SPECTROSCOPIC STUDIES OF SOME COORDINATION COMPOUNDS

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Summary.

In part one, spectroscopic methods are used in a study of the products of some metal-promoted reactions of 2-cyanopyridine. This compound reacts exothermically with copper(II) chloride in methanol to give dichlorobis[O-methylpyridine--2-carboximidate]copper(II). Methyl 2-picolinate and pyridine-2-carboxamide may both be obtained in good yield via metal-promoted reactions of this type. Some proposed mechanisms for these reactions are discussed. Nine new complexes of O-methylpyridine-2-carboximidate are characterised by spectroscopic, magnetic, and conductimetric methods. Spectroscopic evidence for the electron-rich nature of this ligand is used in an explanation of its unusually high d-orbital splitting capacity.

In part two, infrared and Raman data for triphenylamine, tri(2-pyridyl)amine, tri(2-pyridyl)phosphine and tri(2-pyridyl-arsine) are presented, and vibrational assignments are proposed. A literature survey focuses attention on inter-ring vibrational coupling in these molecules.

In part three, assignments for metal-ligand vibrations in a closely related series of complexes of the type bis[tri(2-pyridyl)amine]$M^{2+}2X^{-}$ are made by comparing infrared and Raman data obtained in both solid state and in solution. Most of the "ligand" vibrations of the centrosymmetric cations (D_{3d} symmetry) are accidentally degenerate, but splittings are observed in the low-spin complexes. Variable temperature magnetic and spectroscopic studies of bis[tri(2-pyridyl)-amine]cobalt(II) perchlorate show that an equilibrium bet-

between ^4T and ^2E spin states exists in this complex. The dependence of the susceptibility on the crystal structure in complexes of this type is attributed, in part, to variations in the abilities of different lattices to accommodate the predicted Jahn-Teller distortions in the low-spin isomers. Explanations are given for the unusually high Δ value produced by terdentate tri(2-pyridyl)amine, and for its tendency to form diacidobis(bidentate) complexes.

Preface

The work described in the first part of this thesis, although not directly related to the other two parts, enabled me to gain some experience in the experimental and theoretical methods used in the characterisation of transition metal complexes. The topic selected arose out of a chance observation which I made while working as a vacation student at the (then) National Chemical Laboratory. At that time (1963), the development of far-infrared instrumentation was in its infancy, and laser Raman spectrometers were unknown. However, we had access to a machine which would scan to 375 cm^{-1}, and it seemed logical to prepare complexes using the highly purified organic bases then available at Teddington and to examine their spectra. I found to my surprise that the infrared spectra of copper complexes prepared from 2-cyanopyridine were markedly different from the spectrum of the free base, and from the spectra of copper complexes of 3- and 4-cyanopyridine. A few preliminary infrared spectra and analyses were obtained at Teddington, but the complete characterisation of all the complexes was carried out during the tenure of my Research Assistantship at Aston. I will remain grateful to Dr. J.H.S. Green (N.P.L., Teddington) for stimulating my interests in spectroscopy and coordination chemistry, and for the many useful discussions we had during the early stages of the work.

Parts Two and Three describe the results of an attempt to apply the latest and most sophisticated vibrational spectroscopic methods to the investigation of a set of complexes of a chelating heterocyclic ligand. This involved careful selection of a group of complexes which could be studied in both infrared and Raman, and in solution as well as in the solid state. The eventual choice of the tri(2-pyridyl)amine complexes was fortunate in that the coordination chemistry of this ligand had been studied in this department for some time. If Part Two seems unduly long, this is because I considered it essential to arrive at a definitive assignment for a closely related molecule (triphenylamine) before proceeding to work on the ligand and its complexes.

The use of sophisticated instrumental techniques involved visits to no fewer than five other Universities, and it is a pleasure to record my appreciation of the unstinted assistance I was given wherever I went. In particular, I am grateful to Drs. D.M. Adams, B.J. Hathaway, and A.E. Underhill for their advice and encouragement. Thanks are also due to Drs. J.A. Creighton and G. Davidson for allowing me to use Raman spectrometers at Canterbury and Nottingham, respectively, and to Dr. R.R. Smardzewski for obtaining low-temperature Raman spectra. The variable-temperature magnetic susceptibility measurements were carried out under the watchful eye of Mr. (now Dr.) R.J. Dosser, and I am grateful for his cooperation, which is acknowledged elsewhere.

Many students and staff at Aston contributed help and advice, and space does not allow me to mention them all. However, I must thank Drs. A.W. Downs, G.C. Kulasingam, W.R. McWhinnie, and J.D. Miller for their constructive advice and friendly criticism throughout the course of this work. I am particularly grateful to Dr. McWhinnie, who read an early draft of Part One and most of Part Two, and made many valuable suggestions at Aston and subsequently in correspondence.

Mrs. B. Taylor performed some C, H, and N microanalyses: I am also grateful to Dr. A.E. Underhill for arranging for some of this work to be done at U.C.N.W. when our instrument broke down. Solution spectra on the Unicam SP 700 were obtained by Mrs. V. Shearsby.

Finally, I must express my sincere appreciation of the continuing encouragement given by my supervisor, Dr. A.V. Golton, throughout the five years it has taken to bring this work to a conclusion. I must also thank my head of department, Professor W.G.S. Parker, for his encouragement – particularly in correspondence after I had left Aston.

This thesis was typed by my mother-in-law, Mrs. Anne Wallis, and no praise can be too high for the work which she produced, often from an appallingly rough manuscript and in working conditions which were far from ideal.

In a work of this size, mistakes must occur, and I should be grateful if readers would bring them to my attention.

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PART ONE.

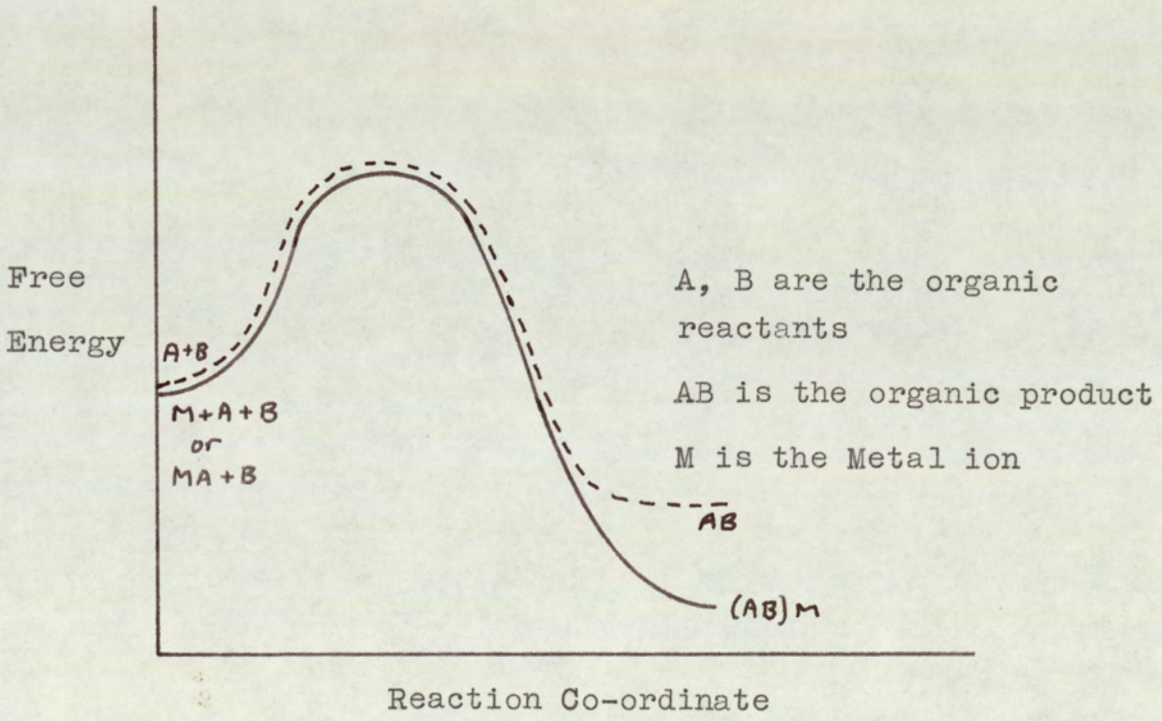
SOME METAL-PROMOTED REACTIONS OF 2-CYANOPYRIDINE.

CHAPTER ONE : Introduction.

The study of reactions of organic compounds which are homogeneously catalysed by transition metal complexes has constituted a topic in which interest has rapidly increased during the past few years. The extent of this recent development may be gauged by the fact that three books dealing with the metal-catalysed or metal-promoted reactions of organic substrates have been published during the course of this work.[1 - 3] This expansion of interest in a previously neglected field of chemistry has been stimulated by two principal considerations. Firstly, it has been found that certain transition metal compounds can effect the homogeneous catalysis of some industrially important reactions of simple organic molecules (e.g. the Hoechst-Wacker and Oxo processes) and in this context it is, perhaps, significant that the lengthiest of the three books previously referred to was written by three members of the research staff of I.C.I. Ltd.

The second spur to the development of interest in metal-catalysed reactions has been provided by an increasing awareness of the role which transition metal ions play in many biological processes. Together, these factors have been tending to break down the traditional barriers between organic and inorganic chemistry.

However, until recently, the use of stoich~~i~~eometric quantities of transition metal ions to promote (rather than catalyse) organic reactions has received little systematic attention possibly because of the difficulties involved in classifying reactions of this type. Some of these difficulties have been described by M.M.Jones[1], who has pointed out that a very general, but nevertheless useful, classification may be derived from a consideration of whether the changes which result when a metal complex is added to an organic reaction system occur as a result of changes in the kinetic or in the thermodynamic factors governing the reactions. Thus, if a co-ordinated product has less free energy than an uncomplexed product, then a reaction will be thermodynamically promoted by the addition of a suitable metal ion. (Fig.1.)



A, B are the organic reactants

AB is the organic product

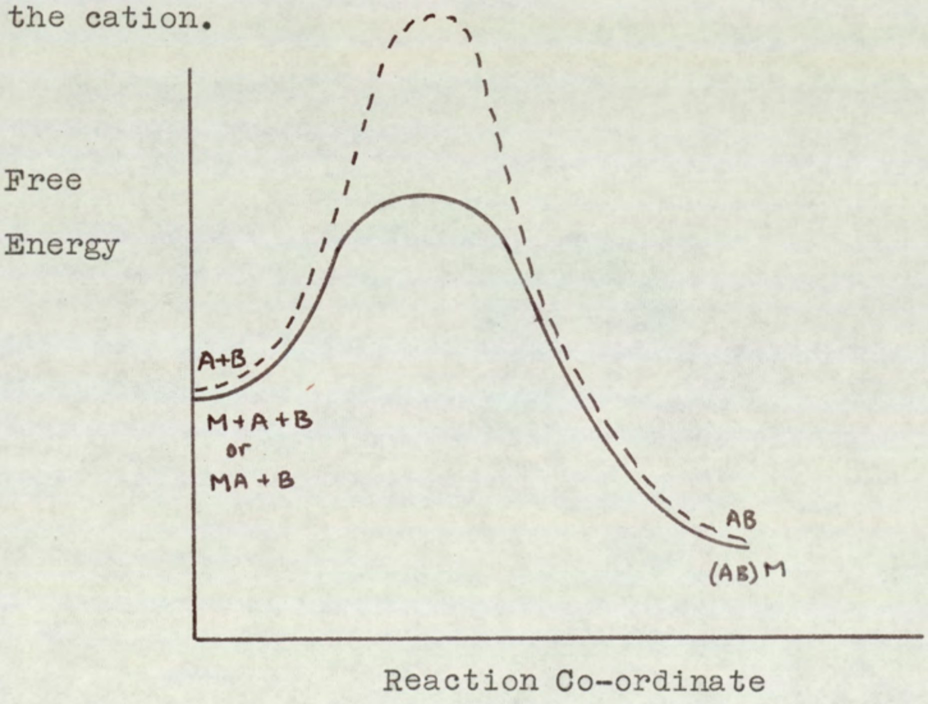
M is the Metal ion

Fig.1.

Alternatively, the free energy of activation for the reaction may be reduced by the introduction of a metal ion. Since

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \quad ,$$

a reduction in the free energy of activation, and hence an increase in the rate of the reaction, can occur if either (a) the enthalpy of activation is reduced (e.g. if complex formation facilitates charge delocalisation in the transition state) or (B) the entropy of activation is increased e.g. if complex formation causes the reactants to come together in a complex in positions favourable for reaction to occur between them (Fig.2), or if (as is generally observed) the reduction in the net charge on a cationic complex, caused by the addition of a nucleophile, leads to release of water or other molecules from the solvation shell around the cation.



<u>Fig.2</u>.

Frequently, kinetic and thermodynamic effects occur together and the resulting energy profile would have the form shown in Fig.3.

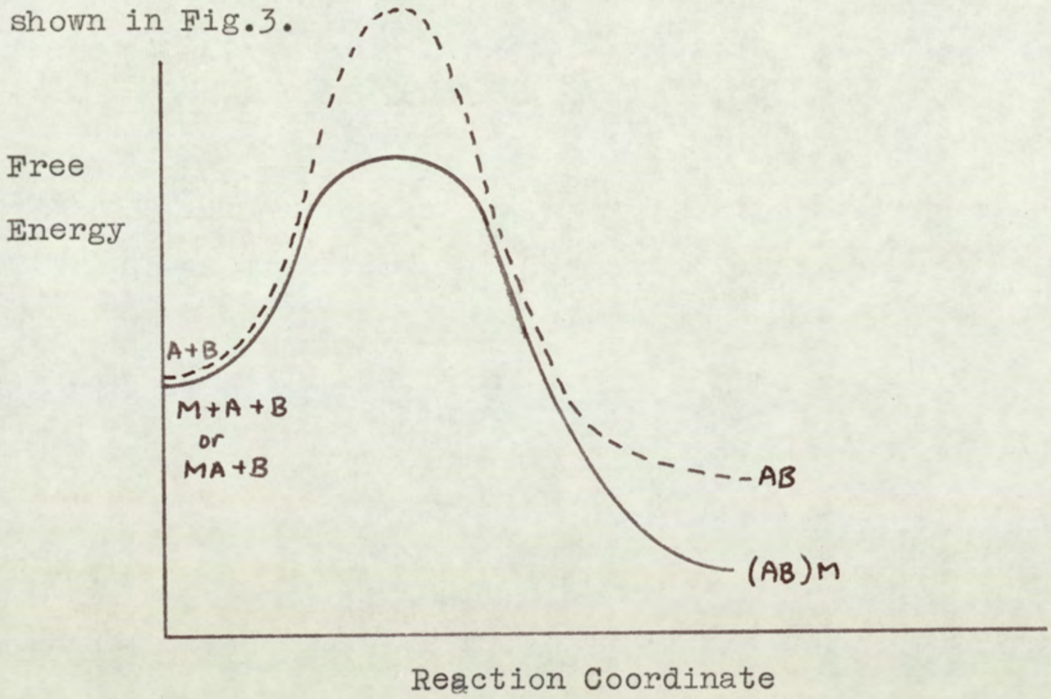
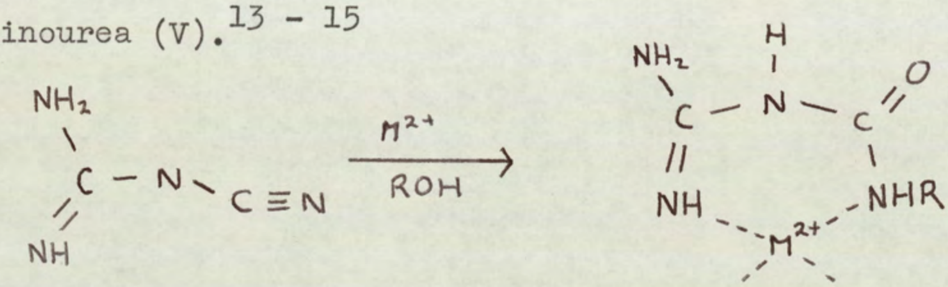


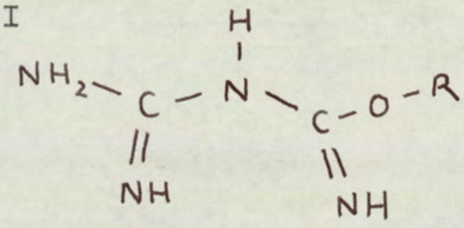
Fig.3.

In 1963 it was observed that 2-cyanopyridine, when added to an aqueous solution of copper(II) chloride, rapidly dissolved to give a deep blue solution, whereas the 3- and 4-cyanopyridines slowly formed green solid complexes under these conditions. This observation prompted an investigation of the reactions of 2-cyanopyridine with metal ions in various solvents, since it seemed likely that both kinetic and thermodynamic effects might favour the formation of a chelating amide complex in the system 2-cyanopyridine-water-copper(II). The results of this investigation are set out in the first part of this thesis, and they are also summarised in a recent publication.[4]

There are only a few examples in the literature of metal-promoted addition reactions of carbon-nitrogen triple bonds. The first such example to be studied was undoubtedly the platinum-promoted hydration of acetonitrile[5] which has been shown[6] to proceed to the amide stage. This reaction is also promoted by mercuric sulphate.[7] Various transition metal ions have been found to promote the addition of alcohols across the triple bond in dicyandiamide(III). It was originally thought that the resulting complexes were derivatives of guanylurea (IV)[8 - 12] but further studies have shown that the structure (IV) is incorrect and that the ligand in the resulting complexes is, in fact, an O-alkyl-1-amidinourea (V).[13 - 15]



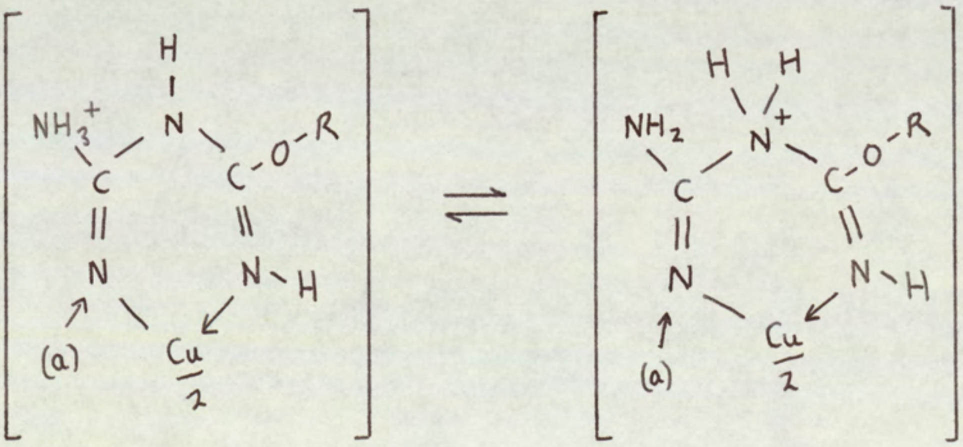
III IV



V

This result could have been predicted. No reasonable mechanism for the reaction of a nitrile with an alcohol to give an N-alkylamide can be written down; indeed, no alkylamide has ever been prepared by such a method, yet both acid-[16] and base-catalysed[17] addition of alcohols to nitriles give O-alkyl-carboximidates (or salts thereof), and the ligand V is an example of this class of compounds. Moreover, the copper (II) complexes of this ligand are <u>pink</u>. Since the molecules are planar, this should have suggested that the ligand is able to produce a very high degree of ligand field splitting, yet amides are known to be weak-field ligands.[18]

We note that the authors of two recent books[19, 20] describe the products of these reactions incorrectly. The strong-field nature of the O-alkyl-1-amidinoureas has been confirmed by studies of the electronic spectra of their planar nickel(II)[15] and copper(II)[21] complexes. The strength of the ligand field in the copper(II) complexes is illustrated by the unusually high position (approximately 20,000 cm^{-1}) of the principal d $\leftrightarrow$ d transition in their spectra, and E.S.R. results[21] for the copper(II) complexes show that the very high value of produced by these ligands is attributable to a marked degree of σ-covalency in the metal-ligand bonds. Infrared studies[21] have shown that the form VI probably represents the structure of the ligand in the complex (VI $\Leftrightarrow$ VII). The high Δ value, and the σ-covalency, were attributed to the anionic character of the nitrogen atoms (a) in VI and VII.



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VII

The chemistry of these complexes has been reviewed.[22]

During the course of this work, kinetic studies of some metal-promoted hydration reactions of 2-cyano-1, 10-phenanthroline[23] and 2-cyanopyridine[24] were reported. A metal-promoted "alcoholation" reaction of the first compound was described. Although the metal complexes formed were not characterized, these studies are of direct relevance to the present work. Their results will be discussed at some length in Chapter Six.

Another metal-promoted reaction of 2-cyanopyridine was reported by Watanabe and Sakai.[25] These workers obtained a blue complex by heating 2-cyanopyridine with an aqueous suspension of Raney nickel. Its I.R. spectrum indicated that it was a complex of pyridine-2-carboxamide, but it was not characterized by elemental analysis. This work was followed up, and in a report which was published during the course of this work[25a], the effect of metal ions on the hydration of 2-cyanopyridine to pyridine-2-carboxamide was investigated.

The hydration of 2-, 3-, and 4-cyanopyridine to the corresponding amide was found to be catalysed by nickel oxide. In the case of the 3- and 4-isomers, the rate of hydration was markedly reduced when thiophene was added, but no such effect was observed with the 2-isomer. Since thiophene is known to poison many heterogeneous catalysts, these results are consistent with a heterogeneous mechanism for catalysis of the hydration of the 3- and 4-isomers, with homogeneous catalysis by metal ions in the case of 2-cyanopyridine. When stoicheiometric quantities of metal ions were used to promote the hydration of 2-cyanopyridine, the bis(pyridine-2-carboxamide) complexes described in this thesis were obtained. When smaller quantities of copper(II) or nickel(II) ions were used, chelated complexes were formed first, followed by catalysis of the hydration of 2-cyanopyridine to pyridine-2-carboxamide.

Although complexes of 3- and 4-cyanopyridine have been investigated quite extensively[26 - 30], only two systematic studies of the coordination behaviour of 2-cyanopyridine have been reported, and in neither of these was any evidence found for metal-promoted reactions of the ligand. Walton has described complexes of 2-cyanopyridine with some d^8 transition metal halides.[26] Unfortunately, however, detailed experimental procedures for the preparation of these complexes were not given, so that it is difficult to assess whether or not metal-promoted reactions of the ligand might have been expected to occur. It was concluded that the ligand was monodentate and that it coordinates via the pyridine ring nitrogen atom. This result is in contrast to the findings of Farha and Iwamoto, who showed, from an infrared examination of the 2-cyanopyridine complexes of copper(I), silder(I), and gold(I) perchlorates, that the metal ions are coordinated via the nitrile nitrogen atom[30]. Complexes of substituted 2-cyanopyridines[31] and 2-cyanopyridine-N-oxide[32] have also been studied, but again, no evidence for any metal-promoted reactions of the ligand was presented.

The basicity of 2-cyanopyridine is almost negligible[33]: in this respect, and in its steric requirements, it might be expected to resemble the 2-halogenopyridines in its coordination behaviour. Complexes of these ligands with the cobalt(II) halides have been shown to be pseudo-tetrahedral[34 - 36], whereas the copper(II) chloride and bromide complexes[35, 36] are believed to be approximately square planar, except for $CuCl_2$(2-chloropyridine)$_2$ which may be square-pyramidal in structure[37]. The feeble coordinating tendency of the halogenopyridines is reflected in the fact that the preparations of these complexes must be carried out in non-aqueous media, and also by the failure of Billing and Underhill to obtain nickel(II) complexes with these ligands. Nickel(II) complexes can, however, be prepared in the absence of solvent, and the colours of these labile products suggest that they have pseudo-tetrahedral structures[38].

CHAPTER TWO : Experimental.

2.1. Physical Measurements.

2.1.1. Electronic Spectra.

Spectra in the region 30,000 - 5,000 cm^{-1} were recorded on a Perkin-Elmer 350 Spectrophotometer, modified by the substitution of a 250W quartz-iodine lamp for the standard tungsten source. Solution spectra were obtained using matched cells of path lengths varying between one and four centimetres. Solids were examined as thick Nujol mulls, after it had been established that the detector system of the diffuse reflectance accessory supplied with the instrument could under no circumstances be induced to provide enough energy to enable acceptable resolution in the vital near-infrared region to be maintained. In order to reduce radiation losses due to scattering, the mulls were spread on the outside surface of an empty 1 cm. liquid cell, which was mounted behind the lens at the detector side of the sample compartment so that the mull was within five millimetres of the surface of the detector (Fig.4). An empty cell smeared with Nujol was placed in the reference beam. This mull technique has two advantages over the more conventional method for obtaining the spectra of solid complexes. Firstly, much less sample is required, and secondly, the same mull can often be used for an infrared spectrum. However, the method is only applicable to spectrophotometers in which it is possible to place the scattering sample in close proximity to the detector(s).

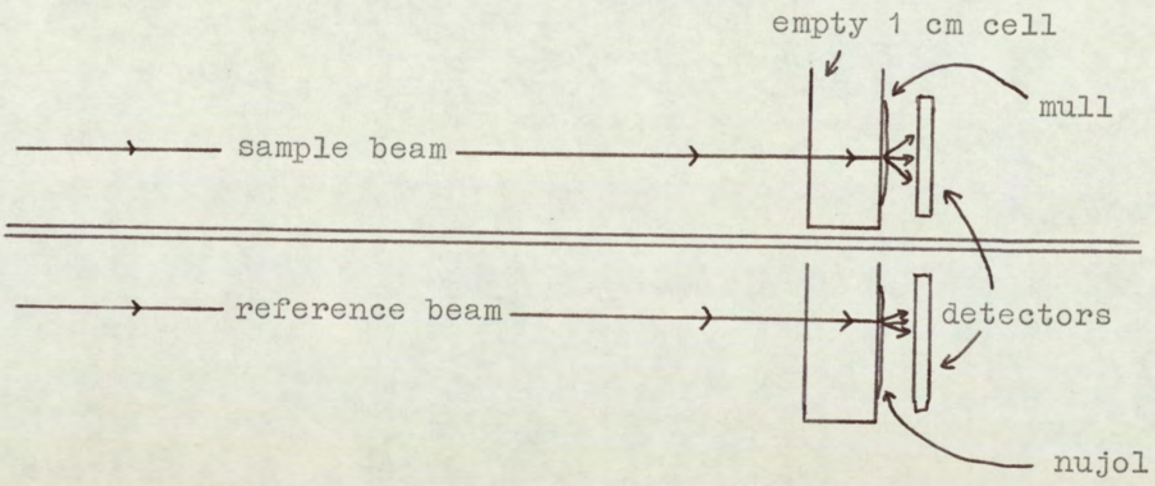

Fig. 4. Adaptation of the P.E. 350 spectrophotometer for diffuse transmittance.

The wavenumber scale on the instrument was checked by reference to the published spectra of benzene (for the near-infrared region)[39] and holmium glass (for the visible region)[40]. Some solution and diffuse-reflectance spectra were also recoorded on a Unicam S.P. 700 spectrophotometer; in general, good agreement was obtained between data for a given compound obtained on both instruments.

The results of these measurements are presented in Tables 1 and 2.

2.1.2. Infrared Spectra.

Infrared spectra (4000 - 195 cm^{-1}) were obtained on a Perkin-Elmer 225 Spectrophotometer. Liquids were examined as capillary films and in 0.05 mm. liquid cells : caesium iodide windows were used. Solids were examined as mulls in Nujol and also, in some cases, as mulls in a fluorinated hydrocarbon. Potassium bromide plates were used to support these mulls in the region 4000 - 400 cm^{-1}; rigid polyethylene plates were used in the 410 - 200 cm^{-1} region. In the latter case, a pair of similar plates with a drop of Nujol between them was placed in the reference beam. The instrument was calibrated by reference to the published spectra of indene[41] and water vapour[42], and the calibration was frequently checked using a polystyrene film. Our reported values are considered to be accurate to within ± 2 cm^{-1} : they are presented in Tables 3 and 4.

2.1.3. Magnetic susceptibilities.

Magnetic susceptibilities were determined by the Gouy method at 289K. The apparatus uses a Stanton model SM 12 semi-micro balance in conjunction with a Newport Instruments Electro-Magnet. A novel method for packing the Gouy tube with powdered solids was found to give reproducible results far more quickly than the recommended[43] "tapping" procedure. In this method, about 0.1 g of the powdered sample is introduced into the tube (e.g. through a drawn-out glass funnel; see Fig.5A); the tube is then held in the fingers and placed lightly against the top of the vibrating unit of R11C "Grindex" infrared sample grinding machine. A piece of rubber should be interposed in order to reduce the risk of fracturing the tube (Fig.5A).

When the tube containing some powder is caused to vibrate, the powder behaves like a liquid and rapidly settles to a constant level. In this way, the tube could be filled in two minutes so as to give susceptibilities reproducible to within 2%; this may be contrasted with the ten minutes or so required to fill a tube by the "tapping" procedure. The

Fig. 5A

Fig. 5B

PLATE 1.

Table 1. Solid-state electronic spectra (30 → 5 kK).*

Complex (for key, see next page)	No.	$\nu_{max.}$ (kK)*
$[(Mepy)CuCl_2]$ (method 1)	1	27.6vs; 14.3s; 13.0sh
$[(Etpy)CuCl_2]$	2	27.9vs; 14.2m; 13.0sh
$[(Bupy)CuCl_2]$	3	26.6vs; 14.8m; 13.1sh
$[(Mepy)_2(H_2O)_2Cu]Cl_2$	4	15.45s; br;
$[(Mepy)_2(H_2O))BrNi]Br$	5	17.1m; 15.8w; 12.2w; 8.65m,br
$[(Mepy)CoCl_2].H_2O$	6	20.3w; 19.35vw; 18.75w; 18.0vw; 16.3sh; 15.9s; 15.7sh; 15.0vs; 14.1s; 10.5w; 6.7sh; 6.2m; 5.55w; 4.90w; 4.65w
$[(Mepy)_2Cu](ClO_4)_2$	7	16.95s,br
$[(2CP)_2CuCl_2]$	8	16.5vs,br
$[(Mepy)_3Ni](ClO_4)_2$	9	18.65m; 12.6sh; 11.4m
$[(Mepy)_3Co](ClO_4)_2$	10	21.75s; 18.55sh; 10.6m
$[(Mepy)_2CoCl_2]$	11	20.6sh; 19.25m; 10.4vw; 7.2w
$[(Mepy)_3Fe](ClO_4)_2.H_2O$	12	26.1s; 19.6vs; 18.0vs
$[(NP)CuCl_2]$	13	26.3vs; 12.95m,br; 10.6sh
$[(NP)_3Ni](ClO_4)_2$	14	16.8m; 13.0w; 10.3m

Key to Table 1.

* 1kK = 1000 cm^{-1}.

Mepy = O-methylpyridine-2-carboximidate

NP = N-methylpicolinamide

2CP = 2-cyanopyridine

Etpy = O-ethylpyridine-2-carboximidate

Bupy = O-_n_-butylpyridine-2-carboximidate

Table 2. Solution spectra and conductivities.

Complex No.*	$\nu_{max.}$ (kK); $\varepsilon_{approx.}$ in parentheses	$\Lambda \times 10^{4}$†	solvent
1	26.85(800); 14.6(100); 13.8(110); 13.1(100)	3	CH_3NO_2
1	13.7(30); 12.7sh	220	H_2O
2	26.6(900); 21.7(90); 14.8(110) 13.8(100)	6	CH_3NO_2
3	26.4(1000); 14.8(80); 13.3(60);	5	CH_3NO_2
4	25.1(400); 13.2(150); 10.0sh	35	CH_3NO_2
4	15.2(60); 13.2sh	230	H_2O
5	17.7(10); 15.8(8); 13.2(6); 10.8(12): 9.7(10)	120	DMF
6	21.9(10); 16.8(15); 16.2(20); 15.8(80); 15.5(80); 14.9(150); 14.5(100); 6.4(80); 5.95(180); 4.68(160); 4.26(160)	30	CH_3NO_2
7	15.9(700)	160	CH_3NO_2
7	15.2(60); 13.2sh	200	H_2O
8	22.9(200); 10.8(100)	27	DMF
9	25.5(17); 18.5(14); 12.8(8) 11.5(10)	180	CH_3NO_2
10	25.5(120); 21.5(40); 18.5(15); 10.6(6)	180	CH_3NO_2
11	20.85(30); 18.9sh; 9.9(10)	122	CH_3OH
12	26.1(4200); 19.9(7700); 18.7(7600)	180	CH_3NO_2
13	22.9(250); 20.7(70); 10.4(120)	25	DMF
14	17.0(14); 13.1(3); 10.4(10)	190	CH_3NO_2
S.1		88	CH_3NO_2
S.1		76	DMF

* see Table 1.

DMF = N,N'-dimethylformamide.

† units are $\Omega^{-1} m^2 mol^{-1}$. K measured for 0.001 M solution.

S.1 = $[(C_4H_9)_4N]I$

Table 3.

Principal bands in the i.r. spectra of the ligands and complexes.

Compound No.§	ν(N-H)	ν(C=N)	νC-O-C	Other bands (cm^{-1}).
Mepy	3292vs	1652vs	1365vs	
NP	3395) 3350) vs			1674vs†; 1532vs‡
1	3378s	1658vs	1380vs	
2	3385m	1650vs	1379s	
3	3220m	1649vs	1375s	
4	3220s,br	1650vs	1378m	3380s.br (H_2O)
5	3230w,br	1650vs	1380vs	3400w,br (H_2O)
6	3270s,br	1648vs	1388vs	3450m,br (H_2O)
7	3318s	1651vs	1376m	1120) 1041) s*; 926m*; 620s*
8				2236m (C≡N)
9	3300s	1651vs	1382vs	1085vs*; 930vw*; 621vs*
10	3292s	1650vs	1382vs	1085vs*; 930vw*; 621s*
11	3210s,br	1649vs	1378vs	
12	3270s	1640vs	1400vs	1085vs*; 932vw; 623*; 3350m (H_2O)
13	3350m 3300sh			1635s†; 1460s‡
14	3340s,br			1639vs,1643sh†; 1460s‡ 1060vs; 930w*; 621s*

† "amide I" band; ‡ "amideII" band; * bands due to perchlorate.

§ see Table 1.

Table 4. Infrared spectra(500 - 200 cm^{-1}) of the ligands and complexes.

compound‡	Principal absorption bands, cm^{-1}
Mepy	475vw;436vw;404m;371w;348m
NP	487w;440w;405m;364m;312s
2-CP	473m;397s;358m
1	452w;418w;378w;320s*;303vw*;285m;279sh;26ow;255vw;228vw
2	490m;415w;365w;320sh*;309m*;273m;235vw;205vw
3	450w,br;412vw;339w;326m*;303m*;285m;274m;205w
4	495w;438w;420w;378w;351s;330sh;250vw;225vw
5	485vw;440w;420w;370w;318m;297s,br;246vw;227vw
6	420m;371w;320s,br*;292s*;285s;247vw;220w
7	450m;440w;417m;378w;323m;257vw;235w
8	491w;435s;403vw;363w;330sh;320vs*;256sh;243m;227w;220m
9	450w;410m;372m;287s;278s;247vw;225vw
10	412w;365m;267s;248s;228w
11	510w;421m;368w;290sh*;284m;235vw;220w
12	546w;475vw;460m;428w;380m;364m;337w;260m;233m
13	595s;513m;451w;426w;412w;367w;316s*;276m*;250w
14	505w;450w;410w;360m;286m

‡ for abbreviations, see Table 1.

* metal-chlorine vibrations

Table 5.

Data used in the calculation of magnetic susceptibilities.

Temperature of measurements = T = 298 K

Specimen volume = V = 0.653×10^{-6} m^3

χ_{mass} (298 K) for tris(1,2-diaminoethane)nickel(II) thiosulphate = 136×10^{-9} m^3kg^{-1}.

χ_{mass} (293 K) for mercury tetrathiocyanatocobaltate(II) = 207×10^{-9} m^3kg^{-1}.

χ_o = volume susceptibility of air = 0.36×10^6.

The tube calibration constant C was calculated from the equation

$$C = \frac{\chi_{mass} m_1 - V\chi_o}{m_2}$$

where m_1 = mass of specimen.

m_2 = apparent change in mass of standard, allowing for the diamagnetism of the tube. The following results were obtained:

(a) using $(en)_3NiS_2O_3$: (i) C = 2962×10^{-9} m^3kg^{-1}
(ii) C = 2983×10^{-9} m^3kg^{-1}
Mean C = 2972×10^{-9} m^3kg^{-1}

(b) using $H_gCo(CNS)_4$: (i) C = 2962×10^{-9} m^3kg^{-1}
(ii) C = 2967×10^{-9} m^3kg^{-1}
Mean C = 2964×10^{-9} m^3kg^{-1}.

Average value for C = 2968×10^{-9} m^3kg^{-1}.

Mass susceptibilites were calculated from the formula

$$\chi_{mass} = \frac{V\chi_o + Cm_2}{m_1}$$

The molar susceptibilities χ_M were then calculated from the relationship

$\chi_M = \chi_{mass}$ x molar mass in kg mol^{-1}.

The molar susceptibility χ_M was then corrected for the diamagnetism of the ligands and anions, and the resulting value of $\chi_M$corr. was used to calculate the Bohr magneton number from the formula:

$$\mu_{eff.} = 797(\chi_M \mathrm{corr} \times T)^{\frac{1}{2}}$$

The following diamagnetic corrections were used

$(ClO_4)^-$ = 40×10^{-11} m^{3}mol^{-1}
Br = 38×10^{-11} "
H_2O = 16×10^{-11} "

Table 6.

Magnetic Susceptibilities.

Compound.	χ_{mass} $m^3 kg^{-1}$	χ_M $m^3 mol^{-1}$	$\chi_{M\ corr}$ $m^3 mol^{-1}$	μ_{eff}	mean μ_{eff}
Mepy	714×10^{-11}	968×10^{-12}			
np	641×10^{-11}	880×10^{-12}			
$(Mepy)_3Ni(ClO_4)_2$	684×10^{-10}	455×10^{-10}	493×10^{-10}	3.02	3.04
	704×10^{-10}	469×10^{-10}	506×10^{-10}	3.07	
$[(Mepy)NiBrH_2O]Br$.	1015×10^{-10}	516×10^{-10}	545×10^{-10}	3.18	3.16
	992×10^{-10}	504×10^{-10}	533×10^{-10}	3.14	
$(Mepy)_3Co(ClO_4)_2$	1814×10^{-10}	1209×10^{-10}	1246×10^{-10}	4.81	4.84
	1855×10^{-10}	1236×10^{-10}	1273×10^{-10}	4.86	
$(Mepy)_3Fe(ClO_4)_2.H_2O$	666×10^{-12}	454×10^{-12}	432×10^{-11}	0.90	
$(np)_3Ni(ClO_4)_2$	761×10^{-10}	508×10^{-10}	542×10^{-10}	3.17	3.12
	712×10^{-10}	475×10^{-10}	509×10^{-10}	3.07	

tube may be emptied rapidly and safely by placing a small beaker or weighing bottle on the vibrating unit and inverting the tube so that, with both tube and collecting vessel held in the fingers, the tube just touches the inside wall of the vessel (Fig.5B). When the tube is set into vibration, the powder rapidly "flows" out.

The tube was calibrated using tris(1,2-diaminoethane) nickel(II) thiosulphate[44] and mercury(II) tetrathiocyanatocobaltate(II)[43]. Most of the measurements were carried out in duplicate (i.e. the tube was emptied and repacked between each set of readings); the calculated susceptibilities generally agreed to within ± 2%. The diamagnetic susceptibilities of the liquid ligands were determined separately. Diamagnetic corrections for the anions were obtained from tables[45]. The results of these measurements are presented in Tables 5 and 6. The presentation of the results in SI units is based on the treatment outlined by Hoppe[45a].

2.1.4. Conductivity measurements.

Solution conductivities were measured at 298K using a Mullard bridge with a "magic eye" balance detector, in conjunction with a dipping cell fitted with bright platinum electrodes of about 1 cm^2 area separated by about 1 cm. The cell constant was determined by measuring the conductivity of an aqueous 0.1M solution of A.R.potassium chloride. The solvents used were purified as follows:-

(a) Nitromethane (Eastman Kodak "Spectro" grade) was dried over anhydrous calcium sulphate and distilled: k = electrical conductivity = 0.65×10^{-3}. $ohm^{-1} m^{-1}$

(b) N,N'-dimethylformamide ("Spectro" grade) was dried by adding one-fifth of its volume of benzene and then distilling at atmospheric pressure; this procedure removes the water as an azeotrope with benzene. The remaining N,N'-dimethylformamide was then distilled under reduced pressure (b.p.373 - 383K/15 - 20 mm Hg) Spectrosol grade methanol (Hopkin and Williams) was used without further purification.

The results of these measurements are recorded in Table 2.

2.2. Analyses.

Most of the carbon, hydrogen, and nitrogen microanalyses were carried out in this department using a Hewlett-Packard F and M Autoanalyser. Other analyses were performed by Messrs.Weiler and Strauss and by the A.Bernhardt Microanalytical Laboratory.

Labile halogens were determined by Volhard's method after warming the sample with excess 6M nitric acid.

After several other methods had been tried and abandoned when they were found to give non-reproducible results, the following procedure was adopted for determining the metal in complexes of metal perchlorates with strong-field ligands:-

Approximately 0.2g of the complex was weighed into a 250 cm^3 beaker. A.R. concentrated nitric acid (5 cm^3) was then added, and the mixture heated gently on an electric hotplate behind a safety screen until the volume was reduced to 1 cm^3. The beaker was then cooled to 0° and A.R.concentrated sulphuric acid (3 cm^3) was cautiously added, followed by A.R. concentrated (s.g. = 1.70) perchloric acid (3 cm^3). The beaker was then placed on an electric hotplate set to maintain the temperature of the contents of the beaker at about 520 K, and the mixture was heated at this temperature in a fume cupboard overnight. The beaker was left partially covered with a watch glass in order to allow acid fumes to escape. The beaker was then cooled to 273 K and the contents were cautiously neutralised (using methyl orange) with 10% sodium hydroxide solution. The resulting solution was then analysed gravimetrically for the metal. Nickel was determined by weighing as its complex with dimethylglyoxime; cobalt and copper were determined by the pyridine-thiocyanate method.

2.3. Materials.

2-cyanopyridine ["pure", m.p.300-301K (lit.29°C[46])] was obtained from Koch-Light Laboratories and was used without further purification. Cobalt (II), nickel(II), and copper(II) perchlorates were prepared by treating A.R.perchloric acid (about 30%) with an excess of the appropriate metal carbonate, filtering *, and evaporating the filtrate (preferably in a rotary evaporator). The hygroscopic crystals which deposited were recrystallised from water. All other chemicals and reagents were of the best quality obtainable.

2.4. Preparations.

Unless otherwise stated, products were obtained in yields of 60 - 80% and solid products were washed with methanol and ether and dried in vacuo over silica gel.

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* If filter papers are used for this filtration they must be thoroughly washed with water before they are disposed of, since they are potentially explosive when dry.

O-methylpyridine-2-carboximidate:- This compound was prepared by the method of Schaefer and Peters[17]. Sodium metal (0.3g) was dissolved in methanol (250 cm^3) and 2-cyanopyridine (52.0g) was added. The mixture was set aside for three days at room temperature and then neutralised to pH 8 with glacial acetic acid. The solvent was then distilled and the residue, a yellow oil, distilled under reduced pressure. A fraction of about 40 cm^3 boiling at 423K/20 mm Hg collected. This fraction was redistilled and gave 30g (45%) of O-methylpyridine-2-carboximidate, b.p. 331-341K/20 mm Hg. (Found: C, 61.8; H, 6.11; N, 20.7. $C_7H_8N_2O$ requires C, 61.8; H, 5.93; N, 20.6 %). The identity of this compound was confirmed by comparing its infrared spectrum with the reported spectrum of methyl benzimidate:[47] the spectra are very similar. The first distillation was stopped when a colourless solid began to collect in the condenser. The contents of the distillation flask also solidified on cooling. These solid residues were combined and recrystallised three times from aqueous ethanol : yield, 9.25g. This substance melts at 517-518K.

The similarity of its infrared spectrum to that of 2,4,6-triphenyl-1,3,5-triazine[48] supports its formulation as 2,4,6-tri(2-pyridyl)-1,3,5-triazine. In subsequent preparations of O-methylpyridine-2-carboximidate the yield was found to vary in an unpredictable manner, and some of the products decomposed to a colourless solid when allowed to stand, even in sealed ampoules. The compound was therefore redistilled under reduced pressure before use in the preparation of complexes.

Picolinic acid N-methylamide:- Methyl 2-picolinate (20 g) was stirred with an ethanolic solution of methylamine (100 cm^3; 33% w/v) at room temperature; an exothermic reaction occurred. The mixture was then set aside at 298K for three days. The solvent was distilled off and the residue distilled under reduced pressure: a fraction boiling at 373-383K/5 mm Hg was collected and redistilled to give 18.0 g (86%) of a colourless liquid, b.p. 378-383K/5 mm Hg. (Found: C, 61.9; H, 5.86; N, 20.8. $C_7H_8N_2O$ requires C, 61.8; H, 5.93; N, 20.6 %)

Dichloro(O-methylpyridine-2-carboximidate)copper(II):

Method 1:- A solution of 2-cyanopyridine (41.6 g, 0.4 mol) in methanol (150 cm^3) was added to a solution of copper(II) chloride dihydrate (68.2 g., 0.4 mol) in methanol (400 cm^3) at 303K. The mixture became warm and after one minute blue-green crystals (97.4 g., 80%) were deposited. Analytical samples were recrystallised from methanol (Found: C, 30.9; H, 3.13; N, 10.3; Cl, 26.6. $(C_7H_8N_2O)CuCl_2$ requires C,31.3; H, 2.98; N, 10.4; Cl, 26.3 %).

Method 2:- Copper(II) chloride dihydrate (1.70 g., 10 mmol) in methanol (100 cm^3) was treated with concentrated hydrochloric acid (2 cm^3). Addition of O-methylpyridine-2-carboximidate (2.5 g., 20 mmol) gave a light green precipitate (Found: C, 31.4; H, 2.92; N, 10.9; Cl, 26.0 $(C_7H_8N_2O)CuCl_2$ requires C, 31.3; H, 2.98; N, 10.4; Cl, 26.3 %).

Dichloro(O-ethylpyridine-2-carboximidate)copper(II) and Dichloro(O-n-butylpyridine-2-carboximidate)copper(II):- These complexes were prepared as described in method 1 (above), but using ethanol, and n-butanol, respectively, as the reaction solvent (Found: C, 32.7; H, 3.71; N, 9.88; Cl, 25.0. $(C_8H_{10}N_2O)CuCl_2$ requires C, 33.7; H, 4.48; N, 8.95; Cl, 22.7%). (Found: C, 38.0; H, 4.50; N, 9.01; Cl, 22.6. $(C_{10}H_{14}N_2O)Cucl_2$ requires C, 38.4; H, 4.48; N, 8.95; Cl, 22.7 %).

O-methyl 2-picolinate:- Dichloro(O-methylpyridine-2-carboximidate)-copper(II) (97 g., 0.36 mol) was stirred with a suspension of disodium ethylenediaminetetra-acetate (126 g., 0.36 mol) in water (200 cm^3). The mixture was warmed to 313K and the resulting blue solution was extracted with chloroform (3 x 100 cm^3). The combined extracts were washed with water (1 x 100 cm^3), dried over anhydrous calcium sulphate, and the solvent removed by distillation on a water bath. The residue was distilled under reduced pressure to give a colourless liquid (38.6 g., 78%) (b.p.361-363K/670 Nm^{-2}) which was identified by its analysis and infrared spectrum[49] (Found: C, 61.4; H, 5.30; N, 10.62. $C_7H_7NO_2$ requires C, 61.3; H, 5.15; N, 10.46%).

Diaquobis(O-methylpyridine-2-carboximidate)copper(II) chloride:- Copper(II) chloride dihydrate (1.71 g., 10 mmol) in methanol (30 cm^3) was heated under reflux with a solution of 2-cyanopyridine (4.0 g., 40 mmol) in methanol (10 cm^3). A deep green crystalline precipitate was formed at first; this slowly dissolved to give a deep blue solution. After heating under reflux for two hours, solid sodium hydroxide (0.05g) was added: the residual precipitate then dissolved. The pale blue complex, which was obtained after concentrating and cooling the solution, was recrystallised from chloroform :

methanol (1 : 1). (Found: C, 37.5; H, 3.63; N, 12.78; Cl, 16.4. $(C_7H_8N_2O)_2CuCl_2.2H_2O$ requires C, 38.0; H, 3.64; N, 12.65; Cl, 16.1 %). A product having an identical appearance and infrared spectrum was obtained, after concentration and cooling, by adding O-methylpyridine-2-carboximidate (20 mmol) to a solution of copper(II) chloride dihydrate (10 mmol) in methanol (50 cm^3).

Dichlorobis(2-cyanopyridine)copper(II):- Ice-cold solutions of copper(II) chloride dihydrate (3.47 g., 20 mmol) in methanol (15 cm^3) and of 2-cyanopyridine (4.20 g., 40 mmol) in methanol (10 cm^3) were mixed. The deep green crystals, which were formed almost immediately, were filtered by suction, washed with ice-cold methanol (2 x 5 cm^3) and dried (Found: C, 41.5; H, 2.48; N, 16.15; Cl, 20.5 $(C_6H_4N_2)_2CuCl_2$ requires C, 42.1; H, 2.34; N, 16.35; Cl, 20.7 %). A product having an identical appearance and infrared spectrum was obtained by addition of a solution of copper(II) chloride dihydrate (3.40 g., 20 mmol) in methanol (15 cm^3) to a solution of 2-cyanopyridine (2.04 g., 20 mmol) in methanol (10 cm^3) containing concentrated hydrochloric acid (5 cm^3). Deep green crystals were formed when the mixture was set aside for several hours at room temperature.

Bis(O-methylpyridine-2-carboximidate)copper(II)perchlorate:- Hydrated copper(II) perchlorate (7.41 g., 30 mmol) in methanol (20 cm^3) was added to a solution of 2-cyanopyridine (6.24 g., 60 mmol) in methanol (20 cm^3) at 298K. The solution became deep blue almost immediately and sufficient heat was evolved to cause the methanol to boil. A deep blue solid separated when the mixture was set aside for one minute. The product was recrystallised from methanol (Found: C, 32.6; H, 3.07;

N, 10.12; Cu, 11.9. $(C_7H_8N_2O)_2Cu(ClO_4)_2$ requires c, 31.4; H, 2.98; N, 10.39; Cu, 11.7 %). Attempts to prepare adducts of this complex with water, pyridine, and acetone invariably led to the recovery of unchanged starting material.

Bromoaquobis(O-methylpyridine-2-carboximidate)nickel(II) bromide:- Solutions of hydrated nickel(II) bromide (3.26 g., 10 mmol) in methanol (20 cm^3) and of 2-cyanopyridine (2.08 g., 20 mmol) in methanol (20 cm^3) were mixed and stirred with 2,2'- dimethoxypropane (50 cm^3) for 30 minutes. The precipitated green solid was purified by dissolution in methanol and reprecipitation with 2,2'-dimethoxypropane (Found: C, 32.9; H, 3.36; N, 9.5; Br, 31.5. $(C_7H_8N_2O)_2NiBr_2.H_2O$ requires C, 33.0; H, 3.54; N, 11.0; Br, 31.5 %). A product having an identical appearance and infrared spectrum was obtained by mixing methanolic solutions of nickel(II) bromide and of O-methylpyridine-2-carboximidate.

Tris(O-methylpyridine-2-carboximidate)nickel(II) perchlorate:- 2-cyanopyridine (3.14 g., 30 mmol) was added to a solution of sodium methoxide (0.1 g., approx.2 mmol) in methanol and the mixture was warmed. A solution of nickel(II) perchlorate hexahydrate (1.82 g., 5 mmol) in methanol (10 cm^3) was then added, and the mixture was heated under reflux for 30 minutes, during which time the colour of the solution changed from green to deep violet. Benzene (30 cm^3) was then added and the mixture was distilled. A pink solid began to separate when about 20 cm^3 of distillate had been collected. The mixture was then allowed to cool to room temperature and the solid which deposited was recrystallised from methanol (Found: C, 37.7; H, 3.76; N, 12.8; Ni, 8.5. $(C_7H_8N_2O)_3Ni(Cl)_4)_2$ requires C, 37.8; H, 3.60; N, 11.6; Ni, 8.8 %).

Tris(O-methylpyridine-2-carboximidate)cobalt(II) perchlorate:- This orange complex was prepared in a similar manner to the corresponding nickel(II) complex (Found: C, 37.5; H, 3.57; N, 12.6; Co, 8.5. $(C_7H_8N_2O)_3Co(ClO_4)_2$ requires C, 37.8; H, 3.60; N, 12.6; Co, 8.8 %).

Dichlorobis(O-methylpyridine-2-carboximidate)cobalt(II):- This orange complex was prepared as described above, but using hydrated cobalt(II) chloride instead of the perchlorate. The product was purified by dissolution in methanol followed by reprecipitation with ether (Found: C, 41.3; H, 4.21; N, 13.6; Cl, 17.5. $(C_7H_8N_2O)_2CoCl_2$ requires C, 41.8; H, 3.98; N, 13.9; Cl, 17.8 %)

Dichloro(O-methylpyridine-2-carboximidate)cobalt(II) 1-hydrate:- A solution of 2-cyanopyridine (4.08 g., 40 mmol) and of hydrated cobalt(II) chloride (9.50 g., 40 mmol) in nethanol (40 cm^3) and 2,2'-dimethoxypropane was heated under reflux for three hours: blue-green crystals were slowly deposited (Found: C,31.0; H, 3.56; N, 9.68; Cl, 24.9. $(C_7H_8N_2O)CoCl_2.H_2O$ requires C, 29.6; H, 3.52; N, 9.85; Cl, 25.0 %).

Tris(O-methylpyridine-2-carboximidate)iron(II) perchlorate 1-hydrate:- The solvents used in this preparation were deoxygenated before use. Iron(II) chloride tetrahydrate (1.98 g., 10 mmol) was dissolved in methanol (20 cm^3) and the solution was treated with iron powder (0.1 g.) and hydrochloric acid (0.5 cm^3; 10%). This mixture was filtered into a solution of 2-cyanopyridine (3.12 g., 30 mmol) in methanol which had been previously warmed with sodium methoxide (0.1 g., approx. 2 mmol). A deep violet colour formed immediately. The mixture was heated under reflux (10 minutes) and then filtered while hot into a solution of sodium perchlorate (10 g.) in water (15 cm^3) at 273K. Violet-black crystals were formed when the mixture was set aside. The product was recrystallised from methanol (Found: C, 36.8; H, 3.76; N, 12.1. $(C_7H_8N_2O)_3Fe(Cl)_4)_2.H_2O$ requires C, 37.0; H, 3.85; N, 12.3 %).

Dichloro(picolinic acid N-methylamide)copper(II):- This bright green complex was precipitated when a solution of the ligand (1.31 g., 10 mmol) in methanol was added to a solution of copper(II) chloride dihydrate (1.78 g., 1) mmol) in methanol (15 cm^3) (Found: C, 30.7; H, 3.06; N, 10.3; Cl, 26.0. $(C_7H_8N_2O)CuCl_2$ requires C, 31.3; H, 2.98; N, 10.4; Cl, 26.3 %).

Tris(picolinic acid N-methylamide)nickel(II) perchlorate:- A solution of the ligand (4.1 g., 30 mmol) in methanol (10 cm^3) was added to a solution of nickel(II) perchlorate hexahydrate (3.64 g., 10 mmol) in methanol (10 cm^3). The pale blue crystals which deposited were recrystallised from methanol (Found: C, 38.5; H, 3.64; N, 11.9; Ni, 8.8. $(C_7H_8N_2O)_3Ni(ClO_4)_2$ requires C, 37.8; H, 3.60; N, 12.6; Ni, 8.8 %).

Diaquobis(pyridine-2-carboxamide)copper(II) chloride:- 2-cyanopyridine (20.8 g., 0.2 mol) was added, with stirring, to a solution of copper(II) chloride dihydrate (17.1 g., 0.1 mol) in water (100 cm^3) at 312K. The 2-cyanopyridine rapidly dissolved, heat was evolved, and the mixture assumed a deep blue colour. The pale blue crystals which separated on cooling (30.1 g., 80 %) were recrystallised from water (Found: C, 35.0; H, 4.0; N, 13.6; Cl, 17.2.$(C_6H_6N_2O)_2CuCl_2.2H_2O$ requires C, 34.7; H, 3.9; N, 13.5; Cl, 17.1 %).

Picolinamide (pyridine-2-carboxamide):- A suspension of diaquobis(picolinamide)copper(II) chloride (4.13 g., 10 mmol) in water (50 cm^3) was treated with disodium ethylenediaminetetraacetate (7.83 g., 12 mmol). The resulting deep blue solution was evaporated to dryness and the residue extracted with benzene. The colourless crystals (1.65 g., 68 %) which separated from the cooled extract were recrystallised from benzene. The solid had m.p. 377-378K and was identified by its m.p. (lit.[50] 105-106°C) and infrared spectrum.[51]

Diaquobis(pyridine-2-carboxamide)nickel(II)chloride:- 2-cyanopyridine (2.08 g., 20 mmol) was heated under reflux for three hours with a solution of hydrated nickel(II) chloride (2.37 g., 10 mmol) in water (50 cm^3). The pale blue crystals which separated on cooling were recrystallised from water (Found: C, 34.4; H, 4.0; N, 13.6; Cl, 17.0 $(C_6H_6N_2O)_2NiCl_2.2H_2O$ requires C, 35.1; H, 3.9; N, 13.6; Cl, 17.3 %).

The effect of pH on the nature of the products of the reaction between 2-cyanopyridine and copper(II) chloride:-
(i) 2-cyanopyridine (2.07 g., 20 mmol) was dissolved in methanol (5 cm^3); this solution was then added to a solution of copper(II) chloride dihydrate (3.45 g., 20 mmol) in methanol

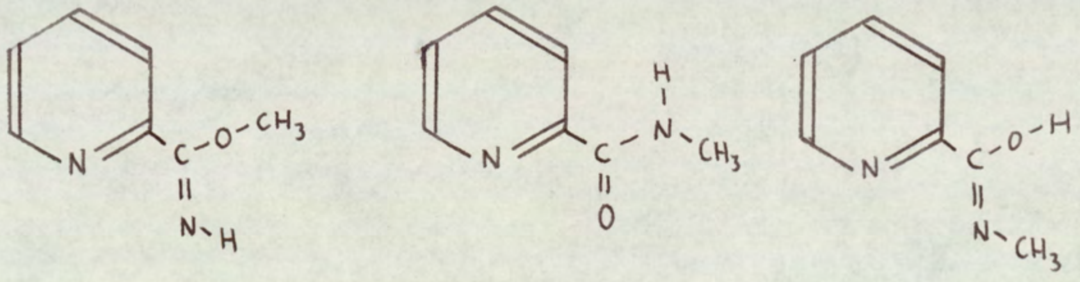
(10 cm^3) containing concentrated hydrochloric acid (1 cm^3). The mixture was warmed to 333K and then left overnight at room temperature. The deep green solid product which deposited was shown, by comparing its infrared spectrum with the spectra of the corresponding pure complexes, to be a mixture of dichlorobis(2-cyanopyridine)copper(II) (major product) with some dichloro(O-methylpyridine-2-carboximidate)-copper(II) (minor product).

(ii) The reaction described in (i) was carried out (omitting the hydrochloric acid) in the presence of sodium hydroxide (0.05 g.) The solid product was shown to be a mixture of diaquobis(pyridine-2-carboxamide)copper(II) chloride (major product) and dichloro(O-methylpyridine-2-carboximidate)copper(II) (minor product).

CHAPTER THREE : Results.

3.1. Copper(II) complexes : The nature of the ligand in the complexes formed by the metal-promoted reactions of 2-cyanopyridine with methanol.

The formula of the complex which is obtained when a solution of 2-cyanopyridine in methanol is added at room temperature to a solution of copper(II) chloride in the same solvent shows that the elements of methanol have been incorporated into the new complex. Moreover, the methanol appears to have undergone reaction with the 2-cyanopyridine, since the infrared spectrum of the new complex (Table 3) shows strong absorption at 3378 cm^{-1} (characteristic of imino N-H) and at 1380 cm^{-1} (characteristic of the $-O-CH_3$ group) but has no absorption assignable to $\nu C\equiv N$. Three possible structures for the new ligand are illustrated in Fig.6.



IX X XI

Fig.6. Showing possible structures for the ligand in the complexes formed by the metal-promoted reactions of 2-cyanopyridine with methanol.

In the absence of metal ions, the reaction of 2-cyanopyridine with methanol, when catalysed by base or acid, should give O-methylpyridine-2-carboximidate (IX) or the salt (XII), respectively[16]. On the other hand, no reasonable mechanism for the reaction of 2-cyanopyridine with methanol to give either structure X (which is N-methylpyridine-2-carboxamide) or structure XI (which is potentially tautomeric with X) can be postulated. It is therefore predictable, on mechanistic grounds, that IX represents the structure of the ligand in the complex. This prediction is conclusively verified by the fact that the same complex can be obtained directly from O-methylpyridine-2-carboximidate, which was separately prepared by the base-catalysed addition of methanol to 2-cyanopyridine.

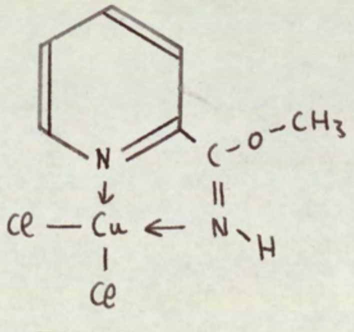
In the preparation of O-methylpyridine-2-carboximidate, varying amounts of 2,4,6-tri(2-pyridyl)-1,3,5-triazine were formed in a side reaction, and some samples of the imidate tended to deposit this substance when kept. In this context, we note that this triazine has been prepared by the reaction of 2-cyanopyridine with another strong base, viz. sodium hydride.[44]

In order to rule out structure X, N-methylpyridine-2-carboxamide was separately prepared, and the spectroscopic properties of a 1 : 1 complex of this ligand with copper(II) chloride were compared with the spectroscopic properties of the complex obtained from 2-cyanopyridine. The first principal d ↔ d absorption maximum (Table 1) in the solid-state electronic spectrum of the amide complex lies 1350 cm^{-1} lower in energy than in the latter complex. This observation, besides confirming that the two compounds are different, indicates that O-methylpyridine-2-carboximidate is a strong-field ligand. The infrared spectrum of the amide complex resembles the spectrum of the free amide (some assignments are given in Table 3) but differs substantially, particularly in the 1700 - 1100 cm^{1} region, from the spectra of both O-methylpyridine-2-carboximidate and the complex prepared from 2-cyanopyridine.

The structure XI for the ligand in the latter complex is a tautomer of structure X; it is most unlikely that a complex containing XI as a ligand could coexist with the copper(II) complex of X. However, the structure XI cannot be completely ruled out, since the -OH, C-O-, and C=N groups in XI could conceivably give rise to infrared absorption in regions similar to those in which the functional groups in structure IX should absorb. For this reason, additional evidence against the formulation XI was sought. The complexes $(C_5H_4N.CN.C_2H_5OH)CuCl_2$ and $(C_5H_4N.CN.C_4H_9OH)CuCl_2$ were therefore prepared by treating 2-cyanopyridine with a solution of copper(II) chloride in the appropriate alcohol; their electronic spectra are virtually indistinguishable from the spectra of the complex obtained from 2-cyanopyridine in methanol solution. This result indicates that the nature of the alkyl group in the ligand does not materially affect the bonding to the copper atom: such an effect would be expected if the alkyl group were attached directly to the atom bonded to the copper atom, so this result provides further evidence against structure XI.

If the structural arguments presented above seem unduly elaborate, it should be remembered that for some time it was thought that the metal-promoted reactions of dicyandiamide (III, p.5) gave derivatives of guanylalkylureas (IV).[8-11] The evidence presented here offers clear support for the correct assignment of the structures of the ligands (V) in these complexes.

The 1 : 1 complex of copper(II) chloride with O-methylpyridine-2-carboximidate dissolves in nitromethane to give an essentially non-conducting solution, and its electronic spectra in this solvent and in the solid state are consistent with a strongly tetragonally distorted octahedral structure. The axial coordination positions are probably filled by halogen atoms from neighbouring molecules in the crystal lattice, and by solvent molecules in solution.



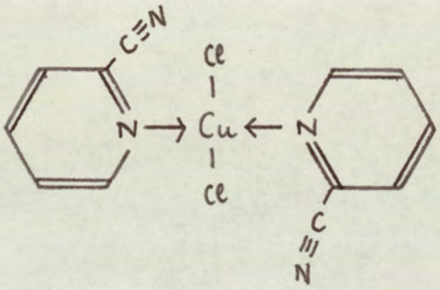
XIII

The far-infrared spectrum of XIII shows a strong band at 320 cm^{-1} which is not present in the spectrum of the free ligand (Table 4). This band is in the position expected for a copper-chlorine stretching frequency:[35-37] presumably the in-plane symmetric and asymmetric frequencies are accidentally degenerate in this complex. Alternatively, a weak feature at 303 cm^{-1} could be assigned to the symmetric stretching vibration. The O-ethyl- and O-n-butylpyridine-2-carboximidate complexes show similar bands in the same regions. A pair of bands at 285(m) and 279 (sh) in the spectrum of XIII are tentatively assigned to "metal-imidate stretching vibrations."

A 2 : 1 complex of O-methylpyridine-2-carboximidate (henceforward referred to as Mepy) can be prepared either by heating an excess of 2-cyanopyridine with copper(II) chloride in methanol for a prolonged period, or directly from the free ligand in neutral solution. The formulation of this complex as diaquobis (Mepy)copper(II) chloride is supported by the similarity of its solid-state (d↔d) spectrum to its solution spectrum in water, in which it dissociates as a 1 : 2 electrolyte, and by the presence of a broad band at 3380 cm^{-1} in its infrared spectrum attributable to coordinated water. Considerable association evidently occurs between the chloride ions and the cations in nitromethane solutions. Similar effects have been previously observed.[53]

If the reactions between 2-cyanopyridine and copper(II) chloride is carried out in methanol at 0°C, a blue-green complex having the formula $(C_5H_4N.CN)_2CuCl_2$ can be isolated. In view of its method of preparation, this complex is presumably an intermediate in the formation of XIII from 2-cyanopyridine since it affords $(Mepy)CuCl_2$ on warming with methanol.

The complex is formulated as XIV since its electronic and far-infrared spectra are similar to the corresponding spectra of some analogous complexes of 2-chloro-and 2-bromopyridine, which have been described as having approximately square planar structures.[35-57]



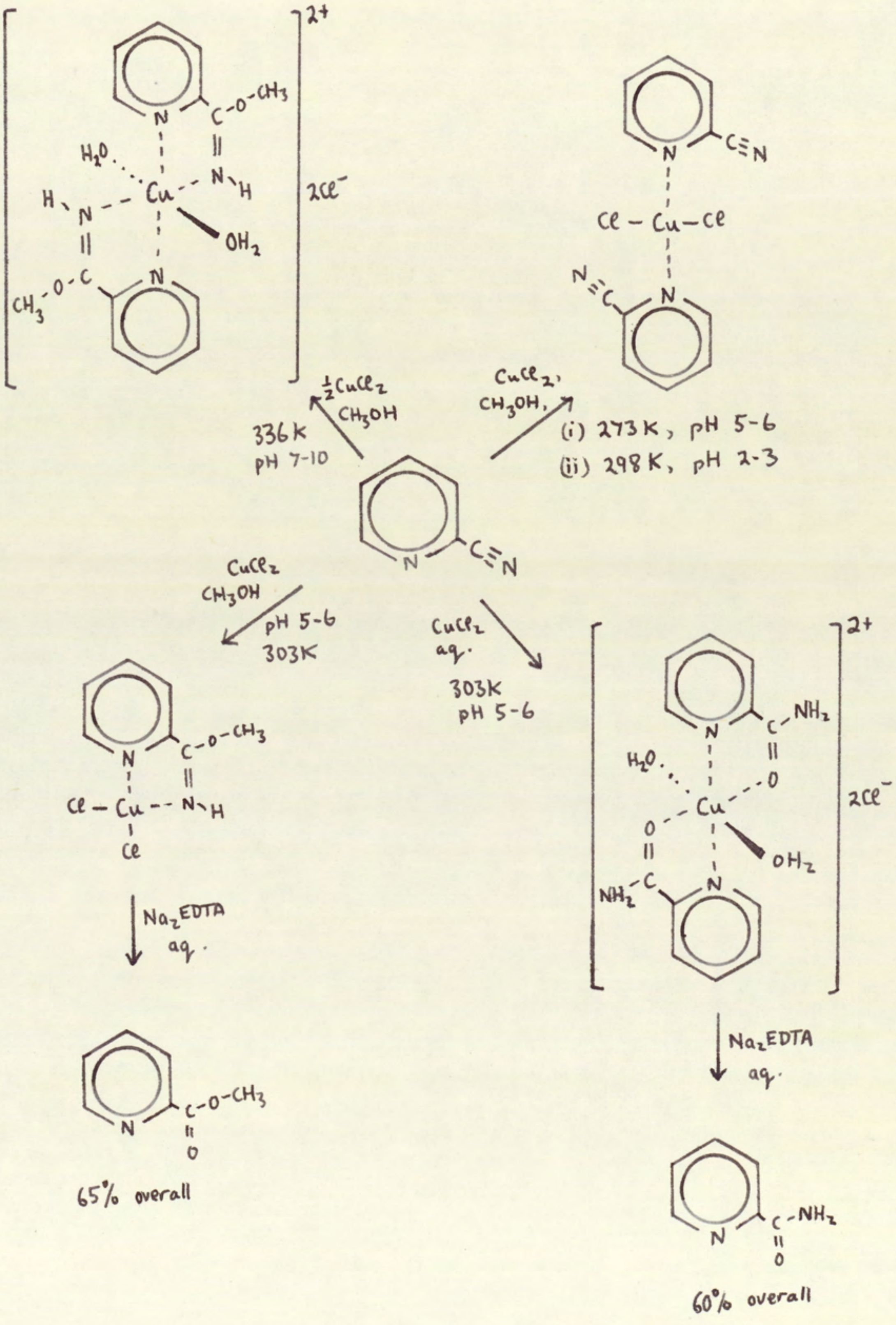
XIV

Also, the C≡N stretching frequency is essentially unshifted on complex formation, indicating that the ligand is coordinated via the pyridine ring nitrogen atom.[26, 30] Strong bands in the infrared spectrum at 320 and 243 cm^{-1} are assigned to ν_{as} Cu-Cl and ν_{as} Cu-N, respectively. In view of the negligible basicity of 2-cyanopyridine (pKa = 0.26± 0.04).[33] which is reflected in the fact that the copper complex can form even in a strongly acid medium, it is at first sight somewhat surprising that the Cu-N frequency is higher in this complex than in the corresponding 2-halogenopyridine complexes $\angle$(2-chloropyridine)$_2$CuCl$_2$; ν Cu-N = 234 cm^{-1}: (2-bromopyridine)$_2$ CuCl$_2$; ν Cu-N = 236 cm^{-1} $\_7$ However, Wong and Brewer have shown[28] that for a closely related series of copper(II) halide complexes of 4-substituted pyridines, π-bonding plays an increasingly important role in the metal-ligand bonding as the electron-withdrawing capacity of the substituent increases; this effect was maximised in the case of 4-cyanopyridine. This hypothesis is supported by Burgess' work on complexes of 3- and 4-cyanopyridines.[27] It is therefore reasonable to attribute the increase in the Cu-N stretching frequency observed in (2-cyanopyridine)$_2$CuCl$_2$ to an increased contribution, from π-bonding, to the copper-nitrogen bond strength in this complex. Some reactions of 2-cyanopyridine with copper(II) chloride are summarised in scheme I.

The predicted splittings for coordinated perchlorate ions[54] are observed in the infrared spectrum of bis(Mepy) Copper(II) perchlorate, but the weakness of any bonding capacity in the z-direction is illustrated by the fact that solid adducts with water, pyridine, or acetone could not be prepared. The complex dissociates as a 1 : 2 electrolyte in nitromethane, but the position of the d$\leftrightarrow$d band in the electronic spectrum in this solvent is shifted to lower frequency relative to the position of the band in the solid-state spectrum, which suggests that the axial perchlorate ligands are replaced by coordinated nitromethane molecules in solution. The behaviour of the perchlorate groups in this complex is considered to represent another example of "semi-coordination".[55, 56]

Hathaway and Billing[56] have pointed out that in copper(II) complexes of σ-bonding ligands such as ammonia and 1,2-diamino-ethane, true square planar stereochemistry is almost unknown. Normally, some further bonding is required for stability. This requirement can be satisfied by the weak axial coordination of anionic ligands (known as "semi-coordination)

Scheme 1. Some reactions of 2-cyanopyridine with copper(II) chloride.



such that the metal-ligand distances are ca.60 pm greater than the in-plane metal-ligand distances, or alternatively by metal-ligand π bonding. The fact that the perchlorate ions in $(Mepy)_2Cu(ClO_4)_2$ are apparently semi-coordinated suggests that the π-bonding capacity of the imidate ligand is limited. A direct comparison of the behaviour of this complex with that of the copper(II) complexes of 2,2'-bipyridyl and 1,10-phenanthroline is not possible, since the $Cu(bipy)_2^{++}$ and $Cu(o\text{-}phen)_2^{++}$ cations cannot, for steric reasons, assume a square planar stereochemistry.[64] No such constraint affects Mepy.

3.2. Cobalt(II) complexes.

In contrast to the copper(II) perchlorate complex described above, the infrared spectrum of $(Mepy)_3Co(ClO_4)_2$ shows that the perchlorate groups are ionic. The complex is a 1 : 2 electrolyte in nitromethane, and the similarity of the solution and solid-state spectra confirm the presence of a tris-chelated cation. The magnetic moment of the complex is in the range usually found for high-spin cobalt(II) complexes of strong-field ligands.[57]

The complex $[(Mepy)_2CoCl_2]$, like the perchlorate complex, can only be obtained in alkaline solution. It is insoluble in nitromethane and in N,N'-dimethylformamide, and its solution spectrum and conductivity in methanol indicate that some reaction of the type

$$[(Mepy)_2CoCl_2] + \text{methanol} \rightleftharpoons [(Mepy)_2Co(\text{methanol})_2] + 2Cl^-$$

is taking place. However, its solid-state spectrum is consistent with an approximately octahedral structure.

$[(\mathrm{Mepy})\mathrm{CoCl_2}].\mathrm{H_2O}$ is blue-green and the position and multiplicity of the bands in its electronic spectrum show that the cobalt atom is in a pseudo-tetrahedral environment; strong bands in the infrared spectrum at 320 and 292 $\mathrm{cm^{-1}}$ are assigned to the asymmetric and symmetric metal-chlorine stretching frequencies, in keeping with previous work.[34-36] Despite the use of 2,2'-dimethoxypropane as solvent, this complex was obtained as the 1-hydrate,. When heated to 393K the colour of the complex changed to deep royal blue, but loss of water was accompanied by decomposition and loss of ligand.

3.3. Nickel(II) complexes: the Ligand Field Strength of Mepy.

Like the analogous cobalt(II) complex, $[(\mathrm{Mepy})_3\mathrm{Ni}](\mathrm{ClO_4})_2$ is a 1 : 2 electrolyte in nitromethane, and its perchlorate groups are ionic: the magnetic moment confirms the essentially octahedral nature of the cation. The electronic spectra of the complex in solution and in the solid state are very similar. The band of lowest frequency in the mull spectrum has a shoulder on its high-frequency side, which is more clearly resolved in solution. This shoulder (12,8000 $\mathrm{cm^{-1}}$) is assigned to the spin - allowed $^3A_{2g} \rightarrow {}^3T_{2g}$ transition, and the main band at 11,500 $\mathrm{cm^{-1}}$ to the spin -forbidden $^3A_{2g} \rightarrow {}^1E_g$ transition. This somewhat unusual assignment is based on our observation that the corresponding iron(II) complex is low -spin. It has been shown that for "octahedral" nickel(II) complexes of polyamine ligands, the critical value of Dq [w.r.t. Ni(II)] for spin-pairing in the iron(II) "octahedral" complex of the same ligand is $1170\ \mathrm{cm^{-1}} \leqslant \mathrm{Dq} \geqslant 1163\ \mathrm{cm^{-1}}$.[58] In other words, if the position of the first (lowest-frequency) spin-allowed band in an "octahedral" nickel(II) complex of a polyamine ligand is at a frequency higher than, or equal to, 11,700 cm^{-1} then the "octahedral" iron(II) complex of the same ligand will be diamagnetic; if the frequency is lower than 11,6301 cm^{-1} then the analogous iron(II) complex will be paramagnetic with a moment corresponding to the presence of four unpaired electrons: no exceptions have been found to this rule. The band which we observe at 11,500 cm^{-1} cannot, therefore, be the spin-allowed transition, since our iron(II) complex is essentially diamagnetic. The reason for the greater intensity of this spin-forbidden transition is not clearly understood, but it probably reflects a considerable degree of spin-orbit coupling in the complex, arising from the fact that the $^3T_{2g}$ and ^1E_g states are almost equi-energetic: Lever has pointed out that the intensities of spin-forbidden bands which gain intensity by a spin-orbit coupling mechanism are inversely proportional to the separation in energy between the states which mix under the influence of this mechanism.[59] A similar phenomenon has been observed to occur in the tris(2-pyridinal-isopropylimine)nickel(II) ion.[60]

The value of Dq = 1280 cm^{-1} shows that Mepy is a strong-field ligand, causing an even higher degree of d-orbital splitting than o-phenanthroline. This value for Dq may be compared with the value of 1040 cm^{-1} obtained from the spectrum of the isomeric nickel(II) complex of N-methylpicolinamide.

No solid complex could be isolated from the reaction of 2-cyanopyridine with nickel(II) chloride in neutral methanol solution, even after heating the mixture under reflux with 2,2'-dimethoxypropane for 48 hours. The reaction under alkaline conditions gave a pink product; analytical results suggested that it was a mixture of $[(Mepy)_3Ni]Cl_2$ with $[(Mepy)_2NiCl_2]$. This substance could not be prepared with a reproducible composition and was therefore not further investigated. The solid-state spectrum and magnetic moment of the complex obtained in neutral solution from nickel(II) bromide are consistent with a tetragonally distorted octahedral structure.[61] The complex is a 1 : 1 electrolyte in solution in N,N'-dimethylformamide, but the electronic spectrum in this solvent is quite different from the mull spectrum. A broad band at 3400 cm^{-1} is observed in its infrared spectrum, but since hydrogen-bonding to bromine atoms could modify the appearance of the O-H stretching bands of lattice water, this result is not diagnostic of coordinated water. Attempts to dehydrate the complex led to decomposition of the ligand, so it is formulated as $[(Mepy)_2(H_2O)BrNi]Br$, with $[(Mepy)_2NiBr_2].H_2O$ as a plausible alternative. This complex is undoubtedly the "unknown product" obtained by Walton,[26] who described it as a complex of 2-cyanopyridine: his analytical data for the "unknown product" agree quite well with our own results. When nickel(II) iodide is used instead of nickel(II) bromide in the above preparation, a similar green product is obtained: this complex was not characterised.

3.4 $[(\mathrm{Mepy})_3\mathrm{Fe}](\mathrm{ClO}_4)_2 \cdot \mathrm{H}_2\mathrm{O}$

This complex is low-spin ($\mu_{\mathrm{eff.}} = 0.90$ B.M.). A slight residual paramagnetism, which persists after recrystallisation, is often found in low-spin iron(II) complexes of chelating heterocyclic ligands.[62] The electronic spectrum of this complex in nitromethane solution (the complex decomposes in aqueous solution) exhibits a doublet band of high extinction ($\varepsilon_m = 7700$) at 19,900 and 18,700 cm^{-1}. This type of band is characteristic of iron(II) complexes containing the α-diimine group, and has been assigned to a $t_{2g} \rightarrow \pi^*$ transition.[63]

3.5. Complexes of pyridine-2-carboxamide.

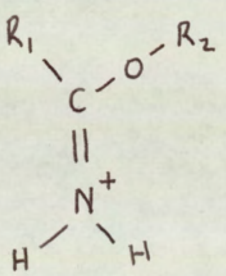
The complexes diaquobis(pyridine-2-carboxamide)copper(II) chloride and diaquobis(pyridine-2-carboxamide)nickel(II) chloride were formed when 2-cyanopyridine was treated with a neutral aqueous solution of the metal salt; the copper(II) complex was formed exothermically, but heating under reflux was required to effect the formation of the nickel(II) complex. These complexes have already been well characterised[25a,64a,65] and their identity was confirmed by comparing their infrared spectra (2000-200 cm^{-1}) with the spectra recently reported.[66] The structure of the nickel(II) complex has been determined by a single-crystal X-ray study, which shows that the ligand is coordinated _via_ the pyridine ring nitrogen atom and the amide oxygen atom.[67]

CHAPTER FOUR : Discussion.

4.1. The Stability of the Complexes.

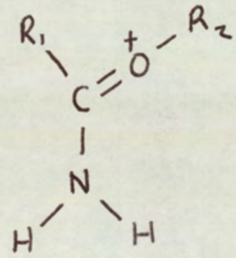
The susceptibility of O-methylpyridine-2-carboximidate (Mepy) to hydrolysis is illustrated by the development of appreciable intensity for a band at 1,722 cm^{-1} - attributable to $\nu C = O$ in methyl 2-picolinate - following exposure of the ligand to moist air for five minutes. By contrast, $[(Mepy)CuCl_2]$ may be crystallised unchanged from 5M hydrochloric acid. On the other hand, $[(Mepy)_3Fe](ClO_4)_2.H_2O$, although it is structurally similar to tris(2,2'-bipyridyl)iron(II) perchlorate, does not share the unusual degree of stability possessed by the latter complex. Thus, $[(Mepy)_3Fe](ClO_4)_2.H_2O$ decomposes rapidly in aqueous solution when exposed to the air, with deposition of iron(III) hydroxide. Also, the deep purple colour of the iron(II) complex is not generated when a solution of $[(Mepy)_3Co](ClO_4)_2$ is treated with aqueous iron(II) ions, in contrast to $[(bipy)_3Co](ClO_4)_2$, which gives the violet colour of the $[(bipy)_3Fe]^{++}$ cation immediately.

A satisfactory explanation for the unusual behaviour of this ligand (relative to other α-di-imine ligands) and for its large Dq value may be derived from a consideration of the synergic mechanism which governs the bonding in complexes in which the ligands can simultaneously donate and accept electrons by σ- and π- bonding, respectively: the function of the π- bonding is to remove the excess charge built up on the metal atom by σ- bonding.[68] The effectiveness of ligands such as pyridine, 2,2'-dipyridyl, pyridine-2-aldehyde alkylimines, and aliphatic α-di-imines is limited by their weak basicity: they are feeble σ-donors and so the potential for stabilisation afforded by the synergic effect cannot be fully exploited. However, O-methylpyridine-2-carboximidate, while retaining the conjugated α-di-imine unit and accordingly having a π^* molecular orbital of relatively low energy for "back-bonding" in its complexes, is also a strong base. The strong basicity of imidates may be considered to result from the enhanced resonance stabilisation of the protonated form (XIV⟷XV). The canonical structure XVII, which is analogous to XV in the unprotenated form, involves charge separation and is therefore less stabilised by resonance than XV.

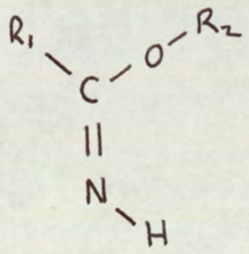


XIV

⟷

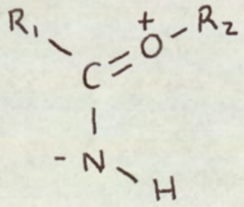


XV



XVI

⟷

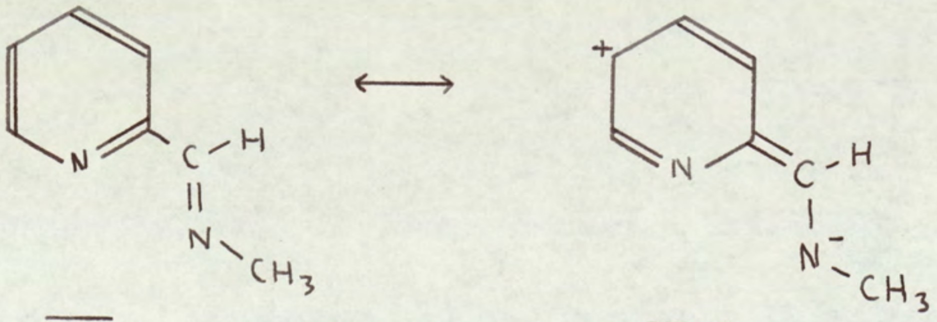


XVII

Mepy may therefore be classified as an "electron-rich α-di-imine ligand" (like biacetyldihydrazone,[60] which has a Dq value of 1,280 cm^{-1}) and its effectiveness as a ligand, particularly in its copper(II) complexes, is attributed to its markedly enhanced σ-donating ability relative to other α-di-imine ligands. This explanation is fully in accord with the reasons given for the unusually high ligand field strength of)-alkyl-l-amidinoureas,[21] and it is supported by the infrared evidence discussed below.

4.2. The Infrared Spectra (3,500 - 1,100 cm^{-1}) of Mepy and its complexes.

ν C=N and ν_{as} C-O-C in Mepy (Table 3) were assigned by comparing the infrared spectrum of this ligand with the reported spectrum of methyl benzimidate.[47] Two general trends are evident from an inspection of Table 3. With the exception of the iron(II) complex (No.12) the C=N frequency is essentially unshifted on complex formation, but the C-O-C frequency increases. A small decrease (12 cm^{-1}) in the C=N frequency is observed in the iron(II) complex. At first sight, this is a surprising result, because the C=N frequency in 2-pyridinal-methylimine (XVI) increases by about 20 cm^{-1} on complex formation with cobalt(II), nickel(II), and copper(II), but decreases by 76 cm^{-1} on complex formation with iron(II).[69]



XVI

XVII

The absence of marked change in the C=N frequency in the complexes of Mepy is considered to arise from the superimposition of two effects, which tend to cancel one another. The first effect is the increase in the bond order on complex formation which was observed by Figgins and Busch;[69] this effect is difficult to explain, but may be visualised as a "quenching" of the normal resonance (XVI↔XVII) in the ligand, with the stabilisation of the form XVI in the complexes of cobalt, nickel, and copper. The second effect arises from the reduction in the bond order which occurs on quaternisation of an imidate nitrogen atom;[70, 71] this is probably a consequence of an increased contribution from the structure XV in the quaternised form. Also, a decrease in the C=N frequency of methyl acetimidate (XIV↔XV, R_1= R_2= methyl) was observed when this ligand formed a pentacarbonylchromium complex.[72]

Support for the existence of the second effect is provided by the observation of an increase in the C-O-C asymmetric stretching frequency of Mepy on complex formation : this is consistent with an increased contribution from structure XV (R_1= 2-pyridyl, R_2= methyl). A similar increase in the C-O-C frequency was observed in the complexes of methyl acetimidate,[72] and in methyl acetimidate hydrochloride.[71] These shifts illustrate the electron-donating effect of the methoxy group, and support the arguments advanced for the "electron-rich" nature of Mepy.

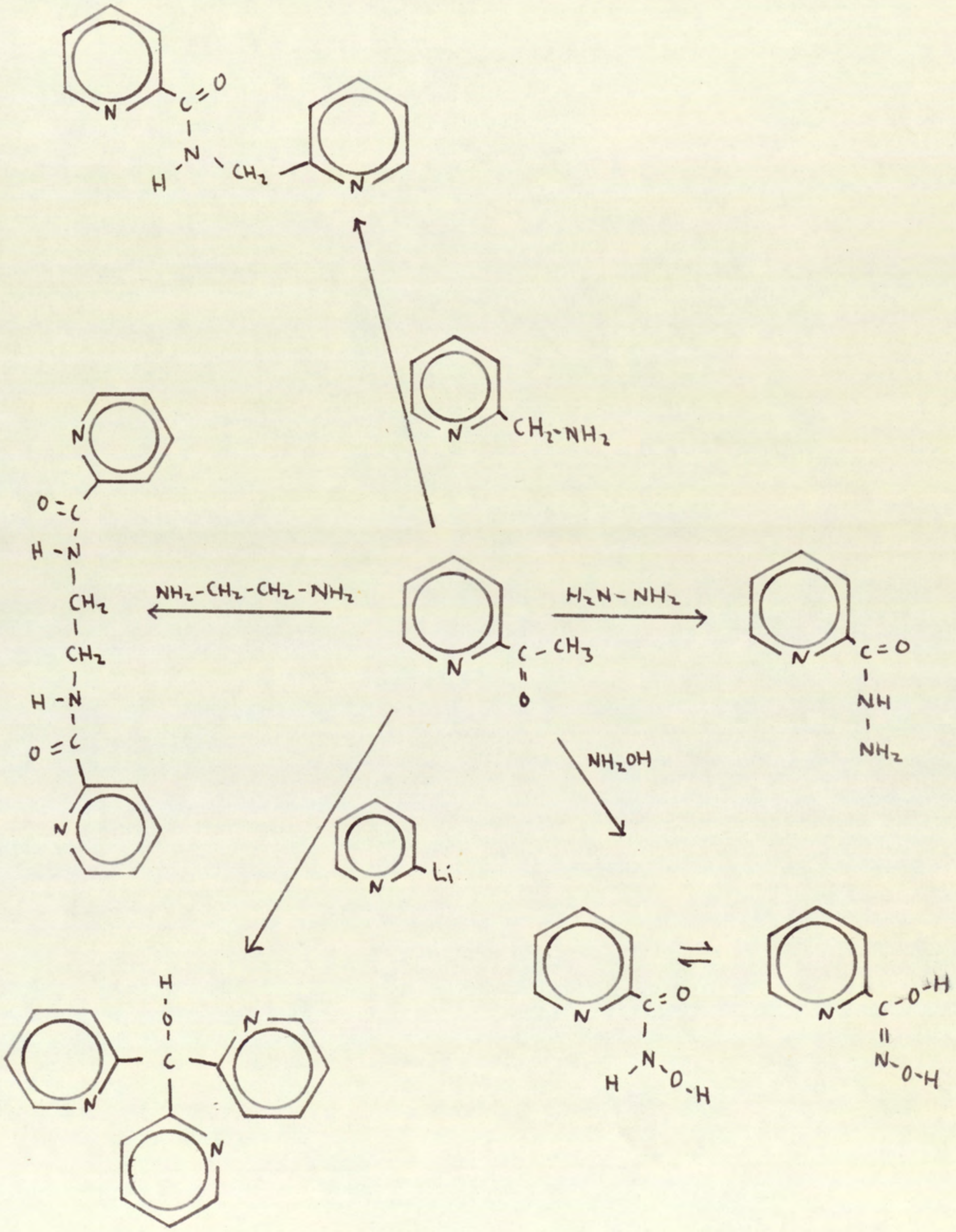
A large reduction in the C=N frequency of 2-pyridinalmethylimine was found to occur on complex formation with iron(II): this was attributed to π-bond formation between the metal and the ligand, with a concomitant reduction in the C=N bond order.[69] The iron(II) complex of Mepy shows a much smaller reduction in the C=N frequency relative to the free ligand. This difference indicates that any π-bonding in the Mepy complexes is much weaker than in the α-di-imine complexes studied by Busch et.al.

Mason has shown that there is a negative correlation between N-H and the π-electron density on the nitrogen atom.[73] Inspection of Table 3 shows that the position of ν N-H for the copper, nickel, cobalt, and iron complexes decreases in the order Cu(II) → Fe(II); this is also the expected order of increasing π-bonding. The positions of ν N-H in the complexes containing labile halogen atoms are probably perturbed by hydrogen bonding effects in the crystals.

4.3. The preparation of ligands via the metal-promoted reactions of 2-cyanopyridine.

Methyl 2-picolinate may be obtained in 78% yield from $[(\text{Mepy})\,\text{CuCl}_2]$ following sequestration of the metal with Na_2EDTA: the imidate group is evidently repidly hydrolysed under these conditions. Since this complex is readily obtainable in good yield from 2-cyanopyridine, these reactions constitute a useful new route to the ester. The procedure recommended by Levine and Sneed,[74] after they had unsuccessfully attempted the preparation of the ester by other standard methods, involves addition of thionyl chloride to solid picolinic acid with stirring, and is difficult to control; we failed to obtain a yield of better than 5% of

Scheme 2. Methyl picolinate as an intermediate in the synthesis of new ligands.



methyl picolinate using this procedure. This ester is reactive, since it has an electron-withdrawing group substituted at the carbonyl function, and it might therefore be a useful intermediate in the preparation of several interesting and, as yet, little-studied ligands. Synthetic routes to some ligands which could, in principle, be prepared from methyl picolinate are summarised in Scheme 2.

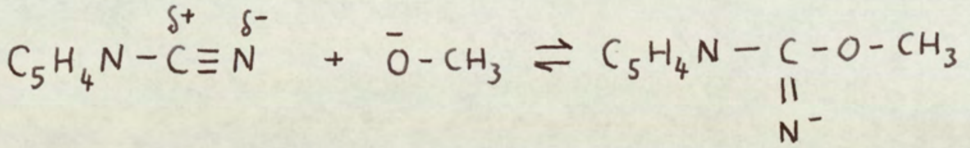
The preparation of pyridine-2-carboxamide <u>via</u> the metal-promoted hydration of 2-cyanopyridine has already been described.[19, 25a] This amide is also difficult to prepare in good yield by standard methods: for example, reaction of 2-cyanopyridine with hydrogen peroxide gives not the amide but pyridine-2-carboxamide-1-<u>N</u>-oxide[50] and an attempt by us to prepare the amide by treatment of 2-cyanopyridine with concentrated sulphuric acid gave pyridine-2-carboxamide in a yield of only 5%

2-cyanopyridine can be prepared from pyridine, <u>via</u> pyridine-<u>N</u>-oxide, by the method of Feely and Beavers,[75] or alternatively by a vapour-phase reaction between cyanogen and butadiene.[76]

4.4. <u>The mechanism of the metal-promoted reactions</u>.

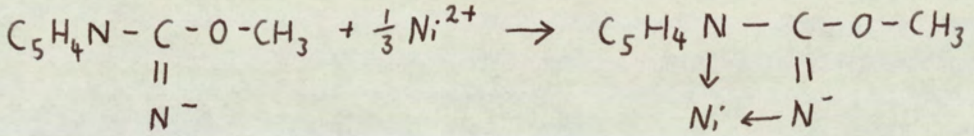
The formation of imidates from nitriles is known to be catalysed by both strong acids[16] and strong bases[17]. This can be used as a basis for an elementary mechanistic distinction between two types of metal-promoted reaction.

The first type of reaction is exemplified by the formation of $(Mepy)_3Ni(ClO_4)_2$ from 2-cyanopyridine and hydrated nickel(II) perchlorate. This complex is not formed unless a strong base is present, and the role of the nickel ion in this case probably consists merely in its ability to form a stable complex with the imidate immediately after its formation by the action of methoxide ion on the nitrile ⌈(1) and (2)⌋.



$$C_5H_4N-\overset{\delta+}{C}\equiv\overset{\delta-}{N} + \bar{O}-CH_3 \rightleftharpoons C_5H_4N-\underset{\underset{N^-}{\|}}{C}-O-CH_3$$

– [1]



$$C_5H_4N-\underset{\underset{N^-}{\|}}{C}-O-CH_3 + \frac{1}{3}Ni^{2+} \rightarrow \begin{array}{l} C_5H_4\underset{\downarrow}{N}-\underset{\|}{C}-O-CH_3 \\ \qquad Ni \leftarrow N^- \end{array}$$

– [2]

To the extent that (1) is an equilibrium process, the nickel ion increases the yield in the forward reaction by removing the imidate. At the same time, further reaction of the imidate (e.g. with water, to give the ester) is prevented. We have already seen how complex formation with copper(II) makes the coordinated imidate remarkably resistant to hydrolysis.

The rapid copper(II)-promoted reactions of 2-cyanopyridine are thought to constitute a second type of reaction. Neither added base nor acid are necessary for these reactions to proceed rapidly to completion. The isolation of the intermediate (2-cyanopyridine)CuCl$_2$ suggests that in these cases the metal ions have a definite catalytic role, as well as being effective in stabilising the product.

The kinetic aspects of the metal-promoted hydration and "alcoholation" reactions of 2-cyano-1,10-phenanthroline,[23,24] and of the metal-promoted hydration of 2-cyanopyridine,[24] have been discussed by Breslow, Fairweather, and Keana. The copper(II)-promoted reactions of these compounds were found to be too rapid for convenient study. However, nickel(II) ions were found to promote the hydration of 2-cyano-1-10-phenanthroline by a factor of 10^7 relative to the hydroxide-ion catalysed hydration in the absence of transition metal ions. This remarkable acceleration was accounted for by a gain of about 35 entropy units in $\Delta S^{\ddagger *}$ relative to the hydroxide-ion catalysed hydration: $\Delta H^{\ddagger *}$ remained unchanged at about 15 Kcal/mole. For the analgous hydration reaction of 2-cyanopyridine, the ratio of second-order rate constants for hydroxide attack on the complexed and free substrate was found to be approximately 5×10^9. Both sets of reactions were found to be first-order in hydroxide ion and were not susceptible to general basic catalysis. Three mechanisms, each of which could account for the observed increase in the entropy of activation of the reaction, were considered by Breslow et.al.

The increase in the entropy of activation in mechanism A was reasonably attributed to the liberation of solvated molecules from around both nucleophile and substrate resulting from the reaction of the nucleophile with a positively

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* 1 e.u. = 4,184 J mol^{-1}

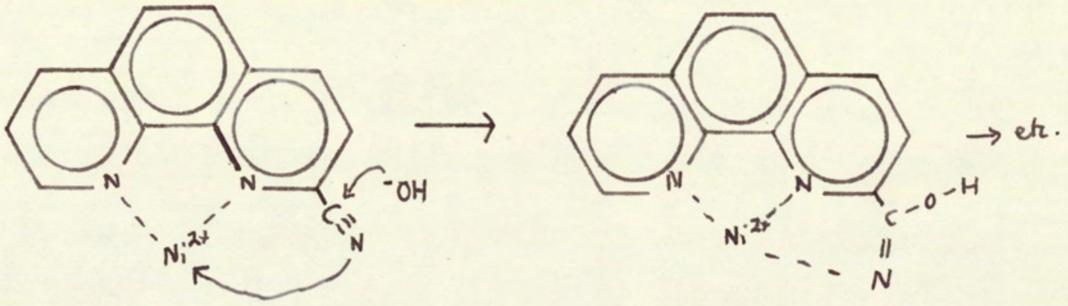
1 Kcal = 4,184 J

charged species. In mechanisms B and C, the increase in the entropy of activation is attributable to a template effect, which reflects the enforced proximity of the nucleophile to the substrate. These three mechanisms are kinetically equivalent, so extra-kinetic arguments were resorted to in an attempt to deduce the correct mechanism.

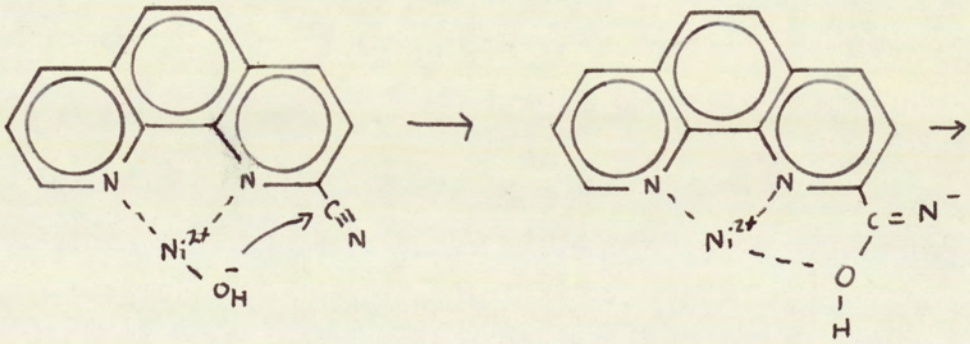
Breslow et. al. decided in favour of mechanism A for two reasons. Firstly, they found that neither ethanolamine nor hydroxyethylethylenediamine were more nucleophilic in the metal-promoted reaction than in the metal-free control: they argued that since these alcohols should have been present in a high concentration in the metal coordination sphere, they should have shown enhanced reactivities, if mechanisms B or C were followed. Secondly, an experiment conducted in 50% aqueous ethanol showed that ethanol was more reactive than water (this is the normal order of nucleophilicities)[77],and they argued that if mechanisms B or C were followed, the preferential coordination of water would have made water more reactive than ethanol. Mechanism C was ruled out because "in the attack on the nitrile, the oxygen, carbon, and nitrogen must remain coplanar as the carbon atom becomes trigonal: stabilisation by the metal in the plane of the molecular complex is therefore geometrically impossible."

The validity of these arguments is questionable. Firstly, no positive evidence in support of mechanism A was presented. Secondly, if a coordinated alcohol such as ethanolamine (bound via the nitrogen end of the molecule as a unidentate ligand)[78] were to react by mechanism B or C, then either the transition

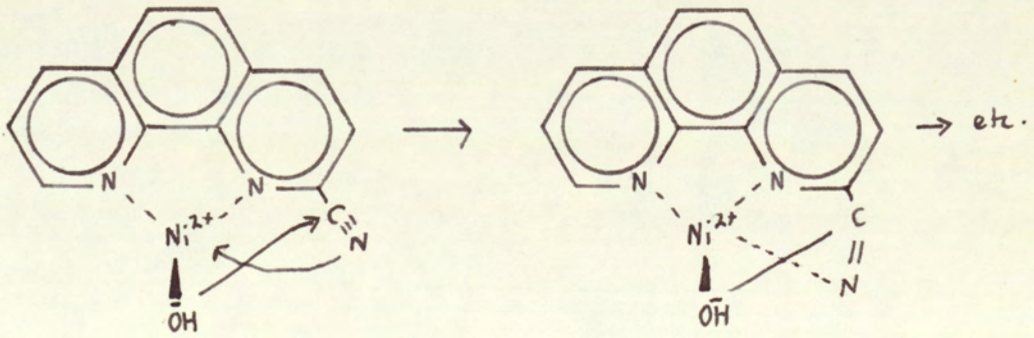
Alternative mechanisms for the metal-promoted hydration of 2-cyano-1,10-phenanthroline.



Mechanism A

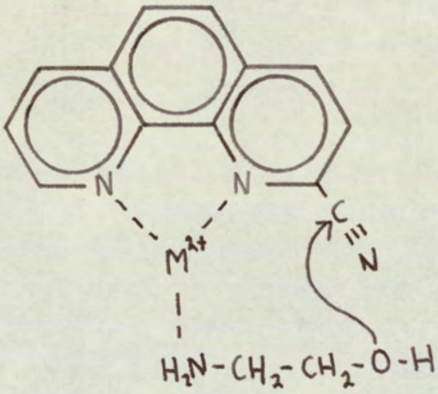


Mechanism B



Mechanism C

state for the reaction (XVII) would contain a (highly strained) seven-membered ring, or else the breaking of the metal-NH_2 coordinate bond would have to be a first step in the reaction: the resulting solvolysis and reaction to form the amide would then be consistent with mechanisms B or C. It is therefore not surprising that these nucleophiles did not exhibit enhanced reactivities.



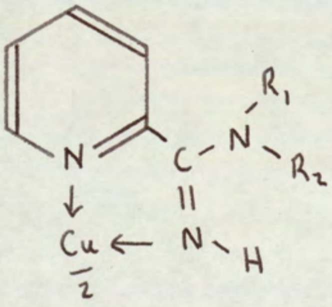
XVII

Thirdly, if the rate of the reaction is governed by the nucleophilicity of the coordinated group, and not by the relative concentrations of the intermediate species containing the different coordinated nucleophiles, then the observed greater reactivity of ethanol is as consistent with mechanisms B and C as it is with mechanism A.

Fourthly, we were not able to prepare an imidate complex from 2-cyanopyridine and nickel(II) chloride in neutral methanol solution, even after heating under reflux for 48 hours, yet the amide complex of nickel(II) chloride was formed readily in aqueous solution: this observation is more consistent with mechanism B or C than with mechanism A. Moreover, when 2-cyanopyridine was treated with copper(II) chloride in methanol containing dissolved sodium hydroxide, the major product isolated was a complex of the amide, not the imidate. Since a substantial concentration of methoxide ions would exist in this solution, a complex of the imidate would be expected as the major product, if mechanism A were correct.

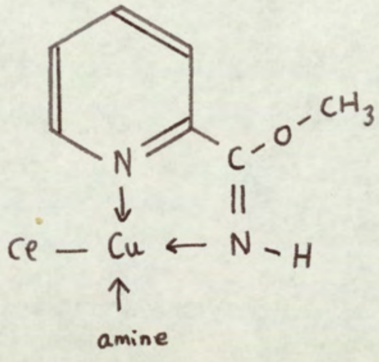
Finally, the statement which "rules out" mechanism C is based on the assumption (for which Breslow et. al. presented no supporting evidence) that the ligand in the amide complex is coordinated via the amide nitrogen atom, since if it were coordinated via the amide oxygen atom, then no steric hindrance would be present. This assumption is almost certainly incorrect, since single-crystal X-ray[67] and infrared studies[79] (including studies on ^{15}N substituted complexes) have shown that the ligands in diaquobis(pyridine-2-carboxamide)nickel(II) chloride are coordinated via the pyridine ring nitrogen atoms and the amide oxygen atoms.

We conclude that it is best to refrain from postulating a general mechanism for these reactions on the basis of the evidence now available. So far, the results of additional investigations have been inconclusive. In a very recent study, Watanabe et. al. attempted to prepare amidine derivatives of the type XVIII



XVIII

by the reaction of various amines with dichlorobis(2-cyanopyridine)copper(II). They succeeded only in obtaining mixed ligand complexes of the type XIX when ammonia, methylamine,



XIX

dimethylamine, ethylamine, and benzylamine were used. When the more sterically hindered and strongly basic amines diethylamine, trimethylamine, and triethylamine were used, then a bis(Mepy)copper(II) complex was formed.

These results can only be used as evidence against mechanisms B or C if it is assumed that the nucleophilicities of the amines are the same as the nucleophilicity of the methoxide ion. If these reactions had been carried out in the absence of water or alcohols as solvent, then the possibility of competition between different nucleophiles would not have arisen. A more useful experiment might be to compare the catalysis of the hydration by nickel(II) ions and palladium(II) ions. Since palladium(II) has very little tendency to coordinate in axial positions, it should be much less effective as a catalyst than nickel(II) if mechanism C is followed, but of comparable activity if mechanism A is correct.

The most rapid metal-promoted reactions of 2-cyanopyridine with methanol in neutral solution were those which were promoted by copper(II) salts: the formation of complexes of Mepy with nickel(II) bromide and iodide and with cobalt(II) chloride took place much less readily, and we were unable to prepare any solid complex of 2-cyanopyridine with nickel(II) chloride. These differences in reactivity may be correlated with the differences in the anticipated stabilities of the corresponding complexes of the metal halides with 2-cyanopyridine. In other words, we are making the reasonable assumption that in the metal-ion-accelerated reactions the formation of an appreciable concentration of a metal complex of 2-cyanopyridine is a necessary first step in its conversion to Mepy. In support of this, we note that copper(II) chloride which reacts rapidly with 2-cyanopyridine in methanol to form $[(\mathrm{Mepy})\mathrm{CuCl}_2]$, also forms a complex with 2-cyanopyridine which was stable enough to be isolated at 0°. The formation of analogous complexes of copper(II) salts with dicyandiamide was quoted as evidence in favour of the "template" nature of the reaction between dicyandiamide, copper(II) salts, and alcohols, to give copper(II) complexes of O-alkyl-1-amidinoureas.[17] The behaviour of cobalt(II) chloride and the nickel(II) halides may be explained by comparing the anticipated stabilities of their (hypothetical) 2-cyanopyridine complexes with the stabilities of the corresponding (known) complexes of the 2-halogenopyridines, since these ligands are sterically and electronically similar to 2-cyanopyridine. The order of increasing tendency to form stable, solid complexes of cobalt(II) and nickel(II) halides with the halogenopyridine is $\mathrm{Co} > \mathrm{Ni}$ and $\mathrm{I} > \mathrm{Br} > \mathrm{Cl}$.[35-37] Trends of this type would account for the formation of $[(\mathrm{Mepy})_2\mathrm{NiBr}_2.\mathrm{H}_2)].\mathrm{Br}$ and $[(\mathrm{Mepy})\mathrm{CoCl}_2].\mathrm{H}_2\mathrm{O}$ and for our failure to obtain any complex with nickel(II) chloride.

4.5. CONCLUSIONS.

A transition-metal promoted reaction of 2-cyanopyridine has been used in a novel preparation of an ester which is difficult to synthesise by other methods. Reactions of this type may find further applications in synthetic organic chemistry, particularly in systems where the use of conventional acidic or basic catalysts might cause undesirable side reactions. The mechanism of the metal-promoted hydration of 2-cyanopyridine has been explained on the basis of a template effect.

The donor properties of O-methylpyridine-2-carboximidate have been investigated, and it has been classified as an "electron-rich" ligand. The investigation of the donor properties of ligands of this type, which can produce large ligand field splittings despite having only a moderate π-acceptor capability, constitutes a topic of some interest, and further research in this field is described in Part 3. of this thesis.

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PART TWO : THE VIBRATIONAL SPECTRA OF TRIPHENYLAMINE, TRI-(2-PYRIDYL)-AMINE, TRI(2-PYRIDYL)PHOSPHINE, AND TRI(2-PYRIDYL)-ARSINE.

CHAPTER FIVE : INTRODUCTION.

5.1. General.

The principal motive for this study was to provide a firm basis for making vibrational assignments in a series of metal complexes of tri(2-pyridyl)amine by establishing a vibrational assignment for the ligand. Previous workers have shown that it is possible to make reliable and self-consistent assignments in large molecules provided that a homologous series of molecules is studied, and to this end, tri(2-pyridyl)-phosphine and tri(2-pyridyl)arsine were prepared and their spectra obtained. These two compounds are also of considerable potential interest as ligands, and it is hoped that the simplified method for preparing these compounds which is described here will facilitate future studies of their donor properties. Triphenylamine was used as a 'model compound' in order to help to relate the spectra of the little-studied tri(2-pyridyl) compounds to the more extensively studied spectra of triphenyl compounds.

5.2. The vibrational spectra of monosubstituted benzenes.

The benzene molecule belongs to the point group D_{6h}. If one of its hydrogen atoms is replaced by a monatomic substituent, the symmetry is lowered to C_{2v}, and the degeneracy of the E vibrations in benzene is lifted. A group theoretical analysis shows that the normal vibrations of this monosubstituted benzene span the irreducible representation

$$\Gamma_{vib} = 11\,A_1 + 6\,B_1 + 3\,A_2 + 10\,B_2$$

The A_1, B_1, and B_2 vibrations are infrared and Raman active, but the A_2 vibrations are Raman active only.

It was noted by Whiffen, during the course of an investigation of the vibrational spectra of the monohalogenobenzenes, that twenty-four of the thirty normal vibrations of these molecules only involve motions of the carbon and hydrogen atoms and therefore remain nearly constant in the series, while the six other modes involving stretching or bending of the carbon-halogen linkage were observed to shift to lower wavenumbers with increasing mass of the halogen.[1] In subsequent investigations of the spectra of other monosubstituted benzenes, it has generally been found that if bands attributable to vibrations of polyatomic substituents are discounted, then their vibrational spectra are similar and resemble the spectra of the halogenobenzenes. Several tables giving average values or ranges of values for the substituent-insensitive vibrations have appeared,[2,3,4] and these tables have been used in making assignments for many monosubstituted benzenes by a 'bingo' procedure involving comparing the position, intensity and degree of depolarisation of an observed feature with the results given in the tables.

Although this empirical procedure has enabled many satisfactory and self-consistent assignments to be carried out, some confusion has arisen in the literature largely because different authors have used different systems of nomenclature for describing the forms of these vibrations. Three systems of nomenclature are currently in use.[1, 3, 5.] It might be thought that the comparison of these three systems would be quite straightforward, since the identification of the forms of the vibrations can be checked by comparing assignments for similar molecules made using different systems. However, inconsistencies are present in the comparisons already published. For example, Stephenson et. al.[3] say that their vibration No.5 (described by Langseth and Lord[5] as No.13) is the same as Whiffen's Z_2[1], and they describe it as a C-H stretching vibration belonging to the A class, yet Varsanyi describes Langseth and Lord's mode No.13 as the "C-X stretching" mode[4], which Whiffen calls q. On the other hand, Varsanyi considers that the Langseth and Lord mode 7a contributes to C-X stretching, yet Stephenson classifies 7a as a C-H stretching mode.

This apparent confusion is explicable if we remember that the only "correct" description of the normal modes of a molecule is that which is given by the potential energy distribution calculated using a "correct" force field. In other words, although Whiffen (for example) draws two A, C-C stretching modes a and b[2], the actual modes will in fact be linear combinations of these idealised motions. Thus, the only "correct" representations of the vibrations of monosubstituted benzenes are those calculated for chlorobenzene by Scherer[5], for Toluene by Bogomolov[6], and for a monosubstituted benzene with a substituent of mass 15 - 19 by Schmid[7]. Even these calculated representations are "correct" only to the extent that the force fields are themselves correct.

Further ambiguity can result from the quite inappropriate attribution of certain specific frequencies to 'C-X stretching' and similar hypothetical vibrations. This point can be illustrated by reference to the three substituent-sensitive A_1 vibrations. Fourteen years ago, Whiffen pointed out that <u>three</u> modes (q, r and t) involve appreciable C-X stretching, and that there is no justification for calling any <u>one</u> of them the C-X stretching frequency.[1] Nevertheless, there have been controversies in the literature since then concerning, for example, whether the Sn-C stretching frequency in triphenyltin chloride lies near 1100 cm^{-1} or near 450 cm^{-1}.[8, 9] In fact, as Varsanyi points out in his review, the vibrational form in which the largest change in the C-X distance takes place can be either mode 13 (LL) or mode 7a (LL), depending on the mass of the substituent.[10] There is, of course, no sudden change from one to the other: this has been demonstrated by the work of Becher and Hofler, who calculated the potential energy distribution of the C-X stretching coordinate in the three substituent-sensitive A_1 vibrations of the halogenobenzenes using a model of the type[11]

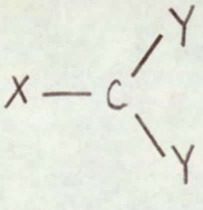


Table 5.1.

The potential energy distribution of the valence force constants in the three A_1 x-sensitive vibrations (from ref.1) of the halobenzenes.

Substituent X	Approximate fraction of phenyl-X stretching incorporated in q, r, and t		
	q	r	t
F	1.0	0.02	0.08
Cl	0.47	0.18	0.39
Br	0.31	0.12	0.59
I	0.23	0.10	0.68

The two groups Y were chosen to represent the phenyl ring and were assigned masses equal to double the mass of a carbon atom. Some of their results are reproduced in Table 5.1, which shows the potential energy distribution of the C-X stretching force constant in the three substituent-sensitive A_1 vibrations of the halogenobenzenes. These results indicate that in fluorobenzene the C-X stretching vibration is concentrated in mode 13 (LL) = q (W) = 12 (SWC), but that in the other halogenobenzenes each of the three vibrations includes a C-X stretching component, which becomes concentrated in mode 6a (LL) = t (W) = 18 (SWC) as the mass of the substituent increases. Although many approximations are made in this treatment, the results clearly demonstrate the need for care in assigning specific frequencies to modes which can couple strongly with other modes.

To sum up, the assignments of the vibrations in monosubstituted benzenes are generally well established, apart from some ambiguities involving vibrations containing contributions from C-X stretching and, to a lesser extent, C-X in-plane bending modes. A comprehensive discussion of these assignments is given in a recent book by Varsanyi.[4] This author reviews assignments for a wide variety of compounds under a separate heading for each normal mode, and compares his own nomenclature - based on that of Langseth and Lord - with the descriptions of vibrations used by other authors. This comparison is not, however, presented in the table in which Varsanyi lists the frequency regions to be expected

Table 5.2. The Vibrations of Monosubstituted Benzenes.

	Light Substituents.												Heavy Substituents.		
C_{2v}	V	LL	W	WSC	vib. type	frequency range	IR	Ra	LL	W		vib. type	frequency range	IR	Ra
1	2	3	4	5	6	7	8	9	11	12	13	14	15	16	17
A_1	1	1	r	2	(α CCC (β C-H (ν C-X	620-830	m-s	s,p	13	q	12	(α CCC (β C-H (ν C-X	1060-1100	w-m	m-s,p
A_1	2	2	z_1	1	ν C-H	3030-3070	m	vs,p							
B_2	3	3	e	3	β C-H	1270-1331	w	w,dp					1253-1275	w	vw,dp
B_1	4	4	v	8	φ C-C	680-700	vs	vw,dp							
B_1	5	5	j	7	γ C-H	970-1000	w	vw,dp							
A_1	6a	6a	t	18'	(α CCC (ν C-X (β C-H	300-530	m-s	m,p	1	r	2	(α CCC (ν C-X (β C-H	650-710	w	m-s,p
B_2	6b	6b	s	18	α CCC	605-630	w	m,dp							
A_1	7a	7a	z_3	15'	ν C-H	3000-3060	w	vp,p?‡	6a	t	18	(α CCC (ν C-X (β C-H	260-420	w-m	m-s,p
B_2	7b	7b	z_5	15	ν C-H	3030-3060	w	vw,dp‡							
A_1	8a	8a	k	16'	ν C-C	1574-1614	m	m-s,p*							
B_2	8b	8b	e	16	ν C-C	1562-1597	w	w-m,dp							
A_1	9a	9a	a	17'	β C-H	1170-1181	m	m,p							
B_2	9b	18b	u	14'	β C-X	200-410	w-m	m,dp					160-300		
A_2	10a	10a	g	11	γ C-H	810-860	vw	vw,dp							
B_1	10b	10b	i	11'	γ C-H	880-910	w	vw,dp	16b (17b)	x (y)	20'	(γ C-X (φ C-C	140-200	w-m	m,dp

1	2	3	4	5	6	7	8	9	11	12	13	14	15	16	17
B_1	11	11	f	4	γC-H	720-760	s	vw,dp					720-830		
A_1	12	12	p	6	ring	990-1010	m	vvs,p							
A_1	13	13 (20a)	q	12	(νC-X (αCCC (βC-H	1100-1280	s	s,p	7a	z_3	15	νC-H	3020-3040	w	vw,p?‡
B_2	14	14	o	9	νC-C	1300-1350	m	w,dp							
B_2	15	9b	c	17	βC-H	1150-1160	w	m,dp							
A_2	16a	16a	w	20	φC-C	390-420	vw	vw,dp							
B_1	16b	17b (16b)	y (x)	19'	(γC-X (φC-C	430-560	m	vw,dp							
A_2	17a	17a	h	19	γC-H	940-980	w	vvw,dp							
B_1	17b	16b (17b)	x (y)	20'	(γC-X (φC-C	140-250	w-m	m,dp	10b	i	11'	νC-H	880-940	w	vw,dp
A_1	18a	18a	b	14	βC-H	1018-1030	m	s,p							
B_2	18b	15	d	10	βC-H	1065-1082	w-m	w,dp							
A_1	19a	19a	m	13	νC-C	1470-1515	m	m,p							
B_2	19b	19b	n	13'	νC-C	1440-1470	s	w,dp							
A_1	20a	20a (13)	z_2	5	νC-H	3070-3110	s	m,p‡							
B_2	20b	20b	z_4	12'	νC-H	3020-3080	vs	m,dp‡							

for the thirty normal modes of monosubstituted benzenes. We have therefore attempted to summarise Varsanyi's textual comparison by including it in an expanded version of his own table. Our tabulated comparison (Table 5.2) differs from that of Stephenson et. al. in that by adopting Varsanyi's distinction between molecules containing light and heavy substituents, consideration is given to the effect of the substituent mass on the extent of coupling and hence on the nature of the substituent-sensitive vibrations.

Key to Table 5.2 : The Vibrations of Monosubstituted Benzenes.

Column No.1 : C_{2v}.

This column gives the species of the vibrational irreducible representation to which each vibration belongs. The choice of the B_1 and B_2 labels follows from the use of the recommended axes for molecules of C_{2v} symmetry.[12]

Column No.2 : V

The numbers in this column refer to the numbers used by Varsanyi to label his drawings of the vibrations of benzene, the components of degenerate vibrations being separated. They are similar to, but not identical with, the drawings used by Lord and Langseth. It must be remembered that these drawings are no more "correct" than any other set.

Light Substituents.

These are defined, for in-plane vibrations, (A_1 and B_2) as those in which the first atom has a mass of less than 25 a.m.u., except for $-CF_3$ and $-NSO$ which are classified as heavy substituents. For out-of-plane vibrations (A_2 and B_1)

the only substituents considered to be "light" are monatomic ones having a mass of less than 25 a.m.u., and polyatomic ones such as toluene in which free rotation is possible around the bond connecting the first "light" and non-branching atom with the ring.

Columns 3 and 11 : LL

The numbers in these columns are those used by Langseth and Lord in their description of the vibrations of benzene. The numbers in parentheses refer to alternative attributions which other workers have used.

Columns 4 and 12 : W

Whiffen's illustrations of the vibrational modes of mono-substituted benzenes are given in Ref.1. The permutation of modes x and y is discussed by Wilcox.[13]

Columns 5 and 13 : SWC

These columns contain the numbers used by Wilcox, Stephenson and Coburn in their notation, which is based on Herzberg's illustration of the vibrational modes of benzene. The SWC notation has been adopted by Durig and his co-workers.[28]

Columns 6 and 14 : Vibration Type.

In these columns, an attempt is made to give an approximate indication of the form of the vibrations. Some of these modes are "purer" than others. Thus, modes marked νC-H are essentially pure carbon-hydrogen stretching vibrations; the large difference between the frequencies of these vibrations and the other vibrations inhibits coupling. By contrast, the out-of-plane deformations ν16b and ν17b (x and y) are so strongly coupled that it is inaccurate to describe either of them as the "out-of-plane C-X bend". αCCC = in-plane ring deformation; νCC = carbon-carbon (ring) stretching vibrations; νC-X = phenyl-X stretching; ϕCC = out-of-plane ring deformation; βC-H = in-plane C-H bending; γC-H = out-of-plane C-H bending. The "ring" mode 13 (i.e. mode 13 in Varsanyi's notation) is a totally symmetric breathing of the whole ring.

Columns 7 and 15 : Frequency Range.

The values in these columns are reproduced from p.394 of Varsanyi's book; they indicate the region of the spectrum in which the various vibrations may be looked for. They are based on a compilation taken from data available up to 1966. All the data are taken from the spectra of compounds in condensed phases; this presumably accounts for the appearance of ν10a, ν16a, and ν19a in the infrared spectra.

Columns 8 and 16 : IR

The letters w=weak, m=medium, s=strong and v=very give an approximate indication of the relative intensities of fundamental frequencies in the infrared absorption spectra of monosubstituted benzenes. A designation such as w-m means that the relative intensity can vary between weak and medium.

Columns 9 and 17 : Ra

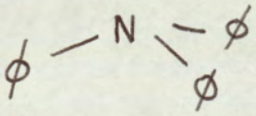
These columns give an indication of the relative intensities and degrees of depolarisation of Raman lines. The letter p indicates a polarised line. In general, vibrations which are derived from the totally symmetric modes of benzene give rise to Raman lines with a degree of depolarisation of less than 0.1; this applies in particular to the vibrations ν2 and ν12. The degree of depolarisation of the other A_1 vibrations varies considerably, that of ν8a (marked p*) exceeding 0.5 in some cases. The Raman lines marked ‡ are not normally observable as separate lines since they are obscured by the extremely intense line due to ν2.

5.3. The Effect of Inter-Ring Coupling on the Phenyl Spectra.

5.3.1. The determination of the species of the phenyl and skeletal vibrations in various triphenyl point groups.

In the discussion which follows, Whiffen's notation will be used, because it has been chosen by most previous workers in this field.

The triphenylamine molecule contains thirty-four atoms and it will therefore have ninety-six fundamental vibrations. If we assume that the molecule has a C_3 axis passing through the nitrogen atom in the direction of the lone pair, then we can regard these fundamentals as being made up of ninety vibrations from the phenyl groups together with six new modes arising from the fact that the three groups are joined at the nitrogen atom. The six new modes will comprise one symmetric and one asymmetric (doubly degenerate) bend of the



system, and one symmetric and one asymmetric torsion of the phenyl groups relative to one another. The degrees of freedom corresponding to stretching of this system are included in the phenyl group vibrations.

Each of the thirty phenyl group vibrations mentioned in the previous chapter will couple through the central atom to give one in-phase non-degenerate vibration and one out-of-phase and doubly degenerate vibration.[15,27] The distribution of the thirty phenyl vibrations among the various symmetry species of the point group D_{3h} was worked out by using a correlation table for the point group D_{3h}. For example, the phenyl vibration q transforms as A_1 in the point group C_{2v} of a monosubstituted benzene (see Table 5.2). By looking down the column under the heading C_{2v} in Table 5.3, we locate the A_1 species and note that it transforms as A_1' and as E' in the point group D_{3h}, as A_1 and E in the point group D_3, and so on.

D_{3h}	C_{3h}	D_3	C_{3v}	C_{2v}	C_3
A_1'	A'	A_1	A_1	A_1	A
A_2'	A'	A_2	A_2	B_1 or B_2	A
E'	E'	E	E	A_1 + (B_1 or B_2)	E
A_1''	A''	A_1	A_2	A_2	A
A_2''	A''	A_2	A_1	B_2 or B_1	A
E''	E''	E	E	A_2 + (B_2 or B_1)	E

Table 5.3. A correlation table for the species of the point group D_{3h} and its subgroups (adapted from ref.32).

A minor complication arises from the fact that the species B_1 and B_2 in the point group C_{2v} are determined by the conventional specification of axes shown in fig.5.2.

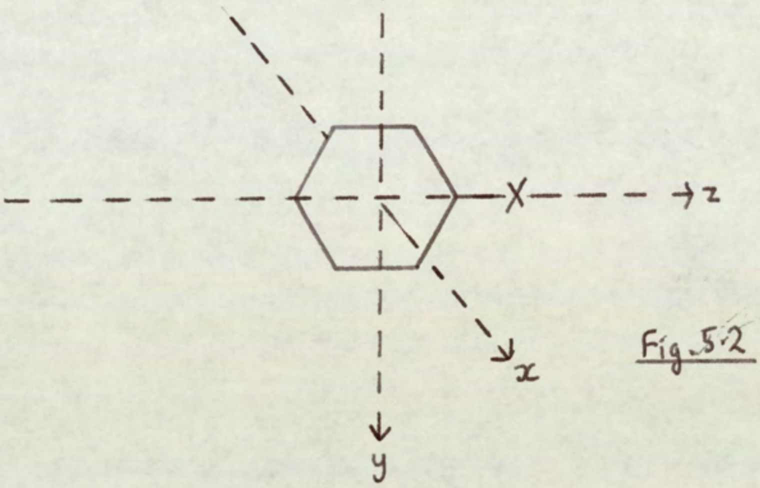
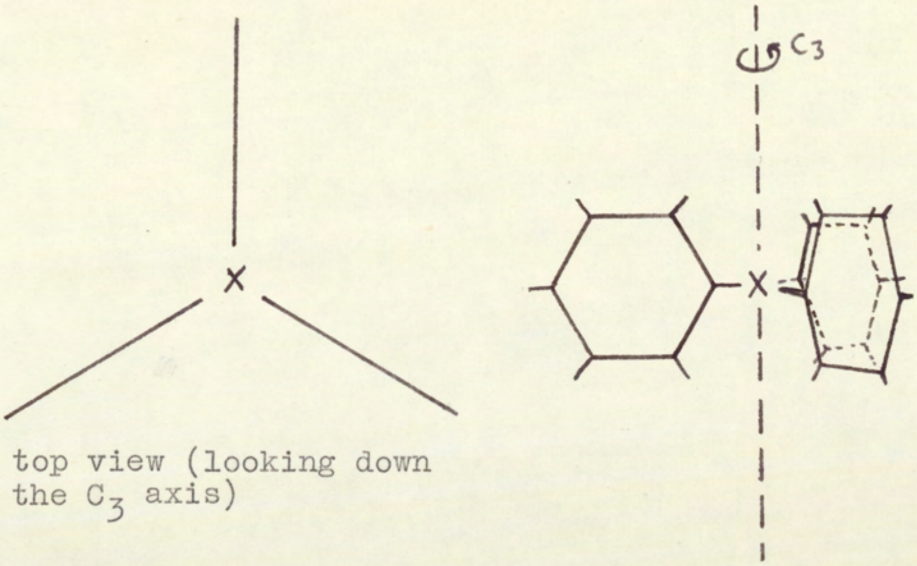


Fig. 5.2

In the vertical D_{3h} structure shown in fig.5.3, the yz planes shown in fig.5.2 are identical with the σ_v planes of the point group D_{3h}. In this case, the first of the alternative sets of species listed in the column under C_{2v} in Table 5.3 must be used. This follows from a comparison of the character tables of the point groups C_{2v} and D_{3h}. The B_2 phenyl vibrations are symmetric w.r.t. reflection in the yz plane; inspection of the D_{3h} character table shows that the non-degenerate species which preserves this feature is A_2''. On the other hand, the B_2 phenyl vibrations are antisymmetric w.r.t. inversion in the xz plane, which corresponds to σ_h in the D_{3h} point group. The degenerate species in D_{3h} which preserves this antisymmetry is E''.

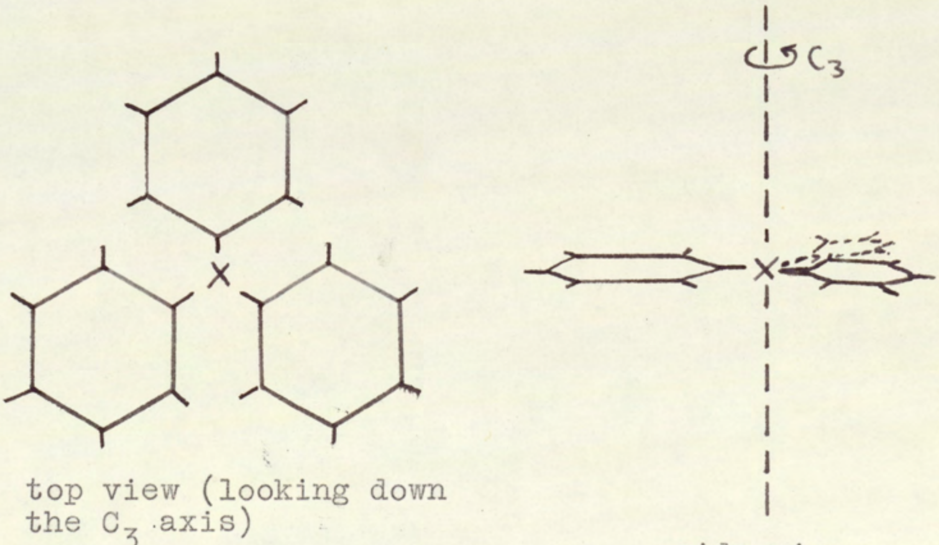
In the 'flat D_{3h}' structure shown in Fig.5.4, the B_2



top view (looking down the C_3 axis)

side view

Fig. 5.3. Vertical D_{3h} structure for a $(\text{phenyl})_3X$ molecule.



top view (looking down the C_3 axis)

side view

Fig. 5.4. Flat D_{3h} structure for a $(\text{phenyl})_3X$ molecule.

phenyl vibrations are now antisymmetric w.r.t. reflection in the σ_v planes of the D_{3h} point group, so they transform as A_2'; the corresponding degenerate species is E', which preserves the symmetry of these vibrations w.r.t. reflection in the σ_h plane. The statements made in the preceding paragraph about the B_2 phenyl vibrations are now true of the B_1 phenyl vibrations instead. In summary, the effect of changing from a vertical D_{3h} structure to a flat structure is to interchange the B_2 and B_1 species, so the second alternative set of species must be used.

A further example should help to show how the considerations described here are applied in practice. The phenyl vibration u can be described as an in-plane bending mode of the phenyl-X linkage. From Table 5.3, we note that it belongs to the species B_2. Looking down the column under C_{2v} in Table 5.3, we note that this vibration splits into A_2'' and E'' components in the 'vertical' D_{3h} structure (choosing the first of the alternatives), and into A_2' and E' components in the 'flat' D_{3h} structure (choosing the second of the alternatives).

The symmetry species of the skeletal vibrations were determined by inspection. The symmetric skeletal bend

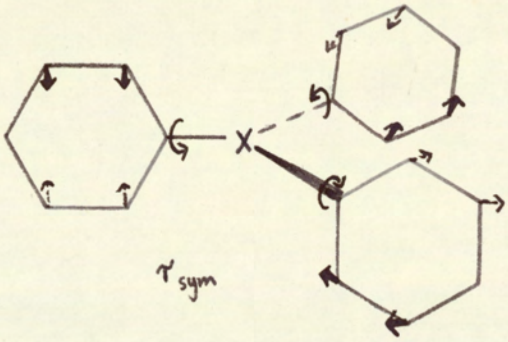


Fig. 5·5

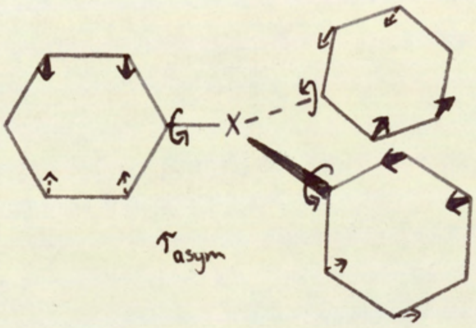


Fig. 5·6

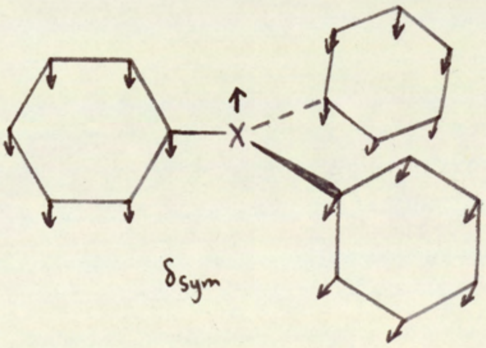


Fig. 5·7

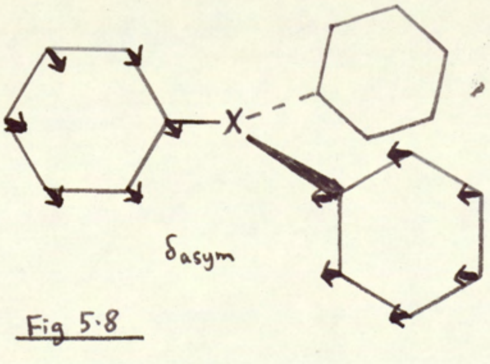


Fig 5·8

(δ_{sym}, Fig.5.7) of the (phenyl)$_3$X unit preserves the three σ_v planes of D_{3h} but is antisymmetric w.r.t. σ_h: the only species in the character table for D_{3h} which incorporates this feature is A_2''. On the other hand, the asymmetric and doubly degenerate bend (δ_{asym}, Fig.5.8) is symmetric w.r.t. σ_h and must therefore transform as E'. The torsions τ_{sym} and τ_{asym} (Fig.5.5 and 5.6) are both antisymmetric w.r.t. σ_h. τ_{sym} is also antisymmetric w.r.t. σ_v. These considerations apply in both the flat and vertical D_{3h} structures, so τ_{sym} transforms as A_1'' and τ_{asym} as E''.

The effect of lowering the symmetry from D_{3h} on the classification of all these vibrations in the point groups of lower symmetry was then determined by using the correlation table 5.3. The distinction between the in- and out-of-plane phenyl vibrations (B_1 and B_2 species) is preserved in the 'flat' and 'vertical' C_{3v} structures which result when the σ_h plane of D_{3h} is lost, and this has important consequences which are discussed in section 5.4.3. These species are, however, mixed in the D_3 and C_3 point groups. The species for C_{3h} are included here because although this is not a feasible point group for a triphenyl compound, it could describe one of the possible symmetries for the tri(2-pyridyl) amine molecule.

The results are summarised in Table 5.4. The infrared and Raman activities of the vibrations were determined by inspection of the character table for the appropriate point group. If the vibration belongs to the same symmetry species as a translation of the molecule, it will be infrared-active; this is indicated by the presence of the symbol $T_{(x, y, \text{ or } z)}$ to the right of the characters for that symmetry species. If the vibration belongs to the same symmetry species as one of the components of the polarisability tensor (denoted by terms such as α_{xy} appearing in the column to the right of the characters) then it will be Raman active.

A final check on the results presented in Table 5.4. was made by setting up molecular models of the 'flat' and 'vertical' D_{3h} structures and then finding the structures of the irreducible representations of the molecular vibrations by the method of Wilson.[33] The numbers of vibrations in each species, calculated in this way, corresponded exactly with the numbers of vibrations assigned to each species by the methods outlined above.

The group theoretical treatment presented here shows that it should be possible, <u>in principle</u>, to assign a point group symmetry to a triphenyl compound by finding the number of components into which assignable phenyl vibrations are split in the vibrational spectra of the triphenyl compound. For example, if strong Raman lines without infrared coincidences are found in the positions expected for the A_1 (in C_{2v}) x-sensitive phenyl vibrations q, r, and t, then reference to Table 5.4 shows that the point group symmetry of the molecule in question is likely to be either D_{3h} or D_3. Examination of the multiplets assignable to the B_1 and B_2 phenyl vibrations should then enable a choice to be made between flat D_{3h}, vertical D_{3h}, and D_3 ; thus, if only one component of the out-of-plane bending vibration x can be identified, and if this is found in both infrared and Raman spectra, then reference to Table 5.4 shows that the likely symmetry is 'vertical' D_{3h}.

In practice, however, the application of these apparently straightforward selection rules must be carried out with some caution, for three main reasons.

First of all, the fact that a splitting is predicted does not necessarily mean that it will be observed. The extent to which a given phenyl vibration is x-sensitive depends on the magnitudes of the changes in the phenyl-x distance and the adjoining bond angles which occur during the vibration. The width of the frequency range given in Table 5.2. is a measure of the x-sensitivity of a given vibration; the larger the range of values, the more x-sensitive the vibration. Since any splitting of a phenyl vibration caused by inter-ring coupling must involve transmission of some vibration through the central atom, it follows that the splitting of phenyl vibrations will increase as the x-sensitivity of the vibrations increase. In other words, a phenyl vibration which is not x-sensitive will not interact appreciably with the corresponding vibrations in the other phenyl rings. This is particularly likely to occur if the mass of the central atom is large, since such atoms should act as effective insulators between the phenyl groups. In general, the magnitude of splittings due to inter-ring coupling should decrease rapidly with increasing mass of the central atom. As a result, the splitting of vibrations of this type is likely to be too small to be observed. It must not be assumed, therefore, that if only one component of a phenyl vibration is observed, the other must be forbidden by the selection rules.

Splitting of vibrations can occur for reasons other than inter-ring coupling. If the compound is being studied in the solid state, splittings may occur as a result of intermolecular vibrational coupling, or because of the situation of molecules on lattice sites of low symmetry. Alternatively, slight separation of frequencies can arise from the presence of molecules in non-equivalent sites in the crystal lattice. Fermi resonance is yet another possible cause. These effects make it very difficult to recognise genuine splittings due to inter-ring coupling in solid-state spectra.

Finally, it is clear from a perusal of Table 5.4 that Raman data ~~is~~ are essential if the symmetric components of all the split vibrations in molecules of D_{3h} or D_3 symmetry are to be located. In the lower symmetry point groups, Raman data is also of considerable value in identifying symmetric components of split vibrations, since the corresponding Raman lines should exhibit some degree of polarisation. In view of these considerations, assignments based solely on infrared data must be treated with circumspection.

To sum up, the credibility of any vibrational assignments in molecules in which inter-ring coupling occurs depends on whether the compound is studied in solution or in the solid state only, and also on whether Raman data are used in conjunction with infrared measurements.

Table 5.4.

Point group	Symmetry Species	Vibrations	No. of vibrations Phenyl	 Skeletal	Activities
D_{3h} flat (Fig.5.4)	A_1	a,b,k,m,p,q,r,t,z_1 z_2,z_3,	11	0	Ra, pol
	A_2'	c,d,e,l,n,s,u,o,z_4 z_5	10	0	inactive
	E'	a',b',k',m',p',q', r',t',z_1',z_2',z_3', c',d',e',l',n',s', u',o',z_4',z_5' δ_{as}			I.R. + Ra depol
	A_1''	g,h,w,τ_{sym}	3	1	inactive
	A_2''	f,i,j,v,x,y, δ_{sym}	6	1	I.R.
	E''	g',h',w',f',i',j', v',x',y',τ_{as}	9	1	Ra, depol
		total	90 +	6 = 96	

C_{3v} flat (Fig.5.7)	A_1	a,b,k,m,p,q,r,t,z_1, z_2,z_3,f,i,j,v,x,y,δ_s	17	1	I.R. + Ra pol
	A_2	c,d,e,l,n,s,u,o,z_4, z_5,g,h,w,τ_s	13	1	inactive
	E	a',b',k',m',p',q', r',t',z_1',z_2',z_3',c', d',e',l',n',s',u', o',z_4',z_5',g',h',w', f',i',j',v',x',y', δ_{as},τ_{as}	30	2	I.R. + Ra depol
		total	90 +	6 = 96	

Table 5.4. (continued)

Point group	Symmetry Species	Vibrations	No. of vibrations Phenyl	 Skeletal	Activities
D_{3h} vert (Fig.5.3)	A_1'	a,b,k,m,p,q,r,t,z_1, z_2,z_3	11	0	Ra, pol
	A_2'	f,i,j,v,x,y,	6	0	inactive
	E'	a',b',m',k',p',q', r',t',z_1',z_2',z_3',f',i', j',v',x',y',τ_{as}	17	1	I.R. + Ra depol
	A_1''	g,h,w,τ_s	3	1	inactive
	A_2''	c,d,e,l,n,o,s,u,z_4, z_5,δ_s	10	1	I.R.
	E''	g',h',w',c',d',e', l',n',o',s',u',z_4, z_5, δ_{as}	13	1	Ra, depol
		total	90 +	6 =	96

Point group	Symmetry Species	Vibrations	Phenyl	Skeletal	Activities
C_{3v} vert	A_1	a,b,k,m,p,q,r,t,z_1, z_2,z_3,c,d,e,l,n,o, s,u,z_4,z_5,δ_s	21	1	I.R. + Ra pol
	A_2	f,i,j,v,x,y,g,h,w, τ_s	9	1	inactive
	E	a',b',k',m',p',q', r',t',z_1',z_2',z_3',c', d',e',l',n',o',s', u',z_4',z_5',f',i',j', v',x',y',g',h',w', δ_{as}, τ_{as}	30	2	I.R. + Ra depol
		total	90 +	6 =	96

Table 5.4. (continued)

Point group	Symmetry Species	Vibrations	No. of vibrations Phenyl	Skeletal	Activities
D_3	A_1	a,b,k,m,p,q,r,t,z_1, z_2,z_3,g,h,w,τ_s	14	1	Ra, pol
	A_2	c,d,e,l,n,s,u,o,z_4, z_5,f,i,j,v,x,y,δ_s	16	1	I.R.
	E	a',b',k',m',p',q', r',t',z',z',z',g', h',w',c',d',e',l', n',s',u',o',z',z', f',i',j',v',x',y', τ_{as}, δ_{as}	30	2	I.R. + Ra depol
		total	90 +	6	= 96
C_3	A	a,b,k,m,p,q,r,t,z_1, z_2,z_3,g,h,w,c,d,e, l,n,s,u,o,z_4,z_5,f, i,j,v,x,y,τ_s, δ_s,	30	2	I.R. + Ra pol
	E	a',b',k',m',p',q', r',t',z'_1,z'_2,z'_3,g', h',w',c',d',e',l', n',s',u',o',z',z',f',i' f',j',v',x',y', τ_{as}, δ_{as},	30	2	I.R. + Ra, depol
		total	90 +	6	= 96

Key. Unprimed l.c.letters = symmetric components of Whiffen's phenyl vibrations.
Primed " " = asymmetric components of Whiffen's phenyl vibrations.
δ_s = symmetric deformation (Fig.5.7)
τ_s = symmetric torsion (Fig.5.5)
τ_{as} = asymmetric torsion (Fig.5.6)
δ_{as}= asymmetric deformation (Fig.5.8)
I.R = infrared active; Ra = Raman active;
pol = polarised Raman lines ($\rho \leqslant 0.75$);
depol = depolarised Raman lines ($\rho > 0.75$).

5.4. The effect of coupling on phenyl spectra : a survey of the literature.

Some idea of the scope of previous work in this field is given in Table 5.5. It is obvious that many of these studies fall far short of meeting the experimental criteria outlined at the end of the previous section.

5.4.1. Triphenylamine

Coupling effects in this molecule must be expected to be quite considerable, in view of the low mass of the central atom. In the absence of Raman data and solution studies, the assignments attempted[14,15,16] for x-sensitive vibrations must be regarded as being largely speculative. Thus, it was suggested that the splitting of infrared bands near 420 cm^{-1} is due to crystal effects,[16] yet we have found that the splitting persists in solution spectra. By comparing the spectrum of triphenylamine with the spectra of compounds believed to have a planar configuration about the central atom (triphenylboron and the triphenylcarbonium ion) and also with the spectra of related compounds which were known to be tetrahedral, Sharp et. al.[14] concluded that the infrared spectrum of triphenylamine favoured a planar arrangement about the central nitrogen atom (D_3 symmetry).

5.4.2. Triphenylphosphine.

In early studies[16,17] of the spectra of this molecule, the effects of inter-ring coupling on the x-sensitive vibrations were not fully appreciated. Thus, Goubeau and Wenzel assigned bands at 1090, 687 and 442 cm^{-1} to the three x-sensitive A_1 phenyl vibrations[17]; they then assigned another pair of bands at 397 cm^{-1} and 493 cm^{-1} to $\nu_s PC_3$ and

Table 5.5.

Compound Studied	Physical State(s)	Spectral Range Covered		Coupling effect discussed.	Reference
		I.R. (cm^{-})	Raman ($\Delta\nu$, cm^{-1})		
Triphenylamine	solid	1700-650	-	Yes	14
"	solid	1700-650	-	Yes, in detail	15
"	solid	650-200	-	No	16
Triphenylphosphine	solid	4000-280	1700-600	No	17
"	solid	650-200	-	No	16
"	solid and solution	667-222	-	No	18
"	solid*	1600-375	1600-400	Yes	19
"	solid and solution	550-100	500-50	Yes	20
"	solid*	1500-50	1500-50	No	21
Triphenylarsine	solid	650-200	-	No	16
"	solid	4000-250	-	Yes	22
"	solution	4000-200	1600-50	Yes	23
"	solid and solution	550-100	500-50	Yes	20
"	solid	1500-50	1500-50	No	21
"	solution	-	1600-50	Yes	24
Triphenylboron	solid	1700-650	-	Yes	25
"	solid and solution	4000-400	-	Yes	26
Triphenylcarbonium salts	solid	1700-650	-	Yes	25
"	solid	4000-300	-	Yes, in detail	27

Table 5.5. (continued)

Compound Studied	Physical State(s)	Spectral Range Covered		Coupling effect discussed	Reference
		I.R. (cm⁻)	Raman ($\Delta\nu$, cm^{-1})		
Triphenyl-methane	solid	1700-650	-	Yes	25
"	solid and solution	667-222	-	No	18
"	(not stated)	650-50	650-50	No	27
Triphenyl-silane	(not stated)	600-50	600-50	No	27
Triphenyl-germane	liquid	4000-33	4000-33	Yes, in detail	29

ν_{as} PC_3, respectively. In fact, the degree of freedom corresponding to P-C stretching is incorporated into the three X-sensitive A_1 phenyl vibrations, so that the "ν_{as} PC_3" and "ν_s PC_3" vibrations are spurious.

In more recent studies, coupling effects have been considered, and infrared studies over a wider frequency range, together with Raman data,[19,20,21] have permitted satisfactory assignments to be made for most of the vibrations. In general, small splittings (less than 30 cm^{-1}) were observed in the phenyl vibrations t, u, x and y, and most of the other split components of phenyl vibrations were found to be accidentally degenerate. The assignments were made by comparing the position and intensity of observed spectral features with results obtained for other compounds in which the vibrational assignments are well established. Only one controversial point merits some discussion: this concerns the assignments for x, an out-of-plane bending mode of the ring, and the in-plane ring bending mode u.

5.4.3. The effect of inter-ring coupling on the vibrations x and u.

The majority of workers assign a group of vibrations occurring between 200 and 280 cm^{-1} to u, and the lower frequency group between 155 and 220 cm^{-1} to x. These authors are presumably relying on the results of calculations performed by Whiffen and others, who obtained a reasonable fit with their data for simple monosubstituted benzenes by assuming that the out-of-plane bending force constant is lower than the in-plane deformation force constant.[1,5,7.] This approach certainly seems to give consistent assignments when the spectra of compounds of the type Ph-MX_2 are compared with the spectra of the corresponding di- and triphenyl compounds.[22] The only divergent view is that held by Nakamoto,[20] and it is based on intensity arguments. He states that since the x vibrations of monosubstituted benzenes are generally weak in the infrared but strong in the Raman - whereas u vibrations appear weakly in both infrared and Raman - his x vibrations must be the higher-frequency group, in view of the fact that a strong polarised Raman line appears in this group as a persistent feature.

In our view, the assignment of the higher-frequency group of vibrations to u is more convincing, because an alternative explanation is available for the appearance of a strong polarised Raman line in this group. Unless the symmetry is C_3, with an angle of twist of exactly 45°, the totally symmetric bending vibration δ_{sym} of the $(Ph)_3M$ skeleton should couple strongly and preferentially with either u or x and y. Reference to Table 5.4 shows that preferential coupling of δ_{sym} with x and y will occur if the structure of the molecule approximates to a "flat" C_{3v} or D_{3h} structure. In fact, neither of these ~~are~~ is likely, because of non-bonding interactions between neighbouring ortho-hydrogen atoms, but if this coupling did occur, then some polarisation of the Raman line corresponding to the symmetric component of y (as well as x) should be observed. The majority of workers in this field have failed to identify a polarised component of the Raman line corresponding to y, so the assignment of the polarised lines to the symmetric component of u seems more consistent with all the data available. x is then assignable to the lower group of vibrations.

5.4.4. Triphenylarsine.

This compound has been the subject of several recent detailed studies, and its vibrational assignment seems well established. As expected, the magnitude of the splittings found - generally less than 10 cm^{-1} - was smaller than in the corresponding vibrations of triphenylphosphine.

5.4.5. Triphenylboron.

It is unfortunate that this compound has not been made the subject of a comprehensive infra-red and Raman study, since the results would have been relevant to the present work, in view of the close structural similarity expected between triphenylamine and triphenylboron. Although an assignment has been proposed[26] it is based solely on infra-red absorptions observed between 4000 and 400 cm^{-1}, and accordingly the x-sensitive vibrations t, x and y were left unassigned. However, certain observations[25,26] seem compatible with an overall symmetry of D_3 for this molecule.

5.4.6. Triphenylcarbonium salts.

The triphenylmethyl cation in triphenylmethyl perchlorate is very similar in structure to triphenylamine. An X-ray study has shown that the three central C-C bonds are coplanar, with lengths of 14.54 nM[30]. In triphenylamine, a slight distortion from planarity in the three C-N linkages occurs in the vapour ($\widehat{CNC} = 116^\circ \pm 2^\circ$), and the corresponding bond length is 14.2 nM.[31] The angles by which the aromatic rings twist out of the plane of the central atoms differ somewhat. The angles ($47^\circ \pm 5^\circ$) in triphenylamine are presumably greater than the angles in the triphenylmethyl ion (32^{o}) because of the smaller degree of π-overlap expected in the former compound.

Weston et. al. showed awareness of the effects of inter-ring coupling on the distribution and activity of the phenyl and skeletal vibrations in the various point groups possible for the compounds they studied (triphenylmethyl fluoborate, triphenylcarbinol, triphenylmethyl chloride and their 1 - ^{13}C and -D^{5} analogues),[27] but they failed to appreciate that the magnitude of the splitting of a phenyl vibration depends markedly on the x-sensitivity of the vibration. Alternative assignments for asymmetric components of the r and t modes are proposed in Chapter 7, but it is clear that Raman data are required before the assignment of the vibrations of these molecules can be said to have been completed.

5.4.7. and 5.4.8. Triphenyl compounds of group IVA elements.

The Raman and infrared spectra of a wide range of molecules of the type $(\text{phenyl})_3MX$ have been reported.[25, 28, 29] (M = C, Si, Ge, Sn and Pb; X = H, Cl and CH_3). Splitting of the phenyl modes t, u, x and y was almost always observed. The magnitude of these splittings decreased in the order $t \gg u > x > y$ and, as expected, $C \gg Si > Ge > Sn > Pb$.

Chapter 6 : Experimental.

6.1. Spectroscopic Methods.

6.1.1. Infrared Spectra.

6.1.1.1. 4,000 - 195 cm^{-1}

Spectra in this range were recorded on a Perkin-Elmer 225 Spectrophotometer. Scale expansion was used so that each of the sub-ranges 4,000-2,000 cm^{-1}, 2,000-1,000 cm^{-1}, 1,000-400 cm^{-1}, and 410-195 cm^{-1} (these sub-ranges are determined by various combinations of gratings and filters) was accommodated on about 50 cm. of chart paper. The slit programme was set so that the spectral slit width varied from 1 cm^{-1} at 4000 cm^{-1} to 4 cm^{-1} at 195 cm^{-1}. The average spectroscopic slit width throughout the whole range was about 1 cm^{-1}, but it tended to increase to about 4 cm^{-1} in the first and last 10 cm^{-1} of each sub-range. In order to reduce the risk of recording distorted band shapes, artefacts, or other spurious features, each trace was repeated using different settings of the scanning speed, gain, and time constants. The instrument was calibrated as described in part one: the frequencies recorded in the tables are considered to be accurate to within ± 2 cm^{-1} for sharp bands in the region 4,000 - 1,000 cm^{-1} and to within ± 1 cm^{-1} in the region 1,000 - 195 cm^{-1}. The interior of the instrument was continuously purged with dry air while spectra were being recorded.

Solid-state spectra were obtained at ambient temperatures for samples in the form of nujol and fluorocarbon mulls supported between caesium iodide plates, and for some samples as discs pressed in a caesium iodide matrix. Spectra were recorded for saturated solutions in matched 0.5 mm or 1.0 mm cells with caesium iodide windows. Some spectra were also obtained in an 0.5 mm cell with potassium bromide windows, used in conjunction with a variable-path cell with potassium bromide windows. The solvents used were of spectroscopic grade and were dried over 4Å molecular sieves.

Spectra at 120 ± 10 K were measured for samples in the form of nujol or vaseline mulls using a RIIC VLT-2 variable-temperature cell holder. The silicone elastomer seals provided for the entry of heating and thermocouple wires were found to leak and they were accordingly replaced by permanent joints made with Araldite. The temperature of the sample in the beam was estimated by inserting the tip of a chromel-alumel thermocouple into a small blind hole drilled in the caesium iodide mull support plate, and the cell was set up so that this hole was facing the entrance slit of the spectrophotometer (Fig.6.1). The temperature estimated in this way was found to differ appreciably (10 - 20 K) from the temperature of the cell holder measured at the point A as recommended by RIIC. Moreover, the magnitude of this temperature difference was observed to be a function of the thickness and absorbtivity of the sample. However, for the purpose of this work, an accurate knowledge of the temperature of the sample was considered to be less important than an ability to ascertain when the sample had reached a steady temperature. In the low-temperature work described here, the 'hot' junction of the thermocouple was kept in an ice-bath while liquid nitrogen was poured into the coolant reservoir until the thermocouple e.m.f., which was traced on a recording millivoltmeter, reached a steady value. Between twenty and twenty-five minutes was required to

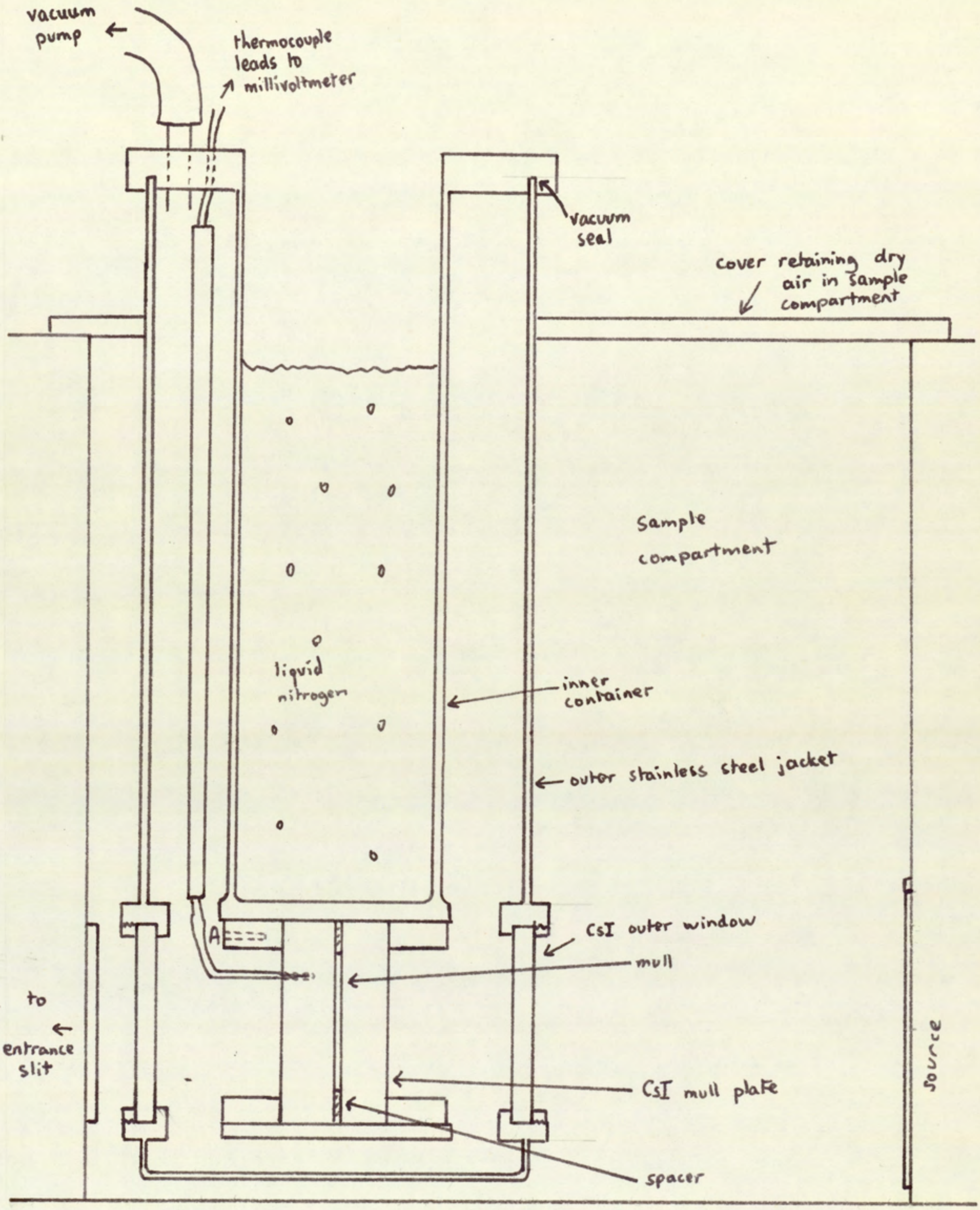


Fig. 6.1. The R.I.I.C. VLT-2 Low-temperature Cell

cool the sample from ambient temperature to a steady temperature. The calibration of the thermocouple was checked by immersing the 'cold' junction in boiling nitrogen. The heating effect of the intense beam of radiation from the Globar source is demonstrated by the observation that with no external heating or cooling, a typical nujol mull sample reached a temperature of between 310 and 320 K after being allowed to stand in the beam for an hour. The precise temperature reached was found to depend on the colour and thickness of the sample, the concentration of the mull, and the thickness and condition of the mull plates.

6.1.1.2. 400 - 40 cm^{-1}.

Spectra in this region were computed from Fourier transforms produced by an RIIC FS-720 Fourier Spectrophotometer. The computation was carried out on an ICL 1905 computer using a program written by RIIC and modified to output drawn spectra on a graph plotter. The transmitted intensity was recorded on punched tape for a total of 1024 positions of the moving mirror, giving an effective resolution of 2 cm^{-1} on the computed spectra. A full description of this instrument, its operation, and of some problems encountered in its use has been prepared by Thompson.[35] The wavenumber calibration was checked by comparing a recorded spectrum of atmospheric water vapour with published data,[36] and also by comparing the positions of sharp bands observed in the region of overlap with the Perkin-Elmer 225 spectrophotometer (400 - 195 cm^{-1}). An interferogram (i.e. a continuous recording of a voltage proportional to the transmitted output of the Golay detector) was traced for each run, and data tapes obtained for runs in which sharp 'spikes' appeared on the interferogram eleswhere than at the zero path difference position were rejected, since these tapes were found to give a meaningless saw-tooth pattern when computed. Separate data tapes were obtained for each sample by causing the moving mirror to travel in both directions through the zero path position, and the risk of recording spurious bands was reduced further still by obtaining spectra for each solid sample as mulls in vaseline at different solid concentration, so that four computed spectra were obtained for each sample. The mulls were supported in vacuum-tight cells using an 0.1 mm spacer between 'Rigidex' polythene supports. Background runs of vaseline between these plates showed no distinctive features other than a sharp band at 72 cm^{-1} and another weak and broad absorption centered at about 380 cm^{-1}. These spectra were indistinguishable from a spectrum of the empty cell. Vaseline was therefore preferred to nujol as a mulling agent, since it is less likely to leak into the vacuum of the instrument.

The bands at 72 and 380 cm^{-1} are attributable to polythene and were recognisable in most of the single-beam computed spectra. The interior of the Fourier spectrophotometer was evacuated to better than 0.1 mm/Hg. during each run.

Some far-infrared spectra spectra of common solvents were reported by Wyss. [37] Unfortunately, their results are of limited value in assessing the usefulness of these solvents in interferometric far-infrared spectroscopy. Since the detector in the FS-720 integrates all the radiation it receives in the frequency region below 600 cm^{-1} (the approximate limit set by the black polythene optics), any strong absorption in this region, due, for example, to hydrogen bonding or non-specific dipole-dipole interactions in polar solvents, will reduce the net amount of transmitted light and hence reduce the signal-to-noise ratio in the computed spectrum.

Test spectra show that this effect is sufficiently serious to make purified nitromethane and chloroform useless as solvents at path lengths exceeding 1.0 mm. (Commercial chloroform contains about 2% of ethanol as a stabiliser; this must be removed by passing the solvent over activated alumina. It was found that the transmission properties of nitromethane were also improved by this treatment). Grating spectrometers operating in this region, such as the Perkin-Elmer 301 and the Beckmann I.R.11, do not suffer from this disadvantage, since solute absorption bands can be sought and found in 'windows' of high % transmission in the solvent spectrum. This disadvantage of interferometric spectrophotometers has received scant attention in the literature, yet it is of considerable significance, since many organometallic compounds, complexes, and other compounds having molecular vibrations in the far-infrared are sufficiently soluble for far-infrared solution measurements only in those solvents, such as chloroform and nitromethane, which absorb so strongly below 100 cm^{-1} that the S/N ratio is seriously reduced in computed spectra. This effect, coupled with the low extinction coefficients of the far-infrared absorption bands in the compounds studied in this work, severely curtailed opportunities to observe solution spectra using the FS-720.

6.1.2. Raman Spectra.

Most of the Raman spectra reported here were recorded on the Coderg PH1 Raman spectrophotometers at the Universities of Kent and Leicester, using 632.8 nM He-Ne laser excitation. However, a few solid-state spectra were also recorded on the Cary 81 Raman spectrophotometer at the University of Nottingham, using 632.8 nM excitation, and on the Coderg instrument at Leicester using an Argon ion laser, in order to check for the presence of grating ghosts and non-lasing emission lines in the Raman spectra obtained using the Coderg instruments with 632.8 excitation. No artefacts or ghosts were found in any of the duplicated spectra. However, weak sharp lines near $\Delta\nu = 180$ cm^{-1}, $\Delta\nu = 433$ cm^{-1}, and $\Delta\nu = 828$ cm^{-1} appeared in some spectra obtained using 632.8 nM excitation. The increase in the intensity of these lines observed on removing the interference filter showed them to be non-lasing neon lines, since these lines are expected in these positions.[38]

Explicit instructions in English for the operation of the Coderg Raman instrument are not commercially available, so the procedures used to obtain Raman spectra of solids and solutions will be described here in some detail. The optical layout of the Coderg spectrophotometer is shown schematically in Fig.6.2 ; many components have been omitted for clarity. The sample at X is illuminated by an intense beam of radiation from a gas laser. Two types of laser are currently in general use as Raman sources. The first is a laser containing a mixture of helium and neon which is tuned to emit nearly all of its radiation in a coherent line at 632.8 nM in the red region of the visible spectrum. A few non-lasing emission lines of neon are also excited, but these can be removed if necessary by placing a thin-film interference filter between the source and the sample, The He-Ne lasers used in this work produced a total output power of between 40 and 85 mW. The second type of laser, which can emit monochromatic radiation of greater intensity, but which is more expensive and less reliable emits a series of lines from ionised Argon containing a small proportion of Krypton. Most of the output power of 2 - 3 W is concentrated in a line in the green region of the visible spectrum at 514.5 nM. This laser was found to cause intense fluorescence and photodecomposition of most of the compounds studied in this work, so its use was limited to obtaining duplicate spectra of a few solids as a check on the spectra obtained with the He-Ne laser. The lasers were switched on and allowed to stabilise for one hour before obtaining spectra.

With a few exceptions, solids were examined as samples weighing between 5 and 10 mg in glass capillary tubes. The best spectra (i.e. spectra with high signal-to-noise ratios) were obtained from crystalline solids having a high ratio of volume to surface area. In other words, it was found disadvantageous to grind the sample before introducing it into the capillary tube, and prismatic crystals were found to give better results than needles. The best results of all were obtained for tri(2-pyridyl)arsine; this compound was obtained, after purification, as large prisms (approximately 5 mm x 5 mm x 2 mm). These crystals were mounted with epoxy adhesive on the ends of capillary tubes which were placed in the solid sample holder so that the laser beam impinged directly on the crystal. (No orientation effects were observed with this sample.) After setting the photomultiplier to 1 kV, the amplifier time constant to 3, and the (low-noise) amplifier gain to 5, the chart recorder was switched on and the recorder gain set at 1. The slits were then opened to 4 and the monochromator scanned until movement of the recorder pen showed that a strong Raman line in the sample had been located. The monochromator was then scanned slowly to maximise the intensity for the chosen line. The position of the sample in relation to the laser beam was then adjusted using the eccentrics provided at the base of the sample holder until no further increase in the intensity of the line relative to the background could be observed, taking care not to allow direct reflections from the glass capillary to enter the spectrometer. The scattered light was then focussed on the spectrometer entrance slit using the controls A and B (Fig.6.2) The intermediate slit S_2 was then gradually closed until a sharp and rapid reduction in the signal intensity was observed. This adjustment markedly reduces the amount of stray light reaching the photomultiplier.

The purpose of the 'backing-off' control is to introduce a variable e.m.f. in opposition to the photomultiplier output so that the variation in this output as a function of wavelength (i.e. the photoelectrically recorded spectrum) over a selected e.m.f. interval determined by the recorder gain (in this case 1 mV) can be displayed on the chart recorder for any reasonable value of the total photomultiplier output.

in Figs.6.4 and 6.5, which illustrate the use of this control in obtaining the spectrum of a fluorescent material. This control must not be used indiscriminately, however, since an increase in the backing-off voltage results in an increase in the noise level on the spectrum.

On the Coderg instrument, an indicator light shows, for each setting of the amplifier time constant (this controls the noise level), when the fastest scanning speed which will not cause loss of resolution has been selected. By choosing suitable values for these parameters, and for the slit widths, photomultiplier voltage, and recorder gain, a selection of spectra was obtained for each sample. For example, one run was made with wide slits (8 cm^{-1}) and low recorder gain (5 mV) in order to observe very weak lines above the noise level, and another run was made with narrow slits (2 cm^{-1}) and high recorder gain (0.5 mV) in order to resolve closely spaced lines and to locate lines close to the exciting line.

The arrangement of the sample compartment or 'transfer plate' used in obtaining the Raman spectra of solutions is illustrated in Fig.6.2. Solutions were filtered directly into the liquid cell B, which had a volume of ca. 1.5 cm^3, using a syringe fitted with a 'millipore' filter. The cell was then placed in its holder at C, and the horizontal and vertical inclination of the mirror D were adjusted until at least five light 'tracks', produced by the multipass system, could be seen in the liquid. The Raman and scattered light were then focussed on the entrance slit, and operating parameters were selected as previously described.

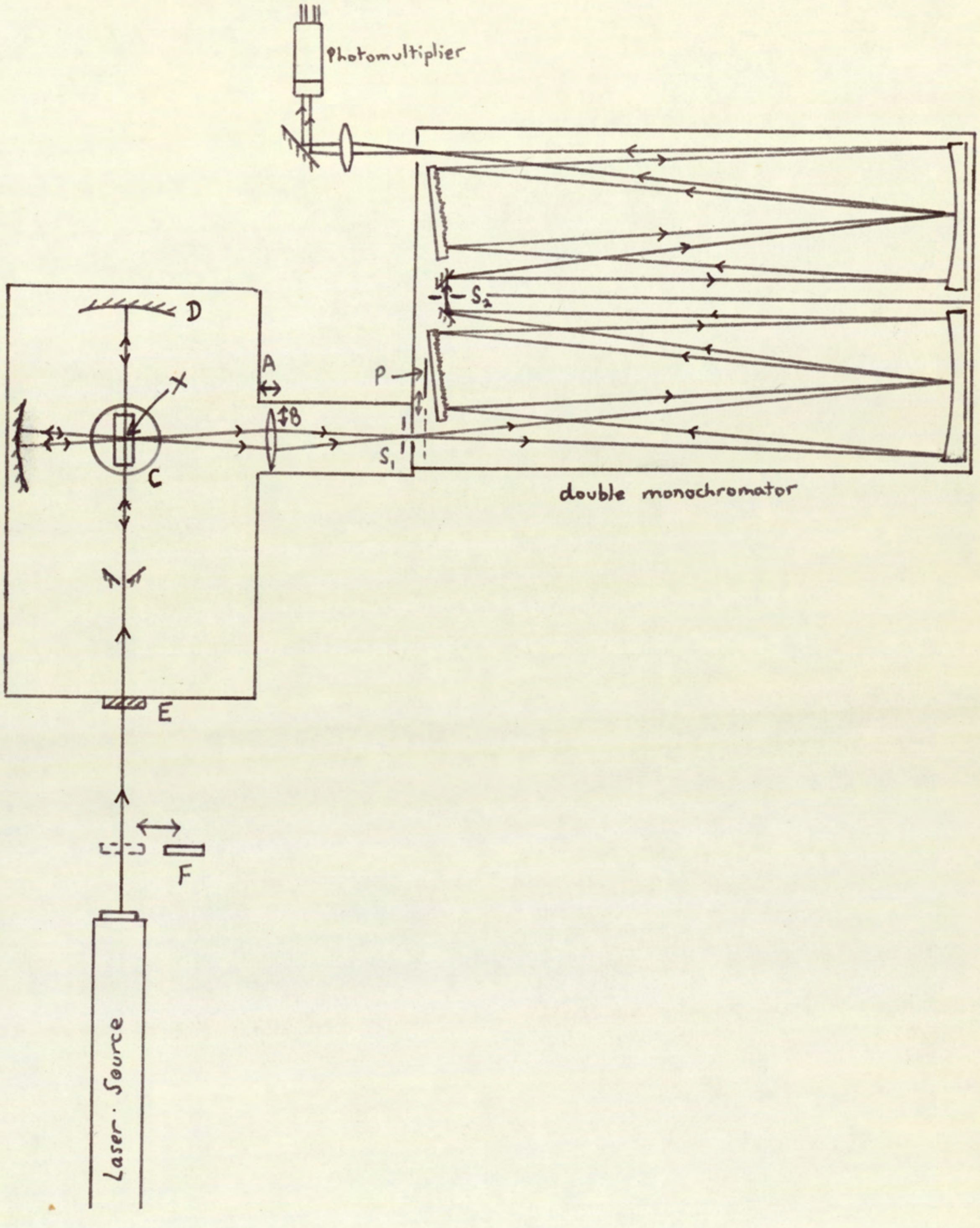


Fig. 6.2. Simplified Optical Diagram of the Coderg Spectrophotometer

The gas lasers used as sources produce light which is 100% linearly polarised in the vertical plane containing the cell filling tubes. Provision is made for rotating the plane of polarisation of the incident light by turning a half-wave plate at E through 90° about an axis coincident with the laser beam. Depolarisation ratios were measured using a polaroid analyser in the scattered beam which passed only vertically polarised light: spectra were obtained first with the half-wave plate set to pass vertically polarised light, and then with the half-wave plate set to pass horizontally polarised light. The use of a polaroid analyser ensures that the accuracy of the depolarisation measurements is a function of the efficiency of the multipass system rather than of the ability of the monochromator to pass only vertically polarised light. The efficiency of this system is demonstrated by the observation that depolarisation ratios of less than 0.01 were obtained for polarised Raman lines such as the ring breathing modes of benzene and pyridine, which indicates that very little of the polarisation of the incident beam is lost in reflections at the multipass mirrors or at the cell interfaces.

A thin-film interference filter was used for solid-state spectra in order to remove the non-lasing He-Ne plasma lines from the incident beam. This filter was removed for solution spectra, thereby achieving a useful gain in the intensity of the incident beam, since much less of the incident light is reflected directly into the spectrometer. The wavenumber calibration of the instrument was established by removing this filter and running a spectrum of the laser source by reflecting a fraction of the incident beam into the spectrometer off an empty glass capillary tube: a spectrum showing the plasma lines was obtained, and the position of the marker lines on the spectra, which are marked every 50 cm^{-1} of the monochromator travel, were calibrated using literature values[38] for the plasma lines. The calibration was subsequently checked from the positions of sharp lines in the spectra of solvents. The values recorded in the tables for the spectra of solids are considered to be accurate to within ± 2 cm^{-1} for strong lines, and to within ca. 5 cm^{-1} for weak lines. The values recorded from solution spectra are accurate to within only ± 5 cm^{-1} for strong lines, since the signal to noise ratio was generally lower than for solids, and it was normally found necessary to employ wider slit widths.

Spectroscopic grade chloroform was purified by passing it through a short column (10 cm x ca. 0.5 cm^2) of 'Camag' activated alumina (Grade 10). Spectroscopic grade pyridine was used without further purification. Details of the purification of the compounds studied are given with the details of their preparation.

2. Preparations.

(1) Triphenylamine.

Triphenylamine (B.D.H.) was recrystallised from aqueous ethanol using decolourising carbon to give pure white leaflets. Traces of a fluorescent impurity were removed from the saturated solution in chloroform used for Raman spectra by passing the solutions through alumina, as described for the solvent.

(2) Tri(2-pyridyl)amine.

This compound was prepared by a modification of the method of Wibaut and La Bastide[39] ; the original procedure involving steam distillation to remove 2-bromopyridine and the solvent mesitylene was found to be unsuitable for large-scale preparations.

(a) Materials.

Di(2-pyridyl)amine was obtained from the Reilly Tar and Chemical Corporation and was used without further purification. It was dried at 0.1 mm Hg/300 K before use. 2-bromopyridine (Koch-Light) was dried over anhydrous potassium carbonate and distilled under reduced pressure. Mesitylene (Hopkin and Williams reagent grade) was dried over anhydrous calcium chloride and distilled. A.R. anhydrous potassium carbonate was dried at 18)^{o} Copper bronze (B.D.H., for organic synthesis), potassium iodide, and disodium ethylenediaminetetra-acetate (Na_2EDTA) were used without further purification.

Procedure.

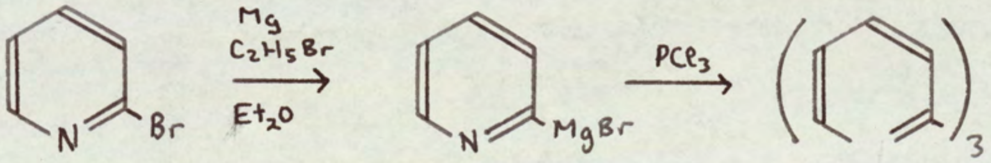
Di(2-pyridyl)amine (15.0 g) and 2-bromopyridine (10 cm^3) were dissolved in mesitylene (1) (200 cm^3) in a 1000 cm^3 three-neck flask fitted with a mechanical stirrer and a reflux condenser with drying tube. Finely powdered anhydrous potassium carbonate (10 g), copper bronze (6 g) and powdered potassium iodide ($\sim$ 0.1 g) were then added, and the mixture was heated under reflux with stirring for twenty hours. After cooling, the mixture was filtered and the residue extracted with boiling chloroform (3 x 100 cm^3). The volume of the combined filtrates was reduced to 100 cm^3 by distilling under reduced pressure. The solid which separated on cooling was filtered off, dried in vacuo, and recrystallised from a dilute aqueous solution (1 g in 500 cm^3) of Na_2EDTA (2) to give 13.9 g (64%) of tri(2-pyridyl)amine, m.p. 130° (lit.[39] 130°) (Found C,72.9; H, 4.90; N, 22.5. $C_{15}H_{12}N_4$ requires C, 72.5; H, 4.84; N, 22.6%). Repeated recrystallisation from water using decolourising carbon gave long (ca.5 mm) colourless needles which were used for Raman spectroscopy. Solutions used for Raman spectroscopy were purified by chromatography as described previously.

(1) A preparation using p-cymene as solvent failed to give an increased yield.

(2) The sequestering agent was added in order to remove copper(II) ions from solution, in order to prevent them from forming complexes with the product.

(3) Tri(2-pyridyl)phosphine.

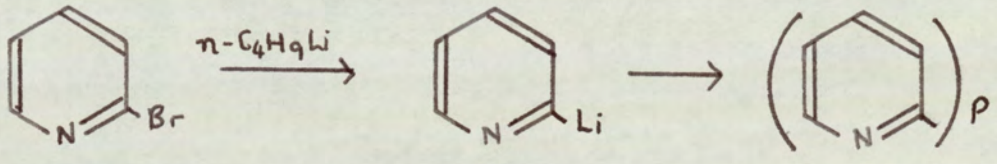
Two preparations of this compound have been reported. The first synthesis, by Mann and Watson,[40] involved the addition of phosphorus trichloride to a 2-pyridyl grignard reagent (II) obtained by the 'entrainment' method from a mixture of 2-bromopyridine and ethyl bromide. (I) ⟶ (III).



I II III

This method suffers from two disadvantages. Firstly, the entrainment procedure involves the formation of substantial quantities of ethyl magnesium bromide, which reacts in stage II → III to give the volatile and highly toxic triethylphosphine, a most undesirable by-product. Secondly, a coupling reaction gives 2,2′-dipyridyl. This is an organic base with a similar melting point to the desired product, and it can only be separated from the phosphine by a fractional distillation <u>in vacuo</u>. An attempt to prepare tri(2-pyridyl) phosphine by this method failed when extensive decomposition of the products occurred at the distillation stage.[41] Attention was therefore directed to the second method, which was employed by Placzek and Tyka. IV → VII[42] .

$$\underset{\text{IV}}{n\text{-}C_4H_9Cl} + 2Li \longrightarrow \underset{\text{V}}{n\text{-}C_4H_9Li} + LiCl$$



VI VII

Several preliminary attempts to prepare tri(2-pyridyl) phosphine by this method were unsuccessful, and it was subsequently found that other workers had experienced considerable difficulties with this preparation.[43, 45] The principal reason for our failure to obtain a measurable yield in preliminary experiments is considered to be the fact that despite taking every conceivable precaution, such as working in an atmosphere of dried argon and rigorously drying and purifying the solvent ether and the 1-chlorobutane, 1-lithiobutane could not be obtained in a yield of greater than ca. 10% in stage IV → V. The reasons for this failure are not understood, since according to Gilman, this reaction proceeds quite smoothly in diethyl ether solution at room temperature to give 1-lithiobutane (n-butyllithium) in 76% yield.[46] As a consequence of the failure at stage IV → V, it was necessary to filter the cooled products from stage IV → V through glass wool in order to remove unreacted lithium, and it is possible that a rise in temperature, occurring during the slow process of filtration, may have made a further contribution to the loss in yield, since 2-lithiopyridine decomposes if the temperature is allowed to rise above 240 K. At the end of stage VI - VII, the reaction products were hydrolysed with dilute acid, and the acid layer separated and made alkaline. At this point, a voluminous white precipitate was formed. At first, it was thought that this precipitate was the desired product, but tests showed that it was actually lithium phosphate, presumably formed from the phosphate ion produced on hydrolysing the excess of phosphorus trichloride. In all probability, the further steps which were undertaken in order to remove this inorganic by-product contributed still further to the loss in the yield of the phosphine.

A review of the probable causes of these failures indicated the desirability of ensuring that the reactants for stages V → VII are present in the correct molar proportions, and in the successful preparation described here, this was achieved by using a known quantity of standardised commercially available 1-lithiobutane solution.

In view of the difficulties previously experienced, full details of the successful preparation are given here.

Materials.

1-lithiobutane (n-butyllithium) was obtained as a nominally 2M solution in hexane from Alfa Inorganics. The actual concentration was found to be 2.34 M by titration.

2-bromopyridine (Koch-Light Laboratories) was dried over anhydrous potassium carbonate and distilled, b.p.466 K/760 mm. The product was distilled under reduced pressure immediately before use, in order to remove coloured impurities.

Phosphorous trichloride (B.D.H., 99% by titration) was redistilled at atmosphere pressure.

Diethyl ether (B,P.) was dried over anhydrous calcium sulphate and distilled. The redistilled ether was allowed to stand over successive fresh portions of sodium wire until effervescence was no longer perceptible. B.O.C. 'White Spot' nitrogen was dried by passing it through concentrated sulphuric acid.

Apparatus.

The equipment used is illustrated in Fig.6.6. Flask A and its attachments were 'flamed out' in a stream of dry nitrogen before adding the reagents. Nitrogen was admitted at C and its flow-rate controlled by observing the rate of bubbling of the liquid paraffin in D. The temperature of the contents of flask A was measured using the alcohol-in-glass thermometer E, and was controlled by raising or lowering the Dewar flask F. A mixture of solid carbon dioxide

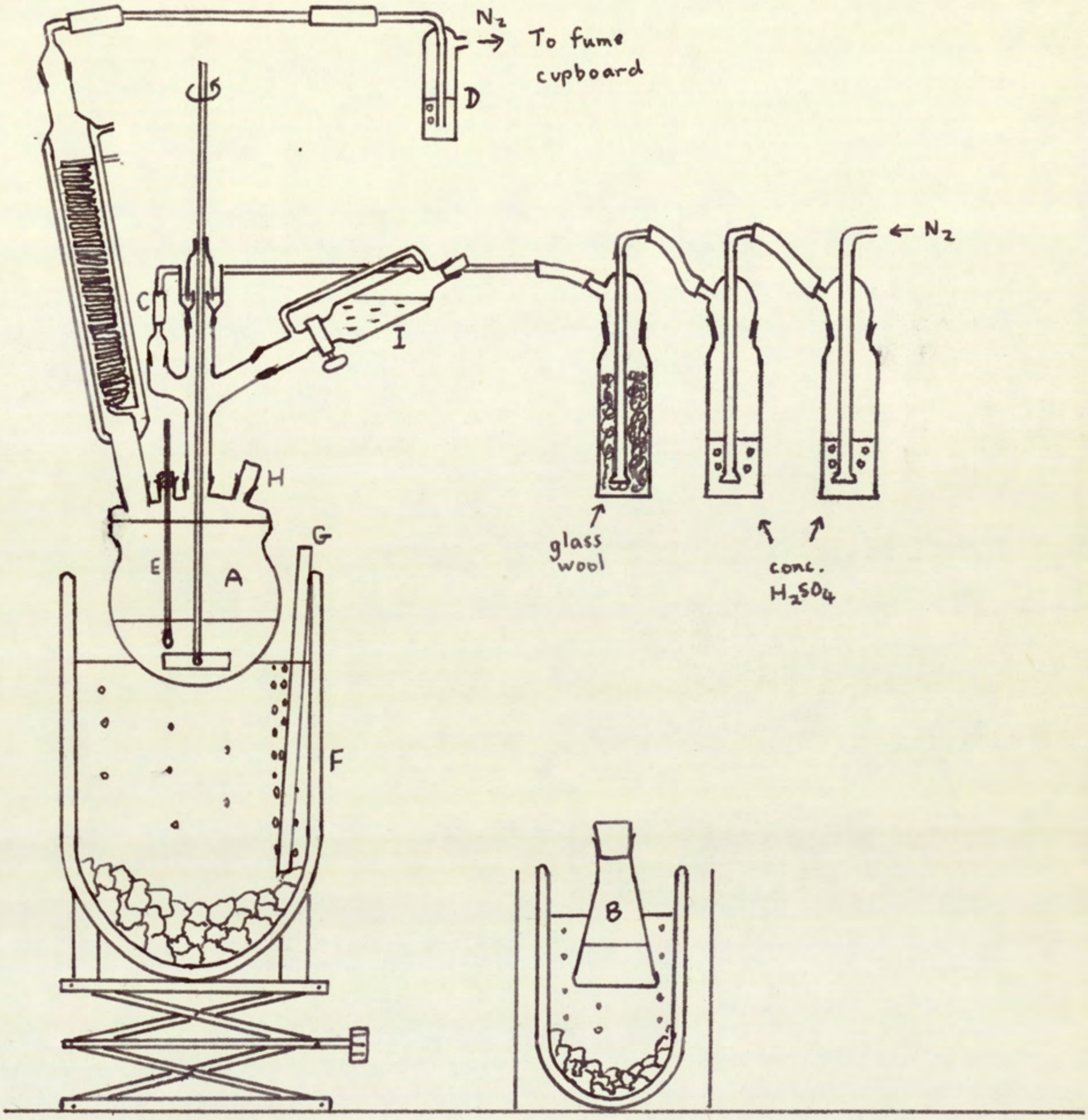


Fig.6.6. Apparatus used in the preparation of tri(2-pyridyl)phosphine and tri(2-pyridyl)arsine.

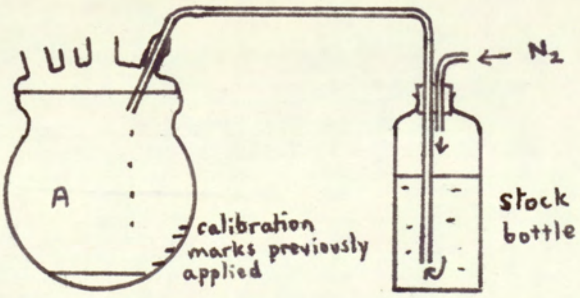


Fig. 6.7. An alternative method for admitting n-butyllithium to the flask A.

and acetone was used as the refrigerant in F, and a roughened metal rod G was inserted in order to prevent violent 'bumping' of carbon dioxide.

Procedure.

Diethyl ether (200 cm^3) was placed in A. 1-lithiobutane (40 cm^3) was then transferred into A by pipetting it from the stock bottle and admitting it at H under a rapid stream of nitrogen (1-lithiobutane can ignite in the presence of moist air). A solution of 2-bromopyridine (10 cm^3, a 5% excess over 1-lithiopyridine) in diethyl ether (50 cm^3) was placed in the flask B. A solution of phosphorous trichloride (4.5 cm^3) in ether (50 cm^3) was placed in I. The stirrer was switched on and the contents of flasks A and B were cooled to 208 K. The contents of B were then added to A through H, under a countercurrent of nitrogen. The addition was completed in 30 seconds and was accompanied by the formation of a deep red colour in A and by a rise in the temperature of A to 233 K. After stirring the contents of A at 218 K for 45 minutes, the contents of I were added dropwise during 30 minutes; this addition caused the temperature in A to rise to 233 K. The addition of the phosphorus trichloride solution caused the deep red colour to be almost completely discharged, and a voluminous white precipitate was formed. After stirring at 233 K for 30 minutes, the Dewar flask F was removed and the contents of A were allowed to warm up to 298 K. The mixture was then stirred at room temperature overnight, and then cooled to 273 K and cautiously hydrolysed by adding ca. 2M sulphuric acid (100 cm^3). The contents of

A were then transferred to a separating funnel, and the yellow acid layer was removed. The ether layer was extracted with two further portions ($30\ cm^3$) of 2M sulphuric acid. The combined acid extracts were cooled at 273 K and cautiously neutralised with a concentrated solution of sodium hydroxide, when a white precipitate was formed together with a small quantity of a dark-coloured oil. The mixture was then diluted to a total volume of 1 litre, when most of the white solid dissolved leaving a small quantity of a biscuit-coloured crystalline solid. The residual solid was filtered off, washed with water, and dried <u>in vacuo</u>. (a). The filtrate was extracted with chloroform ($3 \times 50\ cm^3$), and the chloroform extracts were extracted with 4N sulphuric acid and then worked up as before to give a further quantity of biscuit-coloured solid. (b). Crop (a) was recrystallised three times from cyclohexane to give 1.22 g of colourless leaflets having m.p. 385 K (lit.[42] 386-387 K) (Found: C, 67.8; H, 4.56; N, 16.0; P, 11.7. $(C_5H_4N)_3P$ requires C, 67.9; H, 4.53; N, 15.9; P, 11.7 %), Crop (b) was recrystallised twice from cyclohexane to give 0.76 g of a product having an infrared spectrum identical to that of crop (a). % yield (combined crops) = 23%. A sample for Raman spectroscopy was freed from traces of a fluorescent impurity by passing a solution of the product in chloroform through a short (10 cm x $0.5\ cm^2$) column of activated alumina ('Camag' grade 10), evaporating the eluate, and repeatedly recrystallising the solid from water using decolourising carbon. This purification procedure did not proceed in a yield good enough to enable a satisfactory solution spectrum to be obtained, although sufficient colourless prisms were obtained (ca. 5 mg.) to record a fluorescence-free spectrum of the solid.

Tri(2-pyridyl)arsine.

This compound was prepared and purified in an analogous manner to tri(2-pyridyl)phosphine, using essentially the same apparatus and procedure. In this case, however, 80 cm^3 of 1-lithiobutane was transferred from the stock bottle into A by the method illustrated in Fig.6.7. The flask A was filled to the calibration mark by cautiously applying a slight positive pressure of nitrogen from a separate cylinder through the tube P. 300 cm^3 of anhydrous ether was then added to the 1-lithiobutane. A solution of 2-bromopyridine (20 cm^3) in ether (70 cm^3) was placed in the flask B and a solution of arsenic trichloride (B.D.H. from a fresh bottle) (8.6 cm^3) in ether (30 cm^3) was placed in I. The procedure for tri(2-pyridyl)phosphine was then followed through without modification. At the end of the reaction, the mixture was acidified as before. However, when the acid layer was neutralised, an oil separated but no precipitate was formed. The oil was extracted with chloroform (3 x 50 cm^3), and the chloroform extract was itself extracted with dilute (ca. 2M) sulphuric acid (3 x 50 cm^3). The acid extract was neutralised with concentrated sodium hydroxide solution. The oil which separated crystallised when the mixture was allowed to stand at 278 K overnight. The solid was filtered off, dried *in vacuo*, and recrystallised from cyclohexane to give pale biscuit-coloured leaflets (1.22 g., 6.3%), m.p. 85° C (lit. 85° [42])

(Found: C, 58.5; H, 3.92; N, 13.6. $(C_5H_4N)_3As$ requires C, 58.3; H, 3.88; N, 13.6 %). Samples for Raman spectroscopy were purified by dissolving the compound in benzene and passing the solution through alumina as before. Large colourless plates (ca. 5 mm x 5 mm x 2 mm) were obtained when the benzene eluate was evaporated.

CHAPTER SEVEN : THE VIBRATIONAL SPECTRA OF TRIPHENYLAMINE; RESULTS AND DISCUSSION.

7.1. Results.

Our observed frequencies in the 2000 - 50 cm^{-1} region are given in Table 7.1. Comparison of our results with the earlier data reproduced in columns 1 and 2 shows that good agreement exists in general, provided that about 6 cm^{-1} is added to the values in column 1 between 1150 and 1600 cm^{-1}. Since our I.R. results agree very well with the Raman frequencies obtained using two different instruments, we must conclude that the earlier data contains a calibration error in this region. Also, the existence of weak I.R. absorption near 1530 cm^{-1} and 1204 cm^{-1} was not confirmed, so these bands are presumably due to impurities. The relative intensities given in column 8 are on an arbitrary scale on which the strongest line (996 cm^{-1}) = 500 units. The "depolarisation ratio" (column 9) was obtained by dividing the peak height (measured in mm. above the background) obtained with the incident light in the same plane of polarisation as the analysed light, by the peak height obtained when the plane of polarisation was rotated through 90° by turning the quarter wave plate.

The assignments (columns 11-14) are discussed in sections 7.2 to 7.6. Column 11 gives the species of the vibration assuming that the molecule has D_3 symmetry (see Table 5.6). Column 12 gives the species of the corresponding vibration of a monosubstituted benzene of C_{2v} symmetry. Column 13

Table 7.1. TRIPHENYLAMINE : VIBRATIONAL

INFRARED SPECTRA					RAMAN	
solid previous work[15,16] cm^{-1}		solid this work cm^{-1}	$CHCl_3$ soln cm^{-1}	$CHBr_3$ soln cm^{-1}	solid Cary 81 cm^{-1}	solid Coderg cm^{-1}
						88vs
						103vs
						124sh
						163vs
						179vs
		217vvw	213vw	213vw		220vw
						239sh
241	x	245m	244m	246m*	244s	246vs
		252sh	249sh	252sh*		
			285vw	288vvw*	288m	286m
		326vw	326vw	326vw*		
		335vw	335vw	335vw*	334m	332s
						361vw
405	w	408m	409m	409m	408m	410s,br
431	u	432m	435br	430br		
500	y	501vs	504vs	504vs	504vw	502vw
512sh	t	513m	515m	515m	517vw	516w
			539vw ?			
			550vw ?			
615	s	613s	613s	613s	613m	611s
1	2	3	4	4	5	6

* benzene solution

SPECTRA AND ASSIGNMENTS

SPECTRA				ASSIGNMENT			
soln in $CHCl_3$ cm^{-1}	rel. int.	depol. ratio ρ		D_3 species	C_{2v} species	designation	approximate vibrational form
91	500	0.43	p	A_1			τ_{sym}?
							lattice vibrations
				A_2		δ_{sym}	N-phenyl out-of-plane bend + ϕ_3N deformation
244	45	0.60	dp	E			"
				A_2	B_1	x'	N-phenyl out-of-plane bend + ϕ_3N def. + ring folding
283	27	0.11	p	A_1	A_1	t'	in-plane ring bend + phenyl-N stretch
							2 x 163 = 326
334	29	0.83	dp	E	B_1	x	N-phenyl out-of-plane bend + ϕ_3N def. + ring folding
							2 x 179 = 358
412	38	0.40	p+ dp	A_1+E	A_2+ B_2	w'+W +u	ring folding superimposed on in-plane phenyl-N bend
				A_2	B_2	u'	in-plane phenyl-N bend
				A_2	B_1	y'	out-of-plane ring folding + phenyl-N out-of-plane bend
				E	B_1	y	"
612	40	0.88	dp	A_2+E	B_2	s'+s	in-plane phenyl deformation
7	8	9	10	11	12	13	14

Table 7.1.(continued)

INFRARED SPECTRA					RAMAN	
solid previous work[15,16]		solid this work	$CHCl_3$ soln	$CHBr_3$ soln	solid Cary 81	solid Coderg
		620vs 625sh	620vs 624sh	619vs,br	618m	621m
689vs 694vs	v	695vs 700sh	696vs,br	700vs,br		
					715vs	713vs
		720vw		718vw		
743 749 vs	f	749vs		752vs		
		760sh		763sh	757m	760m
831	g	829w				825vw
		831vw	835w	832w		
					836m	839m
896s	i	891sh 893m	891sh 898m	898m	886vw?	
921m	h	921w	923vw	923w	926m	926w
			941vw			
956m	h	961m	963w	963w		
		975w				
						985w
					996vs	995vvs
1	2	3	4	4	5	6

SPECTRA			ASSIGNMENT			
soln in $CHCl_3$	rel. int.	depol. ratio e	D_3 spe-cies	C_{2v} spe-cies	desig-nation	approximate vibrational form
621	16	0.81 dp	E	A_1	t	in-plane ring bend+phenyl-N stretch
			A_2+E	B_1	v'+v	out-of-plane phenyl deformation
711	120	0.00 p	A_1	A_1	r'	in-plane phenyl def.+ C-C stretch + phenyl-N stretch δ_s+ y' = 718
			A_2	B_1	f'	out-of-plane C-H bend (split by solid-state effects)
757	20	0.60 dp	E	B_1	f	" but unsplit
						2 x u' = 824
			E	A_2	g	out-of-plane C-H bend
837	14	0.46 p	A_1	A_2	g'	"
			A_2+E	B_1	i'+i	"
924	4	0.75 dp	E	A_1	r	in-plane phenyl def.+ C-C stretch + phenyl-N stretch y'+u' = 939; δ_{as}+ v = 940
			A_1+E	A_2	h'+h	out-of-plane C-H bend
			A_2	B_1	j'	"
			E	B_1	j	"
996	500	0.00 p	A_1	A_1	p'	ring breathing
7	8	9 10				

Table 7.1. (continued)

INFRARED SPECTRA					RAMAN	
solid previous work^{15,16}		solid this work	$CHCl_3$ soln	$CHBr_3$ soln	solid Cary 81	solid Coderg
998s	p	998w	999m	999m		1006m,sh
			1017w,sh	1017w,sh		
1025vs	b	1025m	1026s	1026s	1026s	1024vs
						1030sh
1069vs	d	1071s	1073s	1072s		
						1077vw
		1110vw				
1156m	c	1150m	1153m		1156m,br	1152m 1160s
1165m	a	1170s	1173s	1171s	1171s	1171vs
					1187m	1185s
1204 1219m	e	1210w,br		1214s		
1282vs		1273vs,br	1276vs	1276vs	1277m	1279s
		1287m	1290m	1290m	1289m	1290m
1302vs	q	1310m	1311m	1311m	1311w	1311m
1319vs	o	1325m	1327m	1327m		1330vw
1379m	j+ w		1393vw	1390vw		
1	2	3	4	4	5	6

SPECTRA				ASSIGNMENT			
soln in $CHCl_3$	rel. int.	depol. ratio ρ		D_3 species	C_{2v} species	designation	approximate vibrational form
				E	A_1	p	ring breathing
							t + u = 1022
1024	150	0.01	p	A_1+E	A_1	b'+b	in-plane C-H bend
							(w+u) + s = 1031
				A_2	B_2	d'	in-plane C-H bend
1076	4	0.75	dp	E	B_2	d	"
							(w+u) + v = 1105
1155	36	0.75	dp	A_2+E	B_2	c'+c	in-plane C-H bend
1168	145	0.07	p	A_1+E	A_1	a'+a	"
1183	75	0.02	p	A_1	A_1	q'	phenyl-N stretch + in-plane C-H bend + C-C stretch y + v = 1204
1275	50	0.80	dp	A_2+E	A_1+ B_2	q+e'	phenyl-N stretch+ in-plane C-H bend + C-C stretch (superimposed)
1289	38	0.84	dp	E	B_2	e	in-plane C-H bend
1312	27	0.74	dp	E	B_2	o	C-C stretch
1331	10	o.80	dp	A_2	B_2	o'	"
							i+y = 1402; 2 x v = 1390; j+w = 1383
7	8	9	10	11	12	13	14

Table 7.1. (continued)

INFRARED SPECTRA					RAMAN	
solid previous work^{15,16}		solid this work	$CHCl_3$ soln	$CHBr_3$ soln	solid Cary 81	solid Coderg
			1430vw	1430vw		
			1444w	1443w		
			1457w	1456w		
						1480vw
1481vs	m	1489vs 1493vs	1492vs,br	1491vs,br	1493w	1491m
1530w						
1583vs	k	1586vs,br	1586vs,br	1586vs,br	1587s	1585vs
					1601s	1600s
		1640vw	1639vw	1636vw		
		1711vw	1725w	1721w		
		1780w	1791w	1791w		
		1845vw				
		1856vw	1860w,br	1860w,br		
		1930m	1938m	1935m		
		1944m ?				
1	2	3	4	4	5	6

SPECTRA				ASSIGNMENT			
soln in $CHCl_3$	rel. int.	depol. ratio ρ		D_3 species	C_{2v} species	designation	approximate vibrational form
							p'+ u'= 1429
				A_2	B_2	n'	C-C stretch
				E	B_2	n	C-C stretch
1480	17	0.35	p	A_1	A_1	m'	"
1491	20	0.50	p?	E	A_1	m	"
							impurity ?
1586	153	0.74	dp	A_2+E	A_1+ B_2	(l'+l + k)	C-C stretch (superimposed)
1598	122	0.27	p	A_1	A_1	k'	C-C stretch
							f'+ i = 1640
							g + i = 1730
							g + h = 1798; 2 x i = 1796
							2 x r = 1846
							i + h = 1861
							h + j' = 1936
7	8	9	10	11	12	13	14

contains our proposed assignment of the observed frequencies using Whiffen's notation, and column 14 gives the approximate description of the form of the vibrations using the notation explained in section 5.2. p.10. Following Smith[28] we have used primed letters (u', t', etc.) to denote the symmetric components of the split phenyl vibrations. Asymmetric components are denoted by unprimed letters.

7.2. Discussion.

7.2.1. The symmetry of the molecule.

A careful examination of the observed results shows that a consistent assignment of the fundamental vibrations of triphenylamine can only be made if it is assumed that the symmetry of the molecule is D_3. Sheppard and Sharp also interpret the spectra of triphenylamine and the triphenylcarbonium ion in terms of D_3 symmetry, but their spectroscopic evidence in favour of this point group was not convincing, since it relied only on the fact that the 'umbrella' C-H out-of-plane bending vibration (f in Whiffen's notation) is split into two components in the I.R. spectra of these compounds.[25] In fact, this splitting is compatible not only with D_3 symmetry but also with C_3 and (flat) C_{3v} symmetry, and even with D_{3h} symmetry if the molecules are occupying non-equivalent positions in the crystal lattice. This earlier work, which relied solely on solid-state I.R. data, cannot therefore be said to have established the true symmetry of these compounds. Similar criticisms can be directed at the work of Costa and Puxeddu.[15]

Reference to Table 5.4. shows that an immediate distinction between the symmetries D_3 (on the one hand) and C_3 and C_{3v} (on the other) can be made by looking for the presence or absence of certain coincidences between I.R. and Raman frequencies. It was shown in Section 5.4 that coupling effects are most frequently observed in the x-sensitive phenyl vibrations q, r, t, x, y, and u. If the symmetry of triphenylamine is D_3, then each of the three A_1 (C_{2v}) x-sensitive vibrations q, r, and t should give rise to two components, and the totally symmetric $A_1(D_3)$ component should be Raman active but infrared inactive and should give rise to a polarised line. Inspection of the results shows that two strong, polarised Raman lines are indeed found in the regions expected for q and r (at 1183 and 711 cm^{-1} respectively) and that no infrared absorption occurs at the corresponding frequencies, even with concentrated samples. The absence of these coincidences rules out the possibility of any significant distortion from D_3 or D_{3h} symmetry. Moreover, throughout the Raman spectrum, it is observed that polarised lines can only be reasonably assigned as symmetric components of vibrations which originated as A_1 or A_2 phenyl vibrations. Our failure to identify any polarised Raman lines with symmetric components of B_1 or B_2 phenyl vibrations provides further evidence for D_3 symmetry. The all-planar D_{3h} structure can be ruled out by our observation of two components of the in-plane phenyl vibrations d, o, u, and n (only one component is expected in D_{3h} symmetry); by our observation of polarised symmetric components of the A_2 phenyl vibrations w and g (only the A_1 phenyl vibrations give rise to totally symmetric components in D_{3h} symmetry); and by our observation of <u>two</u> I.R.-active components of the out-of-plane phenyl vibrations f, i, x, and y (only one I.R.-active component is expected in D_{3h} symmetry).

Our choice of D_3 symmetry is consistent with the results of the electron diffraction study performed by Sasaki et.al.[31] They found that the phenyl-N-phenyl angle in gaseous triphenylamine differed from that expected for a D_3 structure by only 4°. They commented that their slightly pyramidal propellor-shaped C_3 structure could be interpreted as involving a flat trigonally-bonded nitrogen at equilibrium, the molecule appearing pyramidal because of thermal bending motions. It is quite possible that the D_3 configuration is stabilised in the solid and solution phases by lattice forces and solvation effects, respectively.

7.2.2. <u>Frequency Assignments</u>.

The assignment was made on the basis of the theoretical treatment given in the preceding chapter, with particular reference to the predicted frequency ranges and intensities of the phenyl vibrations given in Table 5.2. One striking and immediately obvious difference between these spectra and the spectra of triphenylphosphine - the closest analogue of triphenylamine to have been studied <u>in detail</u> - is that whereas in triphenylphosphine splittings of phenyl vibrations have been described as "anomalous" and "peculiar"[16, 20], the predicted splittings are more often observed than not in the spectra of triphenylamine, i.e. the "anomalous" cases are those where the symmetric (A_1 or A_2) and asymmetric (E) vibrations are accidentally degenerate. However, in most cases the observed splittings are small enough to enable reasonable assignments to be made by reference to Table 5.2. Much larger splittings are, however, expected in the six x-sensitive phenyl vibrations and in the skeletal modes.

Without a normal coordinate analysis, it is impossible to predict which of the asymmetric or symmetric components of each vibration will have the higher frequency. Our choice has therefore been made by comparing the observed relative intensities of the I.R. and Raman bands of each component with the intensity ratio predicted using the D_3 selection rules given in Table 5.4. However, calculations on simpler molecules of the type MX_3 show that if the mass of M is less than the mass of X, then ν_{sym} is lower in frequency than ν_{asym}, so it is probable that the vibrations involving phenyl-nitrogen stretching (q, r and t) will split so that ν_{sym} is less than ν_{asym}.

Moreover, it is clear that some of the higher-frequency phenyl vibrations behave as if they were "isolated". For example, both components of the A_1 phenyl vibration m appear to give rise to polarised Raman lines, and there are several other cases of departure from the selection rules for the D_3 point group among the higher-frequency vibrations.

7.2.2.1. C-H stretching vibrations.

A study of the C-H stretching vibrations of triphenylamine is essentially irrelevant to the purpose of this work. Accordingly, although well-resolved absorptions were observed in the 3000-3100 cm^{-1} region in preliminary studies, we follow recent workers[18-24] in neither tabulating nor discussing these frequencies.

7.2.2.2. C-C stretching vibrations.

According to Varsanyi,[34] only five vibrations of monosubstituted benzenes (k, l, m, n and o) can be described as C-C stretching vibrations. In fact, a sixth vibration must have some C-C stretching character, but the remaining A_1 vibration (r) will be mixed with C-C-C bending and C-N stretching vibrations (t and q). Of the five simple C-C stretching vibrations, the two A_1 phenyl vibrations m and k can be recognised by the appearance of polarised Raman lines which are assigned to the symmetric components (A_1 in D_3) m_{sym} and k_{sym}. Neither of these Raman lines have any discernible counterpart in the I.R. spectra: this provides further evidence for our choice of D_3 symmetry. The remaining assignments (l, n and o) are made using the data given in Table 5.2, allowing for the possible overlap of some bands.

The sixth C-C mode in a monosubstituted benzene is expected between 620 and 830 cm^{-1}. Since it also contains a strong element of phenyl-N stretching, this vibration can be expected to undergo strong inter-ring coupling: the symmetric component is accordingly assigned to the strong polarised Raman line at 711 cm^{-1}, where there is no corresponding I.R. absorption. The assignment of the asymmetric component presents more difficulty. There is no reasonable alternative assignment for I.R. and Raman frequencies observed near 925 cm^{-1}, since they lie outside all the frequency ranges predicted for the out-of-plane C-H bending modes, and they seem too strong to be due to an overtone or combination mode. It is interesting that both triphenylchloromethane and the triphenylcarbonium ion show I.R. absorption near 900 cm^{-1} which was assigned as the out-of-plane C-H vibration i but which undergoes a red shift of 9 cm^{-1} when the central carbon atom is substituted by ^{13}C. This anomaly was noted but no explanation for it was offered.[27] In our view, the band in this region must be a strong candidate for assignment to r_{asym} since this vibration must involve some movement of the central atom.

7.2.2.3. C-H in-plane bending vibrations.

The five vibrations, a, b, c, d and e are found in the 1000-1300 cm^{-1} region. The A_1 phenyl vibration b is clearly the strong polarised Raman line at 1024 cm^{-1}. The fact that this vibration involves virtually no change in the phenyl-X bond length in monosubstituted benzenes is demonstrated by the very small variation (12 cm^{-1}) in the frequency of b as X is varied. In view of the evident inability of b to couple with the phenyl-X modes, it is not surprising that the symmetric and asymmetric components of b are found to be accidentally degenerate, since inter-ring coupling is only likely to be significant if some effect can be transmitted through the phenyl-N bond.

Similar considerations account for our decision to assign the strong polarised Raman line to 1168 cm^{-1} - which is accompanied by strong I.R.absorption - to both components of the other A_1 phenyl in-plane C-H vibration (a). The only other plausible assignment for a strong polarised Raman line in this region would be to q, which is one of the phenyl-X modes: however, this vibration would be most unlikely to show an I.R.coincidence. In fact, another weaker polarised Raman line is observed at 1183 cm^{-1}, which is not accompanied by I.R.absorption, so this is assigned to q_{sym}.

The non-totally symmetric B_2 vibrations c and d are also insensitive to variations in the substituent (X) in monosubstituted benzenes, so any splitting in c and d is expected to be small. Absorption near 1155 cm^{-1} and 1074 cm^{-1} can be confidently assigned to these vibrations. The other B_2 mode e is more X-sensitive. We assign e_{asym} to a medium-intensity I.R.band at 1290 cm^{-1} which is coincident with a depolarised Raman line. e_{sym} probably contributes to the breadth and intensity of the I.R.absorption at 1276 cm^{-1} which was assigned to q_{asym}.

7.2.2.4. C-C-C in-plane ring bending vibrations.

Two of these (p and s) are not x-sensitive, i.e. their recorded frequencies vary with x by less than 25 cm^{-1}, so appreciable splittings are not expected. The ring breathing mode p is obviously the intense Raman line at 996 cm^{-1}. The third mode t couples strongly with the phenyl-N stretching mode, and a large splitting is anticipated.

Smith finds no splitting in s in the spectra of the tetraphenyl derivatives of the group IVA elements C to Pb, yet all the other vibrations observed below 650 cm^{-1} are split to an increasing extent as the mass of the central atom decreases.[28] This failure of s to split reflects its small x-sensitivity - the range of values given for it is only 605-630 cm^{-1}. In the solution spectrum of triphenylamine, two depolarised Raman lines of medium and strong intensity are observed in this frequency range. Both of these lines, each of which has an I.R. coincidence, cannot be assigned to s without involving a serious and inexplicable breach of the D_3 selection rules, so we prefer to assign one of these frequencies to s and the other to t_{asym}. The stronger of the two I.R. absorption is assigned to t_{asym}, in keeping with Varsanyi's intensity predictions.

A shoulder on the higher-frequency side of this I.R. band may be due to the symmetric component of s. This assignment for t_{asym} is consistent with Smith's assignment of this vibration to a band at 635 cm^{-1} in tetraphenylmethane, and to a band at 598 cm^{-1} in triphenylmethane.[28] Moreover, I.R. absorption bands found at 637 cm^{-1} (medium intensity, unassigned) in triphenylchloromethane, and at 658/647 cm^{-1} (medium-weak combination) in the triphenylcarbonium ion, were found to exhibit red shifts of 20 cm^{-1} and 6 cm^{-1} respectively when the central carbon atom was substituted by ^{13}C.[27] This provides further evidence that t_{asym} is to be found in the 550-650 cm^{-1} range in polyphenyl compounds in which strong inter-ring coupling occurs.

Smith found little variation in the frequency of t_{sym} in the tetra- and tri-phenyl derivatives of the group IVA elements,[28] which is not surprising in view of the fact that the central atom scarcely moves in this vibration. We have therefore assigned t_{sym} to a polarised Raman line of medium intensity at 283 cm^{-1}, in keeping with previous work.[28]
It is interesting that there should be weak I.R. absorption associated with this line in solution but not in the solid state spectra: this suggests that there may be some slight departure from D_3 symmetry in solution, but that the symmetry

of the molecule in the crystal is accurately D_3. Alternatively, some solvation effect involving an interaction between the lone pair of electrons on the nitrogen atom and a solvent molecule could cause a lowering of the symmetry from D_3. In this context, it may be significant that the weak band observed at 285 cm^{-1} in a chloroform solution of triphenylamine is barely perceptible in the I.R. spectrum of a benzene solution in which other bands in the 200-410 cm^{-1} region have the same intensity as in the chloroform solution.

7.2.2.5. C-H out-of-plane bending vibrations.

It is possible to find observed frequencies to fit the intensity and frequency data given in Table 5.2 for the five modes f, g, h, i and j, but the assignments are less certain than those discussed previously, because of the overlapping frequency ranges of some of the vibrations, and because the low intensity of the observed features makes it difficult to use the D_3 selection rules as an aid in their assignment. However, the assignments given in Table 7.1 are supported by the satisfactory assignments of the summation frequencies observed in the 1600-2000 cm^{-1} region. The "umbrella" mode f is known to be particularly sensitive to solid-state effects,[22] and indeed some splitting of one component of this vibration is observed in the I.R. spectrum of a Nujol mull of the solid.

7.2.2.6. C-C-C out-of-plane ring bending vibrations.

Two of these vibrations, v and w, are "x-insensitive" and so no appreciable splitting is expected. v is obvious as the strong I.R. absorption near 700 cm^{-1}; again, this band appears to be split in the solid state. w certainly contributes to the I.R. absorption near 410 cm^{-1}, but it cannot account entirely for its intensity, nor for the intensity of the Raman line observed near 412 cm^{-1}. This Raman line is asymmetric, and the polarisation data suggest that two lines may be superimposed. We therefore suggest that one component of u, an in-plane phenyl-N bending mode, may contribute to these features. The two components of u are expected to occur in this region in view of the trend which can be discerned in the position of u in the polyphenyl derivations of the group IVA and VA elements. The asymmetric component is preferred, as this could account for the observed increase in the intensity of both the I.R. and Raman features; the symmetric component of u should be Raman-inactive.

The third vibration y may be regarded as a ring folding mode which is strongly coupled with an out-of-plane phenyl-N bending mode x, so appreciable inter-ring coupling and splitting can be anticipated. y is normally strong in the I.R. but weak in the Raman; a pair of bands conforming to these requirements is found in the expected frequency range at 504 and 515 cm^{-1}.

7.2.2.7. Skeletal Vibrations.

It was made abundantly clear in the previous chapter that there is no pure vibration corresponding to "phenyl-N stretching". The assignment of the three modes, q, r and t which involve stretching of the phenyl-N bond have been discussed in Sections 7.2.2.3, 7.2.2.2, and 7.2.2.4 respectively. There are two other "phenyl-X" modes u and x, usually described as a phenyl-x in-and out-of-plane bending motions, respectively. Depending on the angle of twist of the phenyl rings about the C_2 axes of the molecule, the skeletal deformations δ_{sym} and δ_{asym} (see Fig.5.4) can couple preferentially with either u or x. In fact, the angles in gaseous triphenylamine are 45^{o}, [31] and there is no reason to expect different angles in the condensed phases, so coupling effects will probably influence both x and u equally. As a result, both x and u can be expected at higher frequencies than are normally found in monosubstituted benzenes having a light substituent attached to the ring, (e.g. C_6H_5F or $C_6H_5NH_2$), whereas the skeletal deformations S_{sym} and ${}_{asym}$ will be found at lower frequencies than in (for example) trimethylamine. In view of the large possible frequency ranges expected for these vibrations, the assignments given in the region 200-450 cm^{-1} are not unequivocal, but they are consistent with the D_3 selection rules and with the trend in the frequencies of u and x predicted from observations on similar compounds.

The symmetric torsional vibration is Raman active and can be assigned to an intense Raman line at 91 cm^{-1} which is polarised in chloroform solution; the asymmetric torsion asym, although predicted to be both I.R. and Raman-active, will cause little effective change in either the dipole moment or the polarisability ellipsoid of the molecule and is accordingly presumed to give rise to spectral features which are too weak to be observed. The strong Raman lines observed between 100 and 200 cm^{-1} are not found in any solution spectra, nor was there any corresponding absorption in the I.R. of the solid. Durig observed similar features in the Raman spectra of solid triphenylgermanium derivatives, and in agreement with his work[29] we assign these Raman lines to lattice modes.

7.3. Conclusions.

(a) The triphenylamine molecule has the point group symmetry D_3 in the solid state and in benzene solution, but a slight distortion to C_3 symmetry may occur in chloroform solution.

(b) A complete vibrational assignment (except for C - H stretching modes) has been made for triphenylamine, and in the light of this new assignment, modifications to the vibrational assignments in triphenylchloromethane and the triphenylcarbonium ion have been proposed.

CHAPTER 8

THE VIBRATIONAL SPECTRA OF SOME TRI(2-PYRIDYL) COMPOUNDS OF THE GROUP VA ELEMENTS.

8.1. Introduction.

8.1.1. General.

The complete assignment of the triphenyl compounds which was discussed in Chapters 5 and 7 provides a basis for the assignment of some vibrations in the analogous tri(2-pyridyl) derivatives, on the reasonable assumption that the extent of coupling, and hence the degree of splitting of those vibrations which are sensitive to the mass of the central atom, will be similar in both classes of compounds. This assumption rests on the close similarity between the phenyl group and the 2-pyridyl group insofar as mass and structure are concerned. However, differences in coupling may arise from the different nature of the bonding which may be expected between the external groups and the central atom, in view of the additional electron-withdrawing capacity of the 2-pyridyl groups.

8.1.2. The symmetry of the 2-pyridyl group.

The other main difference between the 2-pyridyl group and the phenyl group lies in their symmetry. A 2-substituted pyridine has the symmetry of the point group C_s only. Pyridine itself belongs to the point group C_{2v} and has 27 normal vibrations; the vibrations which are missing from those of a monosubstituted benzene correspond to the loss of three degrees of freedom associated with a ring-hydrogen bond; these comprise a stretching frequency, an in-plane bend, and an out-of-plane bend. In pyridine itself, the species divide as in (1)

$$\Gamma_{vib}(C_{2v}) = 10\, A_1 + 9\, B_2 + 3A_2 + 5\, B_1 \quad \text{———} \quad (1)$$

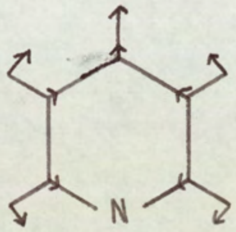
but when the C_2 axis and its associated σ_v plane are removed, as in 2- and 3-substituted pyridines, the vibrational irreducible representation becomes

$$\Gamma_{vib}(C_s) = 19\, A' + 8\, A'$$

As has been pointed out by Green[47], the reduced symmetry of the substituted pyridines results in considerable mixing of the normal coordinates. In other words, the pattern of atomic displacements in the vibrations of pyridine which was illustrated by Long[48] will be altered, and these alterations will be particularly noticeable in vibrations in the mixed classes (e.g. A_1 and B_2) which are close in frequency.

8.1.3. A notational system for the vibrations of the 2-pyridyl group.

In view of the statements made in section 8.1.2., it might be thought that a description of the vibrational modes of a 2-substituted pyridine would be impossible. However, just as Whiffen[1] found that only six vibrations of monosubstituted benzenes are X-sensitive, so Green and his coworkers[47] found that only six vibrations of monosubstituted pyridines are sensitive to the mass of the substituent. The curious feature of their results is that it appears to be possible to make consistent assignments for monosubstituted pyridines, using a notational system adapted for use in pyridine itself, irrespective of the position of the substituent. Thus, reference to the tables of frequencies published for the vibrations of 2-, 3-, and 4-substituted pyridines shows that the vibration 6a in pyridine, drawn as



in ref. 48, is 'X-sensitive' in a very similar manner to the 2-, 3-, and 4-substituted compounds. This is illustrated in Table 8.1.

Position of substituent	Substituent. - H	- D	- Me	- Et	- F	- Cl	- Br
2-	605	600	548	500	556	428	315
3-	605	599	538	488	535	428	319
4-	605	597	514	493	-	414	317
Reference	47	47	47	49	47	47	47

Table 8.1. The effect of varying the substituent position on the frequency of the X-sensitive mode 6a of substituted pyridines.

These results are explicable if it is remembered that varying the substituted position will have no effect on the number of vibrational degrees of freedom permitted, and that any difference arising from different positions of substitution will result only from the different positions of the nitrogen atom relative to the substituent. The mass difference between the N atom and a C-H group is negligible, and no great variation in the ring bonding is expected. Accordingly, although the normal modes will look different on paper, their frequencies will not be markedly sensitive to the position of substitution.

We therefore follow recent workers in using, for 2-substituted pyridines, the nomenclature for the vibrations of pyridine[50] which was itself derived from the notation used by Langseth and Lord[5] to describe the vibrations of benzene. Combining the data provided by Green et. al. with the notational comparison set out in Table 5.2 enables a direct comparison to be made between the notation and expected frequency ranges for the vibrations of monosubstituted benzenes and those of 2-substituted pyridines. This comparison is given in Table 8.2.

Table 8.2. The vibrations of 2-substituted pyridines.

C-H stretching vibrations are excluded.

C_{2v} species (pyridine)	C_s species	WB	W	vibration type	frequency range	I.R.	Raman
A_1	A'	8a	k	ν C-C	1573-1598	s	s
		19a	m	ν C-C ν C-N	1452-1475	s	w-m
		9a	a	β C-H	1143-1150	m-s	m-s
		18a	b	β C-H	1041-1048	s	vs,p
		1	p	ring	991-996	m-s	vs,p
		13	q	X-sens	1104-1249	s	m-s,p
		12	r	X-sens	701-828	s	s,p
		6a	t	X-sens	315-548	m	m-s,p
B_2		8b	l	ν C-C	1565-1568	s	m-s
		19b	n	ν C-C ν C-N	1417-1440	s	w-m
		14	o	ν C-C ν C-N	1253-1376	w-m	w-m
		3	e	β C-H	1282-1300	m-s	w-s
		18b	d	β C-H	1079-1106	m-s	w-s
		6b	s	α CCC	615-629	m	m-s
		15	u	β C-X	265-359	w-m	w-m,dp
A_2	A''	17a	h	γ C-H	960-972	w-m	w
		10a	g	γ C-H	881-886	w-m	w
		16a	w	ϕ C-C	403-406	w-s	vw
B_1		5	j	γ C-H	934-959	w	vvw
		10b	i	γ C-H	749-763	vs	vw
		4	v	ϕ C-C	719-729	w-s	vvw
		11	y	ϕ C-C γ C-X	457-572	m-s	w
		16b	x	γ C-X	152-207	?	vs,dp
1	2	3	4	5	6	7	8

Key to Table 8.2.

Column 1.

These give the species which the vibration would belong to if the substituent were on the 4-position.

Column 2.

These are the actual species of the point group C_s of a 2-substituted pyridine.

Column 3.

Wilmshurst and Bernstein (WB) used a notation for the vibrations of pyridine which was derived from Langseth and Lord's original notation for the vibrations of monosubstituted benzenes. A comparison of this column with column 3 in Table 5.2 shows that the two discarded vibrations which correspond to the loss of the two C-H bending vibrations are 9b = c and 17b = f. A few other discrepancies require comment. Vibrations 1 and 12 are permuted by WB. They allocate the symbol 18b to a C-H bending rather than to a C-X bending vibration, following Varsanyi, so their in-plane C-X bending vibration is numbered 15. This results from a permutation of the assignments for 9b, 18b, and 15. The vibrations 11 and 17b are also ~~permuted~~ reversed.

Column 4.

The letters in this column refer to the "Whiffen vibrations"[1] which correspond in symmetry, vibration type, and frequency range to the WB vibrations listed in column 3.

Columns 5 - 8.

The symbolism used here follows that used in Table 5.2. The data for frequency ranges are taken from values given for the following 2-substituted pyridines: 2-methyl[47], 2-ethyl[49], 2-fluoro[47], 2-chloro[47], and 2-bromopyridine[47].

For the sake of overall consistency, Whiffen's notation is retained in the discussion which follows, despite the use of the WB notation by previous workers [47, 50].

8.1.4. The effect of inter-ring coupling on 2-pyridyl spectra.

The tri(2-pyridyl) compounds of the group VA elements contain 31 atoms, so their molecules will have 87 fundamental vibrations. Triphenylamine has 96 vibrations: the missing vibrations correspond to one symmetric and two asymmetric components of the three vibrations of the missing pyridyl-H group, viz. a pyridyl-H stretch (which will not concern us any further), an in-plane pyridyl-H bend (c) and an out-of-plane bend (f). The procedure used for allocating pyridyl and skeletal vibrations to the different symmetry species of the various point groups possible for the whole molecule closely follows that used in Section 5.3.1., so only the results are presented here.

For a tri(2-pyridyl) compound, there are only three possible symmetry point groups which preserve a C_3 axis passing through the central atom. The highest possible symmetry is C_{3h}. Molecular models show that this structure is possible: it would maximise π-overlap through the central atom, but would leave some non-bonding interaction between the lone pairs on the ring nitrogen atoms and the 5-hydrogen atoms of adjacent pyridyl rings. A C_{3v} structure is unlikely in the free molecules since it would maximise repulsion between the ring nitrogen lone pairs, but it could be important in complexes of these ligands. A C_3 structure represents a propellor-shaped compromise between these two extremes. Various other structures are possible containing at most one plane of symmetry, but these will not concern us any further since from a spectroscopic point of view they are indistinguishable from structures having no symmetry at all.

The distribution and activities of the pyridyl and skeletal vibrations in the point groups C_{3h}, C_{3v}, and C_3 are presented in Table 8.3. C-H stretching vibrations are omitted.

Table 8.3.

Point Group.	Symmetry Species.	Vibrations.	Number of vibrations		Activities
			Pyridyl	Skeletal	
C_{3h}	A'	k,m,a,b,p,q,r,t,l,n, o,e,d,s,u.	15	0	Ra, pol
	E'	k',m',a',b',p',q',r', t',l',n',o',e',d',s', u', δ_{as}	15	1	I.R. + Ra, depol
	A''	h,g,w,j,i,v,y,x,τ_{sym}, δ_{sym},	8	2	I.R.
	E''	h',g',w',j',i',v',y', x', τ_{as}	8	1	Ra, depol
C_{3v}	A_1	k,m,a,b,p,q,r,t,l,n, o,e,d,s,u, δ_{sym}	15	1	I.R. + Ra pol
	A_2	h,g,w,j,i,v,y,x, τ_{sym}	8	1	inactive
	E	k',m',a',b',p',q',r', t',l',n',o',e',d',s', u', δ_{as}, h',g',w',j', i',v',y',x', τ_{as}	23	2	I.R. + Ra depol
C_3	A	k,m,a,b,p,q,r,t,l,n, o,e,d,s,u,h,g,w,j,i, v,y,x,δ_{sym},τ_{sym}	23	2	I.R. + Ra pol
	E	k',m',a',b',p',q',r', t',l',n',o',e',d',s', u',h',g',w',j',i',v', y',x',δ_{as},τ_{as}	23	2	I.R. + Ra depol

The data given in this table shows that it should be possible to assign a point group symmetry to the triphenyl compounds by inspection of their vibrational spectra, subject to the conditions outlined in section 5.4.

8.2. The vibrational spectra of tri(2-pyridyl)amine: results and discussion.

8.2.1. Results.

The observed vibrational frequencies are presented in Table 8.4. The symbols used have the same significance as in Table 7.1. Agreement with previous work [51] is excellent.

8.2.2. The symmetry of the molecule.

Inspection of the results shows that the point group C_{3h} can be ruled out, since in contrast to triphenylamine, all observed vibrations are active in both I.R. and Raman. Reference to Table 8.3 shows that it is more difficult to distinguish between C_{3v} and C_3. If the symmetry is C_{3v}, then the out-of-plane vibrations h,g,w,j,i,v,y,x, and τ should give rise to only one observable component. In fact, only y exhibits definite splitting, and both components of this vibration give rise to depolarised Raman lines: if the symmetry were C_3, then one component of y should exhibit some polarisation. These observations are consistent with C_{3v} symmetry if some other effect (e.g. Fermi resonance: $2x_a = 480\text{cm}^{-1}$) is responsible for the splitting of y. The assumption of C_{3v} symmetry would also account for the observation of marked polarisation in the symmetric component of u. Point groups of lower symmetry than C_3 are ruled out by our failure to observe more than two components in any vibration. Some distortion from C_{3v} to C_3 cannot be ruled out, since a small distortion would give rise to correspondingly small changes in the dipole moment and polarisability in the vibrations derived from the inactive A_2 vibrations in C_{3v} symmetry, so that the corresponding spectral features might be too weak to be observed.

Although C_{3v} symmetry maximises the repulsion between the dipoles on each ring, it minimises the repulsion between the ring nitrogen lone pairs and the amine nitrogen lone pair. Moreover, the electron-withdrawing effect of the 2-pyridyl groups must reduce the π-overlap between adjacent rings which presumably accounts for the D_3 structure adopted by triphenylamine.

8.2.3. Frequency assignments.

The premises on which this assignment is based have been stated in section 8.1.1. Detailed assignments were made by looking for spectral features in the ranges predicted from Table 8.2., then referring to Table 7.1 to find the extent to which the vibration is expected to split, and then comparing the activities of the observed features with the predictions made in Table 8.3.

The general pattern of the spectra is very similar to that found for triphenylamine, so detailed comment on the assignment of each group of vibrations is omitted. Just as was found in triphenylamine, the largest splittings occurred in the x-sensitive vibrations, and vibrations for which only a small range of values is given in Table 8.2. were found to exhibit little or no splitting. Where splitting was observed, the magnitudes of the splittings were found to be consistently similar to those found in triphenylamine. Thus, we find the three 'A_1' x-sensitive vibrations q, r, and t to be split by 77, 202, and 356 cm^{-1} respectively in tri(2-pyridyl)amine, and by 90, 211, and 325 cm^{-1} respectively in triphenylamine.

8.3. The vibrational spectra of tri(2-pyridyl)phosphine.

8.3.1. Results.

The observed vibrational frequencies are presented in Table 8.5. The Raman spectrum of the solid compound was obtained using both He-Ne and A^+ lasers. Apart from a higher level of background radiation caused by more intense fluorescence produced by the A^+ laser, the spectra were identical.

8.3.2. The symmetry of the molecule.

One startling and immediately obvious difference between the spectra of tri(2-pyridyl)amine and tri(2-pyridyl)phosphine is the multiplicity of absorption in the solid-state spectra of the latter compound. These splittings do not persist in solution, so they must be caused by one (or more) of the 'solid-state effects' discussed in section 5.3. It is not possible to state which of these effects is responsible for the splittings: suffice it to say that the data are consistent with the molecules having effectively no symmetry in the solid state, but adopting a C_{3v} or C_3 structure in solution. In view of the greater mass of the central atom, the extent of inter-ring coupling is much less than in tri(2-pyridyl)amine, and as a result there are far more accidental degeneracies between symmetric and asymmetric components. This makes it impossible to distinguish between C_{3v} and C_3 in this case.

8.3.3. Frequency assignments.

Assignments were made by looking for spectral features in the ranges predicted from Table 8.2, and then using the published data for triphenylphosphine [19-21] as a guide to the location of the x-sensitive vibrations and to the extent of the splittings expected to arise from inter-ring coupling. As expected, the x-sensitive vibrations q and r are found at lower frequencies (1124 cm^{-1} and 722 cm^{-1}) than in tri(2-pyridyl)amine (symmetric components at 1250 cm^{-1} and 741 cm^{-1}, respectively). The movement of the central atom in the symmetric component of these vibrations is likely to be small, so these differences presumably reflect the weaker bonding expected in the phosphine.

The position of t_{sym} in tri(2-pyridyl)phosphine appears anomalous at first sight: in view of the trend in the other x-sensitive vibrations, it might be expected to occur at a lower frequency in tri(2-pyridyl)phosphine than in tri(2-pyridyl)amine. In fact, we have assigned t_{sym} to Raman lines at 435 cm^{-1} and 295 cm^{-1} in the phosphine and the amine, respectively. This could be accounted for if the stretching of the pyridyl-N bonds in t_{sym} is accompanied by a relief of non-bonding interactions between hydrogen atoms or lone pairs on adjacent rings. Any such effect would amount to a reduction in the bond stretching force constant, and could explain the observed reduction in the frequency of t_{sym} in triphenylamine. The propellor shape of the triphenylamine molecule [31] clearly illustrates the role of these non-bonding interactions: indeed, an analogous 'inversion' in the positions of t_{sym} in triphenylamine and triphenylphosphine is observed. In support of this hypothesis, we note that in tri(2-pyridyl)amine, where considerable non-bonding dipole-dipole interactions between the ring nitrogen lone pairs is expected in a C_{3v} structure, the splitting of t is 25 cm^{-1} greater than in triphenylamine, whereas the splittings of r and q are less than in triphenylamine.

8.4. The vibrational spectra of tri(2-pyridyl)arsine.

8.4.1. Results.

The observed vibrational frequencies are presented in Table 8.6.

8.4.2. The symmetry of the molecule.

The solid-state spectra exhibit splittings which are similar to those found in tri(2-pyridyl)phosphine. These splittings do not persist in solution, so we again assume that the molecules have effectively no symmetry in the solid state, but revert to a C_{3v} or C_3 structure in solution. We note that similar solid-state splittings were found in the spectra of triphenylphosphine and triphenylarsine.[20]

8.4.3. Frequency assignments.

These require little comment. The downward trend in the frequencies of the X-sensitive vibrations, and the reduced extent of their splittings, are in accord with results obtained for the corresponding triphenyl compounds [19-24]. t_{sym} is at a lower frequency than in tri(2-pyridyl)phosphine. The covalent radii of phosphorus and arsenic are similar [51] so this reduction presumably reflects weaker bonding in the arsine. The covalent radius of nitrogen, on the other hand, is 0.04 nM less: this difference would account for the existence of non-bonding interactions in tri(2-pyridyl)amine but not in the phosphine or arsine.

8.5. Conclusions.

In view of the empirical nature of the methods used in making these assignments, they are clearly not unequivocal, particularly in the region below 400 cm^{-1}, but they are self-consistent and they are in complete accord with the assignments proposed for the analogous triphenyl compounds [19-24].

Table 8.4. TRI(2-PYRIDYL)AMINE: VIBRATIONAL FREQUENCIES (cm^{-1}) AND ASSIGNMENTS.

Infrared Spectra				Raman Spectra				Assignment	
previous work		this work							
solid	soln.	solid	soln.	solid	soln.	rel. int.	ρ	C_{3v} species	
				53vs ?					
		64m ?							
		94m		95s	98	200	0.9dp	E	τ_{as}
		131m 134m 140s 143s		138s,br				A_1	δ_s
				220vw?					
		228sh			232	11	0.8dp	E	δ_{as}
		237s	236br	238s	241	15	0.9dp	E	x_{as}
		297vvw		300w	295	10	0.1p	A_1	t_s
1	2	3	4	5	6	7	8	9	10

1	2	3	4	5	6	7	8	9	10
352m	345w	355m	348br	355m	355	9	1.0dp	E	u_{as}
412s	410s	412s	408m	410m	411	16	0.8dp	E	w_{as}
		422vw		423sh	416	15	0.13p	A_1	u_s
513s 538m	510s 539m	513s 540m	510w 539w	515w 544w	509 540	7 2	0.9dp 1.0dp	E E	y_{as}, split by Fermi resonance (2 x X_{as} = 480)
615m	615m	617m 634w, sh	614m 623w, sh	616w 625w, sh	622br	11	0.9dp	A_1+E	s
		656m	652m 658m	656w	657br	10	0.9dp	E	t_{as}
		710w, br		705vw				E	v
		740sh 744s		741s	742	50	0.04p	A_1	r_s
		779s		783m	780	3	0.8dp	E	i
		832w		832vw					2 x w = 824

Table 8.4. (continued)

Infrared Spectra		Raman Spectra				Assignment	
solid	soln.	solid	soln.	rel. int.	e	C_{3v} species	
876m	866vw		880br	2	?	E	g
940w	945vw	943w				E	r_{as}
956m	960w	958w	950br	2	?	E	j + h
994m	992m	994vs	994	160	0.14p	A_1+E	p
		1029vw					2 x y_s = 1030; s + w = 1026
1050w	1048m	1047s	1050	77	0.10p	A_1+E	b
1084vw	1094w	1084vw	1100	3	0.7dp?	E	d
1100vw	1100vw	1109w				A_1	
115om	1146s	1146w				E	a
1161m	1150s	1159vw	1154	4	0.8dp	A_1	
1208vw							impurity ?
		1246vs	1244	4	0.5p	A_1	q_s split by Fermi Resonance
1256vw	1255w	1253vs	1255	8	0.5p	A_1	(2 x s = 1244)
3	4	5	6	7	8	9	10

3	4	5	6	7	8	9	10
1274sh	1274s		1277	23	0.9dp	A_1+E	e
1281m	1281s	1284vs	1286	20	0.9dp	A_1+E	o
1334m	1332vs,br	1333s	1332	19	1.0dp	E	q_{as}
1366w							r + s = 1361; w + j = 1368
1384w							y + g = 1389
	1426vs						
1431vs	1432vs	1431m	1433	30	0.9dp	A_1	n
	1438s		1441	7	o.7dp?	E	
1465sh	1463s		1465	4	0.7dp?	E	m
1473vs	1470vs	1472w	1471	4	0.7dp?	A_1	
	1490vw						2 x r_s = 1488
1528vw	1520vw						r_s + i = 1523; g + t_{as}= 1532
1565s	1568s	1565s	1570	35	0.9dp	A_1+E	l
1584sh							
1589vs	1590vs,br	1591m	1594	11	0.6p?	A_1+E	k
1600w							t_{as} + r_{as} = 1596
1625vw	1620sh						r_s + g= 1620; q_{as} +t_s = 1631

Table 8.5.

Vibrational frequencies (cm^{-1}) and assignment for tri(2-pyridyl)phosphine.

I.R.Spectra.		Raman Spectra.		Assignment.
Solid	Solution	Solid	Solution	
		22vs		
		61vs		
		92vvs		
		105vs		
		164vs	175 (200,?)	δ_s ?
		184vs		
205m	205m,br	214s		x
249	246m,br	246s	246 (22,p)	u_s ?
259w		259w		
270m	270m			u_{as}
395m) 406m)	394m	395m		w
427m)	426m			t_{as}
433m)		435m		t_s
497s)		495w	}	
503s)	501 sh			
513s)	511s	514m		y
548vw				
619m) 622w)	619w	624m		s
712w	708vw	709m	}	
721w	720w	722s	716 (22,p)	$r_s + v$
742m) 745m) 747m)	744s	746w		r_{as}
765s 773vs 777s	764vs,br	766w		i
		814w,br		

Table 8.5. (continued)

I.R.Spectra.		Raman Spectra.		Assignment
Solid	Solution	Solid	Solution	
894w) 898w) 907w)		894w,br		g
961m				j
985m) 988m)	987m	992vs		p
1046s	1046s	1049vs		b
1084m) 1094m)	1084m	1083w		d
1116sh 1121w	1120m	1124m		q
1131vw				
1147s) 1154s)	1150s	1156m		a
1160m) 1162m)				
1210vw				
1221vw				
1229w		1232w		
1276s	1276s	1276w		e
1284s				
1290vw		1290sh		
1303w				
1360m,br				o
1387w				
1414vs) 1421vs) 1426vs)	1420vs	1419w,br		n
1450s) 1454s) 1456s)	1448vs	1446w,br		m
1556m 1561m	1560s	1560s		l
1570s	1570s	1568vs		k

Table 8.6.

Vibrational Frequencies (cm^{-1}) and Assignment for tri(2-pyridyl)arsine.

I.R.		Raman.				Assignment.
solid	solution	solid	solution	rel.int.	ρ	
		175s				? δ_{sym}
		189vs				
	195m		196br	20	0.9dp	x
229m	231m					
		237vs	238	85	0.06p	u
252m	245sh	254sh				
304m			312			
314	314m,br	313s,br	312	12	0.4p	t
325m			320	10	0.4p	
392sh	388sh	399vw				
397m	396m					w
450m	458sh					
462m						
469s						
475s	474s,br	472w				y
485m,br						
		550vw				t + u = 550

617m	616m	616w	620	15	0.7dp	s
620m						
		630vw,sh	630	6		
695w	696m	696s	obscured by solvent lines			r
698m						
722m,br		712sh				v
738sh						
742w						
744w	744w	742w				as
757s						
759s						
761s	763vs					i
767s						
770s	771sh					
888w		804w				
897w		894vw,br	894br	6	0.7	g
958vw						
974w,br						j
988vs	987s	988vs	988	250	0.06p	p
992sh						
1041s		1044s	1046	160	0.06	b
1046s						

Table 8.6. (continued)

I.R.		Raman.				Assignment.
solid	solution	solid	solution	rel.int.	ρ	
1080sh		1084m	1081	12	0.7dp	d
1083						
1103s						
1106s						
1111s						
1119w		1120s	1120	8	0.5p	q
1150s		1150m	1151	20	0.5p	a
1154s						
1158sh		1158n	1161sh	10	0.8ap	a
1167vw						
1223w		1224w				
1269m		1270w				
1275m						
1280s		1280w	1280br	12	0.5p	e
1300w,br						$t_s + p = 1302$
1365m						
1376s,br						o

1415vs					
1420					n
1425sh					
1440vs					
1445vs		1451br	14	0.1p	
1460vs					
1465vs	1462w				m
1475sh					
1532sh					
1540sh					
1551s					
1555s	1556s	1558	50	0.2p	l
1565vs					
1570	1568vs	1571	70	0.3p	k

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PART THREE: THE VIBRATIONAL SPECTRA OF SOME METAL COMPLEXES OF TRI(2-PYRIDYL)AMINE.

CHAPTER 9 : INTRODUCTION.

9.1. General.

The foundation for this study was laid in Part Two by the assignment of the molecular vibrations of tri(2-pyridyl)amine. There were three main reasons for selecting complexes of this particular ligand for detailed study. Firstly, the coordination behaviour of tri(2-pyridyl)amine has been studied in this department for some time, to the extent that the interest developed in complexes of this and of related ligands has merited a recent review.[1] Despite its exceptionally high ligand field splitting capacity when tridentate (Δ = 12,800 cm^{-1} w.r.t. Ni(II)[2]), the ligand exhibits a marked tendency to form diacidobis(bidentate) complexes with salts containing potentially coordinating anions.[6 - 8] Also, bis[tri(2-pyridyl)amine]iron(II) perchlorate is spin-paired[4], despite the fact that the terdentate ligands cannot accommodate extensive π-delocalisation.

Secondly, the cations in complexes of the type bis[tri-(2-pyridyl)amine]$M^{++}(ClO_4)_2$ (M = Fe, Co, and Ni) are believed to have the symmetry of the point group D_{3d} (not C_{3v}, as was previously suggested)[2]. This follows from the observation[5] that the cobalt(II) and nickel(II) complexes are isomorphous with the iron(II) complex, which was found to exhibit a negligible quadrupole splitting (ΔEq = 0.00) in its Mössbauer spectrum.[4] The centrosymmetric structure of these cations has consequences which, from a practical point of view, are vital to this study. The simplification of the vibrational spectra of the cations arising from their high symmetry causes the total number of infrared-active fundamental vibrations to drop from 183 (assuming no symmetry) to 52 (in D_{3d} symmetry). The number of vibrations in each of the six different species of D_{3d} is sufficiently small to enable the assignments of some low-frequency fundamental vibrations to become a practicable objective. Since coupling can only occur between vibrations of the same symmetry, the small size of each group will enable a more accurate description of the nature of each normal mode to be made. Another advantage results from the high symmetry of these cations. Transitions between centrosymmetric orbitals are forbidden by the Laporte rule: this accounts for the generally feeble intensity of d$\leftrightarrow$d absorptions in octahedral complexes of transition metals.[9] These absorptions can only gain intensity if the higher-energy state can acquire some non-centrosymmetric character, either by vibration of the metal-ligand bonds to give temporary non-centrosymmetric configurations, or by the availability of non-centrosymmetric ligand orbitals for overlap with the metal d-orbitals. Neither of these mechanisms is likely to operate in the bis[tri(2-pyridyl)amine] complexes. The relatively rigid metal-ligand cage system (Plate II) is unlikely to afford opportunities for molecular vibrations to destroy the centre of symmetry, and there are no non-centrosymmetric ligand orbitals available. As a result, the complexes of terdentate tri(2-pyridyl)amine are very pale in colour, in contrast to the well-known tris-complexes of 2,2'-dipyridyl and 1,10-phenanthroline which are

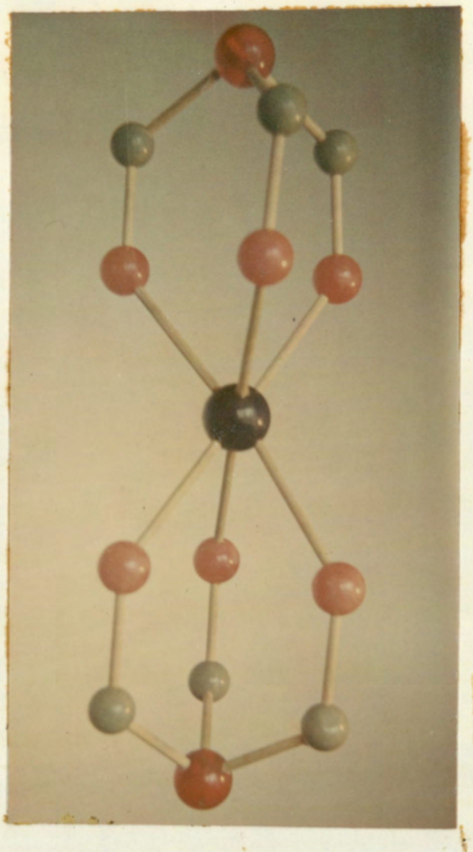

PLATE 2.

The metal-ligand "cage" system.

Large red spheres = amine nitrogen atoms

Green spheres = 2-pyridyl carbon atoms

Small red spheres = pyridine ring nitrogen atoms

Blue sphere = metal atom

of D_3 symmetry and are much deeper in colour. [10] However, some of the intensity of absorption in the latter complexes derives from $t_{2g} \rightarrow \pi^*$ transitions, particularly in the iron(II) and cobalt(II) complexes: even this mechanism is not available in the complexes of terdentate tri(2-pyridyl)amine: the lack of extensive conjugation precludes the availability of a low-energy π^* orbital. These facts, coupled with the exceptionally high Δ value for the terdentate ligand, which brings the $d \leftrightarrow d$ absorption maxima away from the red region of the visible spectrum, enables the nickel(II), cobalt(II), and iron(II) complexes to transmit enough radiation at 635.8 nM to enable Raman spectra to be obtained. In view of the high symmetry of these complexes, Raman data are essential for a complete assignment of metal-ligand vibrations.

The third reason for selecting this system for study was the observation that the iron(II), nickel(II), and cobalt(II) complexes are readily soluble in nitromethane at room temperature without any sign of decomposition or isomerisation. This solvent has little or no coordinating tendency: it has relatively few vibrations of its own to interfere with solution spectra, and many of these can be shifted by using nitromethane-d_3. The advantages of studying the spectra of complexes in solution are that "solid-state effects" can be recognised as such, and that polarisation data can be obtained from the Raman spectra.

Perchlorate and hexafluorophosphate were chosen as the counter-anions for three reasons. Firstly, it has already been mentioned that tri(2-pyridyl)amine has a marked tendency to form diacidobis(bidentate) complexes with anions which can coordinate. These two anions are known to have only a very feeble coordinating tendency:[11] indeed, until very recently no complexes containing coordinated hexafluorophosphate had been isolated, so complexes containing these two counter-anions should preserve the bis(terdentate) configuration of the ligands. Secondly, both anions have very simple vibrational spectra in view of their high symmetry, and no overlapping between their spectra occurs (as occurs, for example, between the spectra of perchlorate and tetrafluoroborate). Thirdly, the anions differ sufficiently in size and mass to cause the frequencies of lattice vibrations in the solids to be appreciably different for complexes of the same cation with the two different anions. This should enable lattice vibrations to be distinguished from low-frequency molecular vibrations in the cations.

This is the first vibrational spectroscopic study of complexes of this type in which solution data have removed the normal uncertainties associated with solid-state spectra.

9.2. The symmetry of the bis[tri(2-pyridyl)amine]M^{++} cations.

By assuming D_{3d} symmetry and then applying the methods described by Wilson[12] to the vibrations of the cation, the representation

$$\Gamma_{vib}(D_{3d}) = 21A_{1g} + 10A_{1u} + 9A_{2g} + 21A_{2u} + 30E_g + 31E_u \quad \text{—} \quad (I)$$

is obtained. Each vibration of the free ligand will, in theory, split to give symmetric (g) and antisymmetric (u) components in the complexes. By applying the methods described in Section 5.3.1., the ligand vibrations can be classified into the appropriate D_{3d} species. For example, the symmetric components of the A_2 ligand vibrations preserve the inversion centre in the point group D_{3d}, but are asymmetric w.r.t. the three σ_d planes, as in the free ligand: they accordingly belong to the species A_{2g} in the point group D_{3d}.

The cations contain 63 atoms and they will accordingly have (3 x 63) - 6 = 183 fundamental vibrations. The splitting of the ligand vibrations gives 2 x 87 = 174 vibrations, so 183 - 174 = 9 vibrations must be associated with the metal-ligand bonds. A check on the distribution of these skeletal vibrations was made by setting up a representation for bond stretching in terms of internal coordinates[13] for the metal-ligand "cage" system illustrated in Plate II. In terms of cartesian displacement coordinates, the representation is

$$\Gamma_{vib}(D_{3d}) = 5\,A_{1g} + 2\,A_{1u} + A_{2g} + 5\,A_{2u} + 6\,E_g + 7\,E_u \quad \text{—— (II)}$$
(cartesian)

In terms of bond stretching, the representation becomes

$$\Gamma_{vib}(D_{3d}) = 3\,A_{1g} + 3\,A_{2u} + 3\,E_g + 3\,E_u \qquad \text{—— (III)}$$
(bond stretching)

This result follows from the fact that there are just three different kinds of bond in the system. By subtracting (III) from (II) we obtain an expression for the number of vibrations in each species which primarily involve deformation of bond angles:-

$$\Gamma_{vib}(D_{3d}) = 2\,A_{1g} + 2\,A_{1u} + A_{2g} + 2\,A_{2u} + 3\,E_g + 4\,E_u \quad \text{—— (IV)}$$
(angle bending)

The problem of redundant coordinates[14] makes it difficult to derive the expression (IV) from first principles.

There will clearly be one stretching vibration for each of the three different types of bond in the cage system, so one can be assigned to the totally symmetric metal-ligand stretching frequency ν_gM-lig. Likewise, in the A_{2u} class one stretching vibration is assignable to ν_uM-lig; in this vibration, the metal nucleus moves with appreciable amplitude. Both of these stretching vibrations should be markedly sensitive to the nature of the bonding between the ligand and the metal. The two bending vibrations in each of these classes are derived from the vibrations u and δ_{sym} of the free ligand. The two bending vibrations in the A_{1u} class are derived from the x vibration of the free ligand and from a metal-ligand torsion, which is illustrated along with the other skeletal vibrations in Table 9.1. The single bending vibration in the A_{2g} class is the symmetric component of the ligand vibration x. The E_g and E_u stretching vibrations can be regarded as metal-ligand rocking modes. The additional E_u bending vibration is illustrated in Table 9.1.

The vibrations of an isolated ML_6 unit of D_{3d} symmetry (Fig.9.1)

Fig.9.1.

would span the representation

$$\Gamma_{vib}(D_{3d}) = 2\,A_{1g} + A_{1u} + 2\,A_{2u} + 2\,E_g + 3\,E_u \quad \text{——} \quad (V)$$

Table 9.1. The vibrations of the bis[tri(2-pyridyl)amine]metal(II) cations.

$\Gamma_{vib}(D_{3d})$ = 21 A_{1g} +	10 A_{1u} +	9 A_{2g} +	21 A_{2u} +	30 E_g +	31 E_u
20 ligand (A_1 in C_{3v}) + ν_g M-ligand	9 ligand (A_2 in C_{3v}) + M-ligand torsion	9 ligand (A_2 in C_{3v})	20 ligand (A_1 in C_{3v}) + ν_u M-ligand	29 ligand (E in C_{3v}) + M-ligand symmetric "rock" ρ_{sym}	29 ligand (E in C_{3v}) +ρasym (M-ligand) +δasym (M-ligand)
 ν_g M-ligand	 M-ligand torsion		 ν_u M-ligand	 ρ_{sym} M-ligand	 ρ_{asym} M-ligand  δ_{asym} M-ligand

Comparison of this result with the number of skeletal vibrations illustrated in Table 9.1. shows that six vibrations are 'lost' when this ML_6 unit becomes part of the cage system of Plate II. These six vibrations are incorporated into deformation vibrations of the ligand: they arise from the loss of six degrees of freedom associated with the closure of the rings in the cage system.

Table 9.2. shows the distribution of the ligand and skeletal vibrations in the various species of the point group D_{3d}, together with the expected infrared and Raman activities. The tables also show the effect on the activities of these vibrations of distortions to S_6 and C_{2h} symmetries. The C_{2h} point group is of particular interest in that systems in which the electronic state of the metal ion is degenerate - for example, bis/̲tri(2-pyridyl)amine/̲copper(II) and the low-spin ^2E form of bis/̲tri(2-pyridyl)amine/̲cobalt(II) - will be required, by the Jahn-Teller theorem [15] to undergo a distortion of this type, in order to lift the degeneracy of the e_g orbitals. A distortion to S_6 would not lift this degeneracy but might arise if a distortion towards C_3 symmetry in the ligand were induced by a lattice effect. However, any such distortion would reduce the amount of overlap between the lone pairs on the ligand nitrogen atoms and the appropriate metal orbital, if the assumption of D_{3d} symmetry in the cations is correct. If necessary, the effects of other distortions can be determined by reference to a correlation table for the point group D_{3d}.

Table 9.2. The distribution and activities of the ligand and skeletal vibrations in the cations bis[tri(2-pyridyl)amine]M^{++}. (omitting C-H stretching vibrations)

9.2.1. Point group D_{3d}

Species	Vibrations	No. of vibrations		Activities
		lig.	skel.	
A_{1g}	k, m, a, b, p, q, r, t, l, n, o, e, d, s, u, δ_{sym}, ν_g M-lig	16	1	Ra, pol
A_{1u}	h, g, w, j, i, v, y, x, τ_{sym}, τ M-lig	9	1	inactive
A_{2g}	h, g, w, j, i, v, y, x, $_{sym}$	9	0	inactive
A_{2u}	k, m, a, b, p, q, r, t, l, n, o, e, d, s, u, δ_{sym}, ν_u M-lig	16	1	I.R.
E_g	k', m', a', b', p', q', r', t', l', n', o', e', d', s', u', δ_{as}, h', g', w', j', i', v', y', x', τ_{as}, ρ_{sym} M-lig	25	1	Ra
E_u	k', m', a', b', p', q', r', t', l', n', o', e', d', s', u', δ_{as}, h', g', w', j', i', v', y', x', τ_{as}, ρ_{asym}, M-lig, δ_{as} M-lig	25	2	

Total: 150 + 9 + 24 C-H = 183

9.2.2. Point group S_6

Species	Vibrations	No. of Vibrations		Activities
		lig.	skel.	
A_g	k,m,a,b,p,q,r,t,l,n,o,e,d,s,u, δ_{sym}, ν_g M-lig,h,g,w,j,i,v,y,x, τ_{sym}.	25	1	Ra, pol
A_u	k,m,a,b,p,q,r,t,l,n,o,e,d,s,u, δ_{sym}, ν_uM-lig,h,g,w,j,i,v,x,y, τ_{sym}, τ M-lig.	25	2	I.R.
E_g	k',m',a',b',p',q',r',t',l',n', o',e',d',s',u',δ_{as},h',g',w',j', i',v',y',x', τ_{as}, $\rho_{sym}^{\text{M-lig}}$	25	1	Ra
E_u	k',m',a',b',p',q',r',t',l',n', o',e',d',s',u',δ_{as},h',g',w',j', i',v',y',x',τ_{as}, $\underset{\text{M-lig}}{\rho_{as}}$, δ_{as}M-lig.	25	2	I.R.

Total 150 + 9 + 24 C-H = 183

9.2.3. Point Group C_{2h}

Species	Vibrations	No. of Vibrations		Activities.
		lig.	skel.	
A_g	k,m,a,b,p,q,r,t,l,n,o,e,d,s,u, δ_{sym}, ν_gM-lig, (k'),(m'),(a'), (b'),(p'),(q'),(r'),(t'),(l'), (n'),(o'),(e'),(d'),(s'),(u'), (δ_{as}),(h'),(g'),(w'),(j'),(i'), (v'),(y'),(x'),(τ_{as}), $\rho_{sym}^{\text{M-lig}}$	41	2	Ra, pol

9.2.3. Point group C_{2h} (continued)

Species		No. of Vibrations lig.	skel.	Activities
B_g	h,g,w,j,i,v,y,x, τ_{sym},(k''),(m''),(a''),(b''),(p''),(q''),(r''),(t''),(l''),(n''),(o''),(e''),(d''),(s''),(u''),(δ_{as}),(h''),(g''),(w''),(j''),(i''),(v''),(y''),(x''),(τ_{as}),ρ_{sym} M-lig	34	1	Ra
A_u	h,g,w,j,i,v,y,x, $_{sym}$, M-lig,(k'),(m'),(a'),(b'),(p'),(q'),(r'),(t'),(l'),(n'),(o'),(e'),(d'),(s'),(u'),(δ_{as}),(h'),(g'),(w'),(j'),(i'),(v'),(y'),(x'),(τ_{as}),(ρ_{as} M-lig),(δ_{as}M-lig)	34	3	I.R.
B_u	k,m,a,b,p,q,r,t,l,n,o,e,d,s,u, ν_uM-lig,(k''),(m''),(a''),(b''),(p''),(q''),(r''),(t''),(l''),(n''),(e''),(d''),(s''),(u''),(δ_{as}),(h''),(g''),(w''),(j''),(i''),(v''),(y''),(x''),(τ_{as}),(ρ_{as} M-lig),(δ_{as}M-lig).	41	3	I.R.

Vibrations marked (') and ('') are the split components of previously degenerate ligand vibrations.

The application of these selection rules to the interpretation of spectra is subject to the reservations outlined in section 5.3.1.

In particular, many of the symmetric (g) and antisymmetric (u) components of each ligand vibration will be accidentally degenerate: in other words, coupling through the central metal atom of the cation is only likely to be significant for vibrations which occur in, or can couple with, the vibrations of the cage system illustrated in Plate II.

9.3. The effect of coordination on the vibrations of 2-substitute pyridines.

The effects of coordination on the ligand vibrations of 2-substituted pyridines have been studied by many workers[16-20]. Unfortunately, studies on the chelating ligand 2,2'-dipyridyl[16-20] are complicated by the change of symmetry from C_{2h} in the free ligand[21] to C_{2v} in the complexes. The effect of this change is to cause previously Raman-active symmetric components of ligand vibrations to become infrared-active, which makes the identification of genuine coordination shifts a difficult task. Although the recent work of Strukl and Walter included normal coordinate analyses of the vibrations of 2,2'-dipyridyl, 2,2'-dipyridyl-d_8, and some complexes of the type (2,2'-dipyridyl)-MX_2, their results cannot be regarded as being conclusive, since no Raman data were used, and their calculations on the complexes were based on an assumed set of bond angles and distances[20, 22]. In a succinct review article, Hart has drawn attention to the sensitivity of calculated vibrational frequencies to small changes in molecular geometry[23]: it was for this reason that in the absence of accurate structural data, no attempt was made to perform such calculations on the complexes which are the subject of this study. It is clear that little or no significance can be attached to the results of calculations which use an assumed force field and which assume a certain molecular geometry.

For molecules of this size, a computer can generate almost any set of frequencies by suitable variations of bond lengths, bond angles, and force constant data which would be within apparently acceptable limits.

In complexes of monodentate 2-substituted pyridines, the symmetry of the ligand does not change markedly on coordination, and - if coupling effects through the central metal atom are ignored - any shifts in the ligand frequencies can be attributed to changes in the electron distribution in the ligand caused by coordination. In general, it has been found that these shifts are relatively small and that no distinct trends occur in the shifts when the metal (M) or the halide ligand (X) is changed in a series of complexes of the type $(2\text{-R-Py})_2MX_2$.[17 - 19] The insensitivity of these shifts has been attributed to π-bonding between the metal and the pyridine ring: it has been suggested that increasing π-bonding counterbalances possible trends caused by the decreasing strength or the σ-bond between the ring nitrogen and the metal ion.[18, 24] Controversy regarding the significance of metal-ligand π-bonding in complexes of heterocyclic ligands has continued for several years. It is difficult to devise experiments which might conclusively decide the issue one way or the other. A recent attempt to investigate the possibility of π-bonding in complexes of 4-substituted pyridines was based on observations of the shift in the frequency of a mode ν_{12} which was described as an aromatic ring vibration without any mass effect of the substituents, and which does not involve any substituent-ring or hydrogen-ring vibrations.[25] In fact, this is the mode which other workers have described as ν_1 (p)[26, 27]. It has been made quite clear that there are three mass-sensitive vibrations in the A_1 class in a 4-substituted pyridine[26,27]: this has been established by reference to the similar spectra of monosubstituted benzenes, and by extensive calculations performed on 4-substituted pyridines.[27] The 'satisfactory agreement' obtained between calculated and observed vibrational frequencies in these complexes[28], based on assignments which include only two mass-sensitive vibrations in the A_1 class, merely serves to illustrate the point made in the preceding paragraph concerning the validity of normal coordinate calculations performed on molecules of this size. Despite the errors implicit in this work, the weight of evidence presented is consistent with the existence of some π-bonding in copper(II) complexes of 4-substituted pyridines: as expected, this type of bonding was found to play a more important role as the electron-withdrawing capacity of the 4-substituent increases.

The most extensive compilation of data in this field was made by Gill and Kingdon[17]: the results of additional studies by McWhinnie[19] and by Goldstein et.al.[18] are in good agreement with their work. The results of their studies on coordination shifts are summarised in Table 9.3. Unfortunately, most of these complexes have distorted tetrahedral or approximately square planar stereochemistries, in contrast to the essentially "octahedral" bond type expected in the bis[tri-(2-pyridyl)amine] complexes. However, it was shown[17] that for 3-, and to a lesser extent, 4-substituted pyridines, the magnitudes of the shifts are insensitive to the stereochemistry of the complex. Reference to Table 9.3. shows that the only obvious differences between the 'tetrahedral' cobalt and zinc complexes and the 'planar' copper complexes are in the magnitudes of the shifts in the out-of-plane modes w and i: in both cases, the shifts are much greater in the copper complexes. Also, splittings are more often in evidence in the 'tetrahedral' complexes: this may mean that they are due to interligand coupling, because the symmetric component of split vibrations should be infrared-inactive in a trans-planar copper(II) complex. Besides, if they are caused by lattice effects, they would not occur with such regularity in a wide range of complexes which are unlikely to be isomorphous. However, in the absence of solution data, these deductions are somewhat speculative.

9.4. Metal-ligand vibrations in complexes of heterocyclic ligands.

In metal complexes of the type (2-pyridine)$_2$MX$_2$, at least two, and sometimes three or four infrared active bands are found between 200 cm^{-1} and 300 cm^{-1} which cannot be attributed to vibrations of the ligands. One or more of these bands is sensitive to the nature of the halogen X leaving the other absorption or absorptions to be assigned as the infrared-active metal-ligand stretching frequencies ν M-N[17 -19]. Tetrahedral complexes will give rise to two such vibrations, both of which will be infrared-active, whereas in theory a planar or octahedral complex should give rise to only one M-N band in the infrared, the symmetric vibration being Raman-active.[29] However,

Table 9.3.

Frequency shifts (in cm^{-1}) of ligand vibrations in complexes of the general formula $(2\text{-R-pyridine})_2MX_2$.

R	et	me	Cl	Br	me	Cl	Br	me	Cl	Br
MX_2	$CuCl_2$	$CuCl_2$	$CuBr_2$	$CuCl_2$	$CoCl_2$	$CoCl_2$	$CoCl_2$	$ZnCl_2$	$ZnCl_2$	$ZnCl_2$
Ref.	18	17	19	19	17	17	17	17	17	17
Mode										
8a=k	+17	+18			+18	+16	+15	+15	+24	
8b=l	+1	+3			-5	-7 -12	-10	-7	-1 -8	
19a=m	+7	+20			+12	+7	+13 +5	+19		+17 +10
19b=n	+3 -10	+14 +20			+7	+4 -6	+4 -6	+11	+10 -1	+6 -5
14=o	+15	+3			+5	+3	+5	+6	?	+6
3=e	-1	+12	+9	-4	+15	+11 +6	+10 +3	+16	+16 +10	+10 +4
13=q	-3	+5	+10	+5	+2	+12	+9	+9 +5	+15	
9a=a	+19	+2	-4	-5	-4	+5	+3	+4	+7	
18b=d	+15	+11	-2	0	+7	+5	+2	+7	+5	
18a=b	+8	+13	+2	+4	+19	+17 +11	+14 +11	+19	+16 +11	
1=p	+40 +19	+34	+29	+32	+28	+37 +32	+35 +30	+35	+27 +27	+34

17a=h	+15	-7			+18	+10		+19	+10	
10a=g	+11	+13 -2	+2	+20	+5 -1	+8 +3	0 -14	+6 0	+9 +4	
12=r	+13	+8 +5	+11	+29	+1		+3	+2		+4
10b=i	+34	+28	+27 +9	+20	+13 +3	+2 -6	+3 -6	+13 +3	+3 -5	+3 -4
4=v	-11	-7			-10	+5	0 -3	-9	+5	0
6b=s	+28	+26	+27	+29	+24	+26	+31 +28	+24 +21	+23	+29 +25
6a=t	-24	+12	+44	-9	+9 +7	+21	+25	+9 +6	+19	+23
11=y	-4	+11	+6	+7	+1	+1 -1	+1 -2	+2	0	+4 +1
16a=w	+29	+36	+30	+29	+19 +15	+16 +12	+15 +12	+18 +14	+15 +11	+15 +11
15=u	-13	+35 +25	+31		+34	+37	+45 +35	+35	+33	+39
16b=x	-5	-3								

these selection rules are unlikely to be strictly obeyed in the solid state.

Far-infrared studies of some tris(chelate) metal complexes of 2,2'-dipyridyl revealed broad bands between 297 cm^{-1} and 264 cm^{-1} which were not, at the time, thought to be attributable to any I.R.active vibrations of the ligand, or of any anion present.[30] The spectra of the low-spin iron(II) complex differed considerably from the others, and assignments of ν Fe-N were made at 423 cm^{-1}, in keeping with the much stronger bonding expected in a complex of this type. These assignments were criticised by Clark [31, 32], largely on the basis of mass arguments: he asserted that because of the greater mass of the ligands, these bands should occur at lower frequencies than the vibrations assigned[29] as νM-N in pyridine complexes. However, McWhinnie has shown that there is a limiting mass dependency for ν M-N: it was pointed out that the overall variation in ν M-N in the complexes listed in Table 9.3, together with the value quoted for ν M-N in (pyridine)$_2$CuCl$_2$[28], was only 29 cm^{-1} when the mass of the 2-substituent was varied between 1 and 80 a.m.u.[19] It is quite true that <u>symmetric</u> vibrations, in which the metal atom does not move in the tris-chelate complexes, will be sensitive, to some extent, to the mass of the ligands. However, this will be true only to the extent to which the whole ligand, includine any heavy substituents, moves in the vibration.

The asymmetric vibrations, which are the subject of this controversy since they are infrared-active in the tris(chelate) complexes, are of two kinds: an asymmetric metal ligand stretch (A_s in D_3 symmetry) which preserves the C_3 axis of the complex, and two vibrations of species E in which one of the metal-nitrogen bonds lengthens while the other shortens. In view of the relative masses of the metal ion (56 - 65) and the ligands (156 each), the A_2 vibration is likely to consist essentially of the metal ion moving up and down the C_3 axis in a 'box' defined by the ligands. Likewise, the E vibrations probably involve 'rattling' movements of the metal ion which/ destroy the C_3 axis but which do not involve significant movement of the ligands. These considerations could account for the presence of metal-ligand vibrations at frequencies which are mugh higher than would be expected if the frequencies were a function of the ligand mass.

Strukl and Walter, in their studies of complexes of the type (2,2'-dipyridyl)MCl_2, assigned bands at 243, 270, and 318 cm^{-1} to the B_1 asymmetric M-N stretching frequencies where M = Zn, Co, and Fe respectively. These vibrations correspond roughly to the E vibrations of the tris-chelates, but coupling effects will obviously differ appreciably. Their assignments were supported by approximate normal coordinate analyses based on assumed structural data for the complexes[20].

In a recent and very elegant study involving the use of metal isotope effects to locate vibrations involving movement of metal ions, Nakamoto et.al.[33] have essentially confirmed Inskeep's earlier assignments[30]. Of the three M-N stretching frequencies expected, two are observed in some cases and three in other cases. The vibrations were positively identified by the fact that they are the only vibrations above 150 cm^{-1} which exhibit significant shifts (2 - 7 cm^{-1}) on metal isotopic substitution. Although it is not clear whether some of these bands are overlapped on each other or split due to solid-state effects, these studies show definitely that the M-N stretching vibrations in the tris(2,2'-dipyridyl) complexes of iron(II), nickel(II), and zinc(II) occur in the regions 381-376, 292 - 266, and 231 - 184 cm^{-1}, respectively.

CHAPTER 10 : EXPERIMENTAL.

10.1. Preparations.

10.1.1. Materials.

Tri(2-pyridyl)amine was prepared as described in Section 6.2.1. Barium perchlorate 3-hydrate (Hopkin and Williams: G.P.R), cobalt(II) perchlorate 6-hydrate (Koch-Light Laboratories), A.R. grade hydrated metal sulphates, and basic metal carbonates were used without further purification. Nitromethane (Eastman Kodak "Spectro" grade) was used without further purification. Nitromethane-D_3 (CD_3NO_2; about 98%) was obtained from Koch-Light Laboratories, Hexafluorophosphoric acid (65% HPF_6, 5% HF, 30% H_2O) was generously donated by the Ozark-Mahoning Company, Tulsa, Ok., U.S.A. The preparation of other transition metal perchlorates was described in Section 2.2.3.

10.1.2. Bis[tri(2-pyridyl)amine]nickel(II) perchlorate, bis[tri(2-pyridyl)amine]cobalt(II) perchlorate, bis[tri(2-pyridyl)amine]copper(II) perchlorate, and bis[tri(2-pyridyl)amine]zinc(II) perchlorate.

The preparation of these complexes has been described[2, 34]. Yields in normal recrystallisation procedures were found to be unsatisfactory, owing to the flat solubility curves of the complexes, so, with the exception of the nickel complex, which was successfully recrystallised from water, the following procedure was adopted: the impure product was washed with water and then ethanol, and sucked dry on a No.4 sinter. The minimum volume of nitromethane required to dissolve most of the solid was then added, and the mixture stirred. The product was then filtered through the sinter. Benzene was then added dropwise with stirring to the filtrate until a faint turbidity appeared. On standing, crystals of the complex were formed, and addition of benzene was continued until the colour of the solution was almost completely discharged. Analytical data for these complexes are given in Table 10.1.

10.1.3. Bis/ tri(2-pyridyl)amine /iron(II) perchlorate.

Iron(II) sulphate 7-hydrate (0.72 g, about 3 mmol) was dissolved in water (5 cm^3) and a solution of barium perchlorate 3-hydrate (0.98 g, 2.5 mmol) was added. The precipitated barium sulphate was filtered off, and a solution of tri(2-pyridyl)amine (1.24 g, 5 mmol) in ethanol (10 cm^3) was added to the filtrate. The orange precipitate was filtered off and purified by the method described in 10.1.2: yield, 0.83 g.

10.1.4. Bis/ tri(2-pyridyl)amine /nickel(II) hexafluorophosphate, bis/ tri(2-pyridyl)amine /cobalt(II) hexafluorophosphate, and bis/ tri(2-pyridyl)amine /copper(II) hexafluorophosphate.

The method used was the same in each case. Hexafluorophospheric acid (0.4 cm^3; about 1 mmol) was diluted with an equal volume of water, and the appropriate basic metal carbonate was added in small portions until effervescence was no longer perceptible. The mixture was then filtered through a No.4 sinter, and a solution of tri(2-pyridyl)amine (0.50 g, 2 mmol) in ethanol (7 cm^3) was added. The resulting precipitates were filtered, washed with water and ethanol, and then purified by repeated dissolution in nitromethane, filtering, and reprecipitation with benzene. This procedure was necessary to remove traces of a nitromethane-insoluble complex, possibly arising from the presence of hydrofluoric acid in the starting material. Colours and analytical data for these complexes are given in Table 10.1. Yields of about 0.7 g of pure products were obtained.

10.1.5. Bis[tri(2-pyridyl)amine]iron(II) hexafluorophosphate.

Potassium hexafluorophosphate was prepared by neutralising the acid with A.R.potassium carbonate: the resulting solid was recrystallised from water. 1.12 g (6.5 mmol) of the pure crystalline salt was dissolved in water (25 cm^3) and iron(II) chloride 4-hydrate (0.47 g, 2.5 mmol) was added. This solution was then added to a solution of tri(2-pyridyl)-amine (1.24 g, 5 mmol) in ethanol (15 cm^3). The resulting orange precipitate was filtered off, washed with water and ethanol, and purified by the method described in Section 10.1.2. Yield, 1.2 g.

10.2. Vibrational spectra.

The methods used to obtain infrared and Raman spectra at ambient temperatures, and infrared spectra at low temperatures, were described in Chapter 6. The Raman spectrum of bis[tri-(2-pyridyl)amine]cobalt(II) perchlorate at ca. 100 K was obtained by Dr.R.R.Smardzewski, at the University of Leicester, using a Coderg low-temperature cell. The solid sample, which is placed in a glass capillary tube, is cooled by forcing a stream of cold nitrogen gas to flow through the capillary tube holder.

10.3. Magnetic susceptibility measurements.

The magnetic susceptibilities of the two microcrystalline solid complexes bis[tri(2-pyridyl)amine]cobalt(II) perchlorate and bis[tri(2-pyridyl)amine]cobalt(II) hexafluorophosphate were measured at temperatures between 93 K and 373 K using a Newport Instruments variable-temperature Gouy balance. This work was carried out in collaboration with R.J.Dosser, and details of the experimental procedure, including calibration of the Gouy tubes, are given elsewhere[35, 36]. All measurements were made at two different field strengths, but no dependence of the susceptibilities on the field strength was detected in either sample. After the thermostatting device had caused the desired steady temperature to be reached, the force on the Gouy tube was measured and then measurements were repeated at intervals. No time-dependence of the susceptibility was detected in either sample. The reversibility of the effect of temperature on the susceptibility of the perchlorate complex was demonstrated by taking another reading at 173 K after cooling the sample to 93 K and then allowing it to warm up again: the calculated susceptibilities differed by less than 0.2%. The "magnetic moment" μ_{eff} was calculated from the formula:

$$\mu_{eff} = 2.828(\chi_{M'}T)^{\frac{1}{2}}$$

where $\chi_{M'}$ is the molar susceptibility of the cation in c.g.s.

units obtained after applying the following corrections for the diamagnetism of the ligand and anions:

tri(2-pyridyl)amine : 277×10^{6} c.g.s.
(ClO_4) : 34 "
(PF_6) : 64 "

The c.g.s. units system is retained here in order to facilitate comparison of these results with recent work on similar systems.[37 - 39]

10.4. Electronic Spectra.

An attempt was made to obtain the polarised spectra of bis[tri(2-pyridyl)amine]nickel(II) perchlorate and bis-[tri(2-pyridyl)amine]cobalt(II) perchlorate using a Unicam SP700 spectrophotometer at the University of Essex. This work was carried out in collaboration with Dr.B.J. Hathaway and his co-workers, and the experimental methods used are described elsewhere[40]. The effect of rotating the plane of polarisation of the light incident on well-defined external faces of the crystals - grown by evaporation from nitromethane solution - was merely to alter the intensity of all the absorptions by the same amount. In particular, no effects attributable to trigonal distortions of the crystal field were detected.

Table 10.1.

Analytical data for the complexes described in Sections 10.1.2. to 10.1.5.

Complex	Colour	Found			Calculated		
		% C	% H	% N	% C	% H	% N
*$(TM)_2Ni(ClO_4)_2$	pink	47.8	3.21	14.9	47.7	3.15	14.7
$(TM)_2Co(ClO_4)_2$	orange	47.7	3.22	15.1	47.8	3.21	14.8
$(TM)_2Cu(ClO_4)_2$	mauve	46.9	3.15	14.8	47.4	3.16	14.8
$(TM)_2Fe(ClO_4)_2$	red	48.1	3.34	15.2	47.9	3.20	14.9
$(TM)_2Ni(PF_6)_2$	pink	42.0	2.67	13.3	42.6	2.84	13.3
$(TM)_2Co(PF_6)_2$	orange	42.2	2.50	13.2	42.4	2.82	13.2
$(TM)_2Cu(PF_6)_2$	mauve	41.7	2.71	13.0	42.4	2.82	13.2
$(TM)_2Fe(PF_6)_2$	red	43.0	2.84	13.5	42.7	2.85	13.3
$(TM)_2Zn(ClO_4)_2$	white	46.7	3.11	14.6	47.3	3.16	14.7

*TM = tri(2-pyridyl)amine

CHAPTER 11 : RESULTS.

11.1 Vibrational Spectra.

11.1.1 General.

The results are presented in Tables 11.1, 11.2 and 11.3. [redacted] The following general points emerge from an inspection of these results:-

1. Agreement with previous work[2,34] is generally satisfactory, provided that allowance is made for the better resolution achieved by our instrument, and for a calibration error in the 1000-1600 cm^{-1} region in previous work.

2. The spectra of the perchlorate and hexafluorophosphate salts of the same cation are very similar, with the sole exception of the spectra of bis(tripyam[*])cobalt(II) perchlorate and bis(tripyam)cobalt(II) hexafluorophosphate at 100 K (see Fig.11.1). This similarity is particularly significant in the region below 400 cm^{-1}, where effects caused by the interaction of molecular vibrations with lattice vibrations are likely to be important. Where solid-state splittings are evident, these are usually of the order of 3 - 8 cm^{-1} and are readily recognisable as such. These splittings are similar in the perchlorates and hexafluorophosphates. Moreover, the spectra of the complexes in solution in nitromethane closely resemble the corresponding solid-state spectra, and again this is particularly significant in the low-frequency region. The only exception is

[*] tripyam = tri(2-pyridyl)amine

the infrared spectrum of bis(tripyam)zinc(II) perchlorate in nitromethane solution. This contains extra bands in the 400 - 200 cm^{-1} region which indicate that a disolvated species, containing bidentate ligands, may be present.[2]

3. No significant distortions from the expected symmetries of the anions ($ClO_4 = T_d$, $PF_6 = O_h$) are discernible in their vibrational spectra.

4. The infrared spectra of the copper(II) complexes (Raman spectra could not be obtained because they absorb the laser radiations, and the perchlorate complex may isomerise in nitromethane solution[2]) contain more multiplet bands than the other complexes. This additional multiplicity is found in both the perchlorate and hexafluorophosphate, so it may arise from the lifting of the degeneracy of the ^2E_g levels in the complex which is required by the Jahn-Teller theorem[15,41] rather than from "lattice effects". These additional splittings are particularly marked in those vibrations such as w, s, and p, which are known to be "metal-sensitive" (see Table 9.3).

5. The spectra of the other complexes (Fe(II), Co(II), Ni(II), and Zn(II)) can be divided into two classes: those in which the selection rules for a centrosymmetric point group are obeyed in most vibrations of the metal-ligand cage system (PlateII) as well as in the metal-sensitive ligand vibrations (see Table 9.3), and those in which the selection rules are only rigorously obeyed in the metal-ligand vibrations. For this reason, the vibrations of low-spin complexes, which fall into the first category, are tabulated separately

(Table 11.2) from the vibrations of the high-spin complexes, which are in the second category (Table 11.1)

11.1.2. Ligand vibrations.

In general, the spectra of these complexes above 400 cm^{-1} resemble the spectrum of the free ligand, subject to perturbations of the ligand vibrations which are similar to those found in other complexes of heterocyclic ligands (see Table 9.3). Assignments were made by comparing the spectra of the free ligand (Table 8.3) with the spectra of the complexes, and then using symmetry considerations (Table 9.2) and the expected perturbations (Table 9.3) to predict the position and activity of the ligand vibrations in the complexes. The spectra of the high-spin complexes are so similar in the 1000-1650 cm^{-1} region that the positions and assignments of bands in the high-spin cobale(II), copper(II), and zinc(II) complexes in this region are omitted. Table 11.3 contains the assignment of the vibrations of the nickel(II) complexes in this region.

11.1.3. Metal-ligand vibrations.

The assignment of metal-ligand vibrations were based on the following premises:-

1. They should obey the "rule of mutual exclusion", required by a centrosymmetric point group, to a greater extent than the ligand vibrations in the region below 400 cm^{-1}. This follows from the assumption that ligand vibrations will not couple strongly through a heavy central atom.

2. They should be more sensitive to the nature of the metal than ligand vibrations in the same region: in other

words, a change of metal should cause a perceptible shift in these vibrations.

3. A change in spin state, as was found to occur in bis(tripyam)cobalt(II) perchlorate on cooling to 100 K, should produce more pronounced shifts in metal-ligand vibrations than in vibrations derived from ligand vibrations.

11.2. Magnetic Susceptibility Measurements.

The results are presented in Tables 11.4 and 11,5, and the variation of μ_{eff} with temperature is shown in Fig.11.2. Bis(tripyam)cobalt(II) hexafluorophosphate obeys the Curie-Weiss law, but the analogous perchlorate salt exhibits the behaviour previously found to be typical of cobalt(II) complexes in which a temperature-dependent equilibrium between ^4T and ^2E states has been postulated.[37-39] Inspection of Table 11.4 shows that the magnetic susceptibility follows the "minimax" pattern previously observed in these complexes. The equilibrium is reflected in the change observed in the vibrational spectra of the complex on cooling to 100 K. The changes in the spectra and in the susceptibility were found to be smooth, progressive, and completely reversible.

Table 11.1. BIS/¯TRI(2-PYRIDYL)AMINE ¯7M^{2+} $2X^-$(high-spin complexes) VIBRATIONAL FREQUENCIES AND ASSIGNMENTS (50 - 1050 cm^{-1})

11.1.1. M = Co(II) (high-spin).

Infrared spectra			Raman Spectra						Assignment	
X=ClO_4 solid	X=PF_6 solid	X=ClO_4 soln	X=ClO_4 solid	X=PF_6 solid	X=ClO_4 soln(a)	X=PF_6 soln(b)	Rel. Int.	ρ	g or (u)	
			124vvs,br	124vvs,br					g	ρ M-ligand(E_g)
			163vvs	161vvs					g	ν M-ligand(A_{1g})
			180vs	178sh						neon emission
227m 237m	228m	230m,br							u	ρ M-ligand(E_u)
263m	262m	261m							u	ν M-ligand(A_{2u})
285w,br	276w 284w	280w,br	285m,br	282m 286m	281	288	25	dp		x_{as}
			320m	319s	321	326	40	p	g	t_s
325m	325m	323s							u	t_s
344vw	344w	343w 364w?							u	u_{as}
1	2	3	4	5	6	7	8	9	10	11

1	2	3	4	5	6	7	8	9	10	11
			360w	356w					g̀	u_{as}
		407w	406vw?							w (non-coordinated)
433m	431m	431m		436vvw						w (+ neon emission)
	466vvw	466vw	456w,br							u_s + $PF_6(T_{2g}$; δFPF) + ClO_4 (E; δClO)
	491vw?									
513s	509s	500vw	512vw,br	506w,br						y
515s	516s									
	520sh		529vw,br			546?	160(b)dp			
544w		542w								
	558vs			563w						$PF_6(T_{1u}$; δFPF; E_g, δ_sPF)
				601vw?						
621sh		622vs								
624vs										t_{as} + ClO_4 (T_2, δClO)
631s	630s		625m	626m,br						
			629m							
642vw		640m	643m	642m						
646m	646m									
652vw										s
685m	685m	683w	683w	684w						
	722w									v
				738m		744m		p		$PF_6(A_{1g}$, ν_sPF)

Table 11.1.1.(continued) : $(\text{tripyam})_2Co^{2+}$

Infrared Spectra			Raman Spectra						Assignment
X=ClO_4 solid	X=PF_6 solid	X=ClO_4 soln	X=ClO_4 solid	X=PF_6 solid	X=ClO_4 soln(a)	X=PF_6 soln(b)	Rel. Int(a)	e	
744w	741w	740w 746w							
760vs 768vs	756vs 766vs	761vs	757s	756s	758	761 p	70	p	r_s
773sh	775vw	772m	772w	771w					
797s,br	786w 796s	795s							i
			816w,br	811m,br	850		18	p	neon emission
					872?		35	p	solvent combination frequency?
	842vvs,br								$PF_6(T_{1u}, \nu_{as} PF)$
898vw	894w	894w	906w,br	889w 902w					g
912w	911w	912w							
			929s						$ClO_4(A_1, \nu_s Cl\text{-}O)$
936s 939s	933sh 937s 942s	936s	934sh	936m	936	931	100	p+ dp	r_{as}
1	2	3	4	5	6	7	8	9	11

1	2	3	4	5	6	7	8	9	11
950w, sh	959vw			962vw					
968w	966w								j
989w	986w	990vw		982vw					h
1021s	1022s	1021s	1022vs	1024vs	1022	1028 p		p	p

11.1.2. M = Ni(II)

Infrared Spectra			Raman Spectra							Assignment
X=ClO$_4$ solid	X=PF$_6$ solid	X=ClO$_4$ soln	X=ClO$_4$ solid	X=PF$_6$ solid	X=ClO$_4$ soln*(a)	X=PF$_6$ soln(b)	rel. int.(b)	ρ (b)	g or u	
			110s,br 132s,br	125sh					g	ρ M-ligand(E_g)
			166vvs						g	ν M-ligand(A_{1g})
			180sh	187vs						neon emission
248m 254m	250m	248m	240br,sh						u	ρ M-ligand(E_u)
276s	276s	274s							u	ν M-ligand(A_{2u})
289m 293m 301w	289m	286m 300vw	294m 310w	277sh	287	285	39	dp		x_{as}
			325s	325s	323	322	60	p	g	t_s
326s	327s	326s							u	t_s
1	2	3	4	5	6	7	8	9	10	11

1	2	3	4	5	6	7	8	9	10	11
349w	350w	349w	338sh 357w	389w?					u g	u_{as}
			406w,br		506w,br					w (non-coordinated)
438m	437s	438m	437w,br	419vw 434w		435	5	dp		w + neon emission
450vw		457vw	452w 458m	467w		446	6	p?		u_s + $PF_6(T_{2g}, \delta FPF)$ + ClO_4 (E, δClO)
490vw? 513m 516m 555vw	491vw? 509m 516m	514m 560vw	513w,br 530w,br	544w?		519	3	p?		y
	557vs									$PF_6(T_{1u}, \delta FPF; E_g, \delta_s PF)$
621vs 629s 632w	627s 630s 634sh	603m? 621vs 626sh	600w,br? 622m 626m							t_{as} + ClO_4 (T_2, δClO)
646w 666w 686m	646m 664w 680m	640m,br 687m	638m 647s 689w	645m						s
720w	722br	720vw								v

Table 11.1.2 (continued): (tripyam)$_2$Ni^{2+}

Infrared spectra			Raman Spectra						Assignment
X=ClO$_4$ solid	X=PF$_6$ solid	X=ClO$_4$ soln	X=ClO$_4$ solid	X=PF$_6$ solid	X=ClO$_4$ soln*(a)	X=PF$_6$ soln(b)	rel. int.(b)	ρ (b)	
	738w			737m		739	30	p	PF$_6$(A$_{1g}$, ν_sPF)
760s	756m								
	762sh	762s	764s	761s	763	760	53	p	r$_s$
767s	765s								
772sh	778w,br		776w	772m,sh	772			p	
798m	797m	795s				795	4	?	i
			828m,br	826w		827	11	dp	
						851	9	dp	neon emission
						874	11	p	
	844vvs,br								PF$_6$(T$_{1u}$, ν_{as}PF)
896vw	892w	893w							
906vw	901br		907m,br						g
912w	909w	912w							
				918w,br?					
				925m,br?					
1	2	3	4	5	6	7	8	9	11

1	2	3	4	5	6	7	8	9	11
			931vs		931(p)				$ClO_4(A_1, \nu_s Cl\text{-}O)$
936m 940m	936m 940sh	936m	939sh			934	46	dp	r_{as}
968w	958w 965w		974vw			979	3	?	j
989vw	986w	990vw							h
1020s	1023s		1027vvs	1027vs	1026(p)	1026	125	p	p

Table 11.1.3. M = Cu(II) and Zn(II)

M = Cu(II)		M = Zn(II)			
Infrared Spectra		Infrared Spectra		Raman	Assignment
X=ClO_4 solid	X=PF_6 solid	X=ClO_4 solid	X =ClO_4 soln	X=ClO_4 solid	
				126vvs,br	νM-ligand(A_{1g})
				181w	neon emission
198m	196m	206sh		195vw?	νM-ligand(E_u)
238vvw? 260s,br	239vvw? 260s	211s 255vw			νM-ligand(A_{2u})
295m	294m	280m 282m	274m,br	285m 298sh	x_{as}
329m	328m	320s	319s	322s	t_s
343w 348w	343w 349w	340w	339w 355w 364m?	339w,br	u_{as}
409w 414vw	405w 413w	407vw			w (non-ccordinated)
433m 440m	432w 440m	428s 429sh			w
		465vw			u_s
		489w?			
497m 511s,br	497m 508s 514s,br	510m 513m 540w,br			y
	556vs				PF_6(T_{1u}, δFPF)
613m 621vs 629m 634m	615s 621s 630s 634m	621vs,br 628vs		627m	t_{as} + ClO_4(T_2, δClO)

Table 11.1.3. (continued)

M = Cu(II)		M = Zn(II)		
Infrared Spectra		Infrared Spectrum	Raman	Assignment
X=ClO_4 solid	X=PF_6 solid	X=ClO_4 solid	X=ClO_4 solid	
641m	641vs	645vs	645w	
645sh		653vw		s
656m	656m	658s		
681m	681m	680s		
	721m	720w		v
737m	737m	744w		
	739sh			
750m	753vs	759vs		
756vs				
765vs	763vs	767vs		
769sh		771sh		r_s
778vs	775vs		775m	
782sh				
792vs	793vs	797vs,br		
	797sh			i
845w?	840vvs,br	845vw?		$PF_6(T_{1u}, \nu_{as} PF)$
			876w	neon emission?
870vw	876m,br			
909w	890sh	897w	906w	g
916w		912w		
			930m	$ClO_4(A_1, \nu_s ClO)$
934m	934m	937m		
938m	939sh	941m	941sh	r_{as}
950m	950w			
970w	964vw	969w		j
987w	991w	989w		h
1016s	1017s			
1029s	1031s	1021vs	1026vs	p

Table 11.2 LOW-SPIN COMPLEXES: VIBRATIONAL FREQUENCIES AND ASSIGNMENTS

(tripyam)$_2$Fe^{2+}2X$^-$ at room temperature							(tripyam)$_2$Co(ClO$_4$)$_2$ at ca. 100 K		(frequencies marked () are present in the high-spin spectra)	
Infrared Spectra			Raman Spectra						Assignment	
solid X=ClO$_4$	solid X=PF$_6$	soln. X=ClO$_4$	solid X=ClO$_4$	soln. X=ClO$_4$	rel. int.	e	infrared solid	Raman solid	g or u	
			182vs 185vs	183	40	p		170vs,br	g	ν M-ligand(A_{1g})
			229sh	225	4	?	223w (230w)		g	e M-ligand(E_g) + x_{as}(g)?
255vw,br	278vw,br						252m (266w) (292w)		u	x_{as}
309s 320m	300m 309s 322m	304m					301s 312m		u	ν M-ligand(A_{2u}+E_u)
			334w	339	6	p	(332w)		g	t_s
348m	345m	347m					345m		u	t_s
	357w		354m	359	7	dp			g	u_{as}
1	2	3	4	5	6	7	8	9	10	11

1	2	3	4	5	6	7	8	9	10	11
381w	379w						374w 384m		u	u_{as}
	396vw? 412vw?									
							424m (434m)		u	w
			433w	439	10	dp			g	w
456vw	468w	446w	460m, br				454w 460m		g+ u	u_s + w + CeO_4(E, δCeO)
485m 487m	483m						473m 492m		u	u_s
500w	513m	504sh								
	515m	519vs					516s		g+	y
522s	524s	529sh	520m, br	524	10	dp	521s		u	
558w		556s					558vw			
		561sh								
		569sh								
	556vs									PF_6(T_{1u}, δFPF)
622vs 623vs 632m	631m		624s	632	8	dp	618vs 621vs 628vs 634vs		g+ u	t_{as} + CeO_4(T_2, δCeO)

Table 11.2 (continued)

$(tripyam)_2Fe^{2+}2X^-$ at room temperature							$(tripyam)_2Co(ClO_4)_2$ at ca. 100 K			
Infrared Spectra			Raman Spectra						Assignment	
solid X=ClO$_4$	solid X=PF$_6$	soln. X=ClO$_4$	solid X=ClO$_4$	soln X=ClO$_4$	rel. int.	e	infrared solid	Raman solid	g or u	
646sh 648m	643sh 648m		647vs				641s 647w 651m			s_s
	664w?									
694m	695m	700w	700w,br				688sh 691s			s_{as}
721w,br	721w,br								u	v
745vw	738w	743w	735w,br						g	v
765vs 773vs 775vs 778sh	758vs 769vs 774s	766vs							u	r_s
			774vs	774	37	p			g	r_s
792s 798sh	794s 802s	792vs	792w	793	13	dp				i
			827m	829	26	p?				neon emission
1	2	3	4	5	6	7	8	9	10	11

1	2	3	4	5	6	7	8	9	10	11
845w?	845vs,br	840vs?		851?	4	p?				$PF_6(T_{1u}, \nu_{as}PF)$+ combinations
	875s,br	877vw?								
896vw?		885w?		885	1	?				
905w	904w		903m							g
930m 934m	926w 930vw	928m,br	929vs							$r_{as} + ClO_4(A_1, \nu_s ClO)$
963w	951m	975w,br								j
984w	982m		983w							h
1015vw?	1008w?									combinations?
1026m	1027w		1029vvs	1029	150	p		1026w		p
1100vs,br	1061m		1054m							$b + ClO_4(T_2, \nu_{as} ClO)$
			1034vw?							
	1103m 1108m		1103m,br	1101	43	p?				d
1160s	1155sh 1160s		1157m	1154	4	dp				a
			1202vs	1202	60	p			g	q_s
1255s	1254s 1265s		1254s	1253	21	p			g+ u	$q_s(u)$ + o

Table 11.2 (continued)

(tripyam)$_2$Fe^{2+}2X$^-$ at room temperature

Infrared Spectra			Raman Spectra				Assignment	
solid X=ClO_4	solid X=PF_6	soln. X=ClO_4	solid X=ClO_4	soln. X=ClO_4	rel. int.	e	g or u	
1288m	1290s 1293s 1298m		1292m 1295m	1290	10	?		e
1359w,br	1360w		1374w,br					q_{as}
1438m 1448m	1440m 1448m		1444vw					n
1462vs	1464vs						u	m
1474w			1472m	1468	15	p?	g	
	1532w?							
1565m	1569m			1563	30	dp		l
				1580	10	p		
1598s	1598vs		1596vs,br	1599	66	dp		k_{as}
1616s	1617s						u	k_s
			1643s	1646	150	p	g	k_s

Table 11.3. BIS(TRIPYAM)$Ni^{2+}2X^-$: VIBRATIONAL FREQUENCIES AND ASSIGNMENTS (1000 - 1650 cm^{-1}).

Infrared Spectra		Raman Spectra						
X=ClO_4 solid	X=PF_6 solid	X=ClO_4 solid	X=PF_6 solid	X=ClO_4 soln(a)*	X=PF_6 soln(b)	Rel. Int.(b)	e	Assignment
1020s	1023s	1027vvs	1027vs	1026(p)	1026	125	p	p
1058s	1055s 1058sh	1058m	1056m	1047(p)	1051	17	p	b
1083vs,br								$ClO_4(T_2, \nu_{as}ClO)$
1100vs	1102s 1112sh	1105m,br	1103m,br	1101(p)				d
1157s	1155s	1162s	1168w,br		1152	6	p	a
		1208m	1207m	1203(p)	1201	27	p	q_s(g)
1240s	1242m	1236vw,br	1225w, sh		1233	5	p?	q_s(u)
1256m	1255sh 1261s	1260w,br	1270w,br	1252(p?)	1254	8	dp	o
1287m	1288s							
1290m		1293w,br						e
1298w	1296sh							
1	2	3	4	5	6	7	8	9

1	2	3	4	5	6	7	8	9
1350w	1355m							
1365sh	1366m							
	1373sh							q_{as}
1375m	1376s							
	1382sh							
1410vw?		1408vw, br?						
1428sh								
1438vs	1439s							n
	1444sh							
1461vs	1464vs							
	1467sh							
1476s	1476s							m
	1479s							
1500w?		1511m, br?						
1566m	1568m	1558w						l
		1568m						
1598vs	1601vs	1601w			1597	3	dp?	
1613s	1615m	1615w						k(u)
1628m								
					1645	15	dp	k(g)

Key to Tables 11.1, 11.2, and 11.3

1. In every case, the far right-hand column contains assignments for "ligand" and metal-ligand vibrations. Whiffen's notation is retained here for use in the description of "ligand" vibrations (see Chapter 8 for details) in view of the generally small shifts observed on coordination. The subscripts s and as indicate components of pyridyl vibrations which are symmetric and antisymmetric, respectively, w.r.t. the C_3 axes of the cations. The letters g and u are used to differentiate between components of these and other vibrations which are symmetric and antisymmetric, respectively, w.r.t. the centre of symmetry of the cations. It was shown in Table 9.2.1 that some pyridyl vibrations may, in fact, be split into four components in the complexes, e.g. $t_s(g)$, $t_s(u)$, $t_{as}(g)$ and $t_{as}(u)$. It should be borne in mind that this notational system gives only an approximate description of the vibration. For example, the vibrations described by Whiffen as C-C stretching modes will contain an admixture of C-N stretching, resulting from the presence of the nitrogen atoms in the pyridyl rings.

2. Where tables are presented at right angles to the normal direction of reading, a row of numbers is given at the bottom of the first page and at the top of the next page, in order to facilitate visual alignment of the columns. The numbers

have no other significance.

3. No attempt has been made to assign combination modes, in view of the very large number of possible assignments. A number of observed features have therefore been left unassigned, and are shown thus: 569w?

4. All solution spectra (infrared and Raman) were obtained using nitromethane as the solvent, except where an asterisk appears in the column heading, which indicates that nitromethane-D_3 was used.

Table 11.4.

Bis(tripyam)cobalt(II) perchlorate : variation of χ_m' and μ_{eff} with temperature.

T (K)	$10^6 \chi_m'$(c.g.s.)	μ_{eff} (B.M.) ($\pm$ 0.01)
373.4	7771	4.82
333.2	8735	4.83
293.3	9573	4.74
253.2	10807	4.63
213.2	11808	4.48
193.0	11864	4.28
173.3	10345	3.78
173.2 *	10359*	3.79*
163.9	8652	3.37
153.3	7202	2.97
133.2	5887	2.50
113.1	5684	2.27
93.1	6212	2.15

* measurement repeated after allowing sample to warm up : see text (section 10.3).

Table 11.5.

Bis(tripyam)cobalt(II) hexafluorophosphate : variation of χ_m' and μ_{eff} with temperature.

T (K)	$10^6 \chi_m'$ (c.g.s.)	μ_{eff}(B.M.) (± 0.01)
373.1	6383	4.36
333.2	7190	4.38
297.9	7972	4.36
253.2	9586	4.40
213.2	11213	4.37
193.2	12398	4.38
173.1	13845	4.38
153.1	15563	4.36
133.3	17581	4.33
113.2	20538	4.31
93.1	24185	4.30

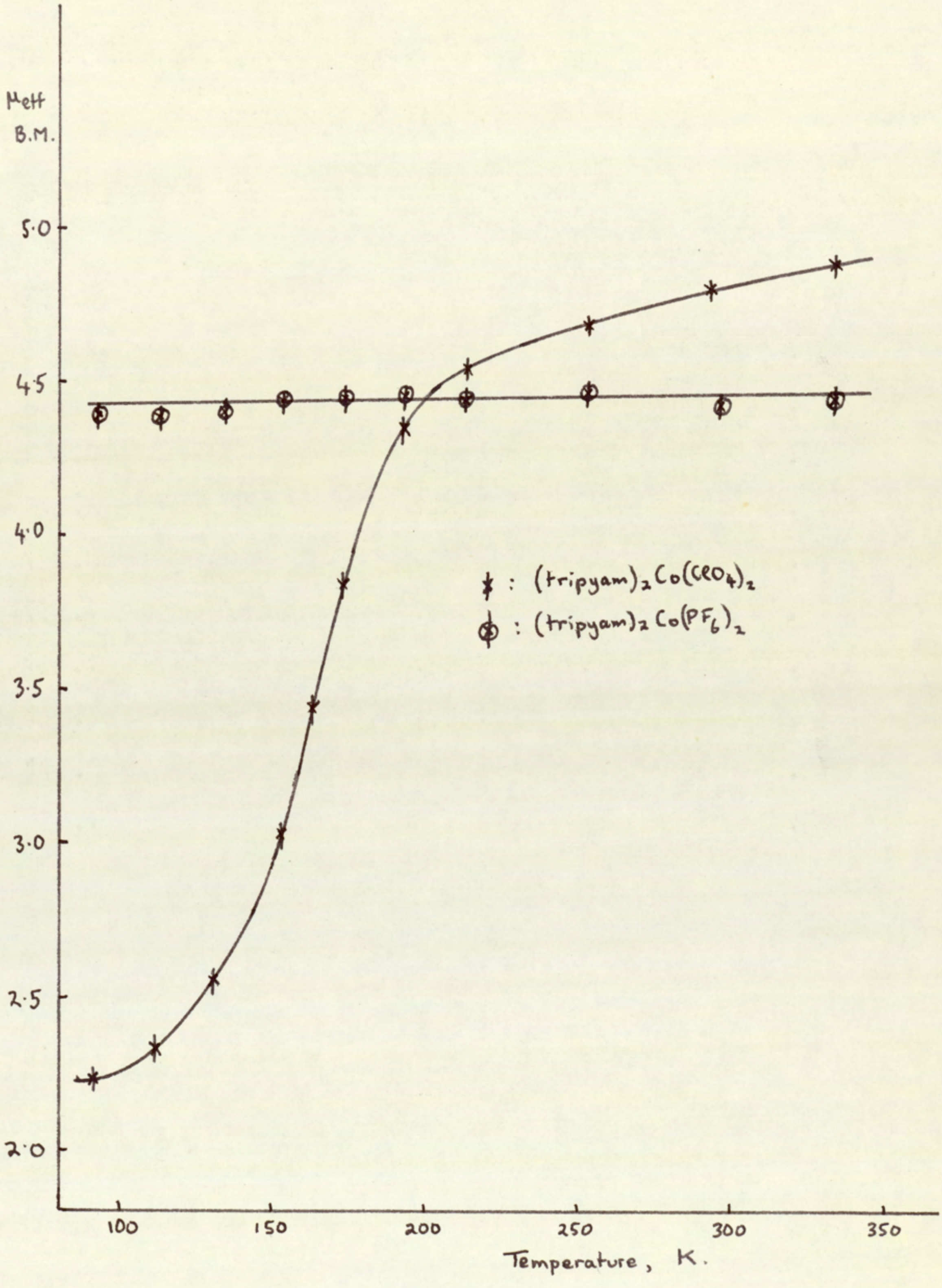

Fig. 11.2. Graphs of $\mu_{eff.}$ vs. temperature for two cobalt complexes of tri(2-pyridyl)amine.

CHAPTER 12 : DISCUSSION.

12.1. Vibrational assignments.

12.1.1. The symmetry of the cations.

The solution spectra of the complexes show that the assumption of D_{3d} symmetry for the complex cations was entirely justified.* In particular, no splitting of degenerate ligand vibrations could be detected in solution spectra, which shows that the C_3 axis present in the ligand must be preserved in the complexes.

12.1.2. Metal ligand vibrations.

The measure of agreement between the results reported here, and previous work outlined in Chapter 10, is very satisfactory. In particular, we find the asymmetric metal-ligand stretching frequencies to be in similar positions to those found by Nakamoto et.al.[33] (see Table 12.1.)

Table 12.1. A comparison of the asymmetric metal-ligand stretching frequencies in bis(tripyam) complexes and tris(2,2'-dipyridyl) complexes.[33]

	M		
$_{as}$ M-lig.	Fe	Ni	Zn
bis(tripyam)M^{++}	304	248, 276	206, 211
tris2,2'-dipyridyl)M^{++}	374, 381	282, 292	186, 235

The assignments of the totally symmetric (A_{1g}) metal-ligand stretching frequencies are more tentative, in view of the difficulties experienced in obtaining solution Raman

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* except in the Cu complexes: see 11.1.1 note 4.

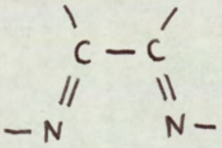
data and infrared data below 200 cm^{-1}. The rising background emission of nitromethane below 200 cm^{-1} reduces the accuracy of polarisation data obtained in this region, and various malfunctions of the R.I.I.C. instrument frustrated attempts to obtain infrared spectra below 200 cm^{-1}. However, a very strong line at $\Delta\nu$ = 130 cm^{-1} in the room-temperature spectrum of bis(tripyam)cobalt(II) perchlorate disappears on cooling, and this change is accompanied by an increase in the breadth and intensity of a line at $\Delta\nu$ = 170 cm^{-1}. These vibrations were by far the strongest lines observed in the spectra of this compound: indeed, all other lines except for p were indistinguishable from background noise. It is unlikely that any vibration other than the totally symmetric metal-ligand of breathing vibration would exhibit such a marked shift with a change of spin state. This observation supports our assignments of ν (M-lig) (A_{1g}) to lines observed near 160 cm^{-1} in the low-spin complexes, and near 175 cm^{-1} in the high-spin complexes. This constitutes the first application of Raman spectroscopy to the study of a spin-equilibrium. The trend in the frequencies of this vibration [Fe(II) $>$ Co(II) (^{2}E) $>$ Ni(II) $>$ Zn(II)] is the same as in the asymmetric vibrations (Table 12.1.) The order of masses of the metals studied is Fe $<$ Co $\sim$ Ni $<$ Cu $<$ Zn, so it is safe to conclude that the observed order of M-ligand stretching frequencies, viz. Fe(II) $>$ Co(II) (^{2}E) $>$ Ni(II) $>$ Co(II)(^{4}T) $>$ Cu(II) $>$ Zn(II) represents the order of the strength of the metal-ligand bonds. This order is not the "natural order" of bond strengths [Fe(II) $<$ Co(II) $<$ Ni(II) $<$ Cu(II) $>$ Zn(II)][41] : the deviations are obvious in the case of the low-spin Fe(II) and Co(II) complexes, in view of the additional ligand field stabilisation energy (L.F.S.E.) known to be present in these complexes, but the order of bond strengths in the high-spin complexes can only be explained if it is assumed that the effect of L.F.S.E. is much more important in these complexes than is normally found to be the case. Copper is an exception in that the Jahn-Teller theorem requires some distortion which will lift the degeneracy of the ^2E levels: this must lead to a distortion of the geometry of the ion which will affect the overall strength of the bonding.

12.1.3. Ligand vibrations.

The most interesting features of our results is the marked difference observed between the "ligand" spectra of the high-spin and low-spin complexes. It is clear that strong coupling of the ligand "cage" vibrations and other metal-sensitive vibrations occurs through the central metal ion in the low-spin complexes, but not in the high-spin ones. The x-sensitive ligand vibrations u, r and t occur at significantly higher frequencies in the low-spin complexes than in the high-spin ones, which suggests that a "tightening-up" of these pyridyl ring vibrations occurs in the low-spin complexes.

The absence of any significant effect on q, which is the vibration most likely to be sensitive to changes in the bond order of the pyridyl-nitrogen bonds in the ligand, confirms that conjugative interactions through the chelate rings in these complexes can be ignored: the conjugation extends to each pyridyl group, but no further.

These results are in accord with previous deductions made from the spectra of complexes of other chelating heterocyclic ligands, in which the profound differences observed between the spectra of high-spin and low-spin complexes were attributed to extensive back bonding between filled t_{2g} metal orbitals and π^* molecular orbitals on the ligands.[30,42-45] There is no reason to suppose that a different mechanism operates in this case. The surprising feature of our results is that spin-pairing occurs in both iron(II) and cobalt(II) complexes of a ligand in which the geometry is unlikely to permit extensive π-delocalisation: this non-availability of a low-energy π^* orbital is confirmed by the relatively high frequency found for the $t_{2g} \rightarrow \pi^*$ charge-transfer bands in these complexes.[46] In only three recent instances have low-spin complexes of iron(II) been prepared using ligands which do not contain the α-di-imine function,[4, 47-48] (I)



(I)

and this is the first report of a low-spin cobalt(II) complex prepared from a ligand which cannot accommodate extensive π-bonding in the chelate rings. This result is particularly surprising when the value of Δ [w.r.t. Ni(II)] for tripyam[46] (12,800 cm^{-1}) is compared with the value of π, the energy required to effect spin-pairing in a cobalt(II) complex (19,500 cm^{-1}).[37]

12.2. The $^4T \rightleftharpoons {}^2E$ equilibrium in bis(tripyam)cobalt(II) perchlorate.

Interest in systems exhibiting "anomalous" magnetic behaviour near the crossover region between high- and low-spin complexes has been sufficient to merit the publication of three review articles in recent years.[37,49, 50.] The various attempts which have been made to fit the experimental magnetic data by using a Boltzmann distribution over the ^2E and ^4T states have only met with limited success. The most recent attempt was successful in obtaining a good fit to the observed graphs of $\frac{1}{\chi_m}$ vs. temperature by assuming values for E, the zero-point energies of the ^4T and ^2E states; $C = \frac{Q_E}{Q_T}$, the ratio of the vibrational partition functions of the two states; $-\frac{3}{2} > \lambda < -1$, the spin-orbit coupling constant for a d^7 ion; and ζ, the one-electron spin-orbit coupling constant. It is not surprising that with these four adjustable parameters at their disposal, a "good fit" was obtained.[39] For this reason, attempts to fit the observed susceptibility of bis(tripyam)cobalt(II) perchlorate will be postponed until structural data for the high- and low-spin isomers are available.

It has been shown that the change from high-spin tris-complexes of 1,10-phenanthroline (Co(II), Ni(II)) to low-spin complexes (Fe(II)) is accompanied by a considerable shrinkage in the volume of the cation.[51] This shrinkage must affect E and C considerably. Moreover, it would account for the marked dependence of the magnetic behaviour of these "cross-over" complexes on the nature of the anion and on the degree of hydration.[37,56] It has already been pointed out that different crystal lattices will differ in their abilities to permit this shrinkage.[52] Another lattice effect which operates in cobalt(II) "crossover" systems has not been considered previously. The ^2E state of cobalt(II) leaves a single electron in the ^2E levels: this is a case of orbital degeneracy which (as in copper(II)) will require some distortion, according to the Jahn-Teller theorem, so as to remove the degeneracy.[15,40] In view of the very high Δ value required to effect spin-pairing, few examples of low-spin cobalt(II) complexes have been structurally characterised. In a very recent study, a static tetragonal "copper-like" distortion was found in dipotassium barium hexanitrocobaltate(II) at 233K[53]: other workers have invoked dynamic Jahn-Teller distortions in order to explain their failure to observe tetragonality in related complexes.[54] It is possible that some of the "anion effects" observable in cobalt(II) "crossover" systems are caused by variations in the abilities of different lattices to accommodate the required Jahn-Teller distortions in the low-spin isomers. In support of this hypothesis, we note that 1,10-phenanthroline, although exerting a very high value of Δ (w.r.t. Ni(II) = 12,700 cm^{-1} [55]), fails to cause spin-pairing in its tris(cobalt) complex[60], whereas other ligands having lower values of Δ cause spin pairing. The ^2E_g level remains degenerate in the rigid D_3 symmetry of the tris(1,10-phenanthroline)cobalt(II) cation, whereas the other ligands referred to [49] are either more flexible and could therefore accommodate the required distortions without difficulty, or else the symmetry of the cations is such that the degeneracy is already lifted. For example, the ^2E_g level becomes $A_1 + B_1$ in the point group

D_{4h}

D_{2d} (not C_{2v}, as previously stated) of the bis(2,2',2"-terpyridyl) complex cations[56]. Since the $^{2}E_{g}$ level also remains unsplit in D_{3d} symmetry, it is possible that this effect may operate in the cobalt(II) complexes of tripyam and its derivatives. Any distortion which removes the degeneracy of the e_g electron must also reduce the effectiveness of π-bonding between the filled t_{2g} metal orbitals and the ligand orbitals.

Recent work has shown (see Part One) that "electron-rich" ligands, which concentrate electron density into orbitals while retaining some π-acceptor capability will produce very high values of Δ (w.r.t. Ni(II)). However, Δ is essentially a quantity which measures the ability of a ligand to destabilise the e_g orbitals of Ni(II) w.r.t. the t_{2g} set, and it depends more on the coulombic charges on the donor atoms than on the ability of the ligand to delocalise t_{2g} electrons by π-bonding. The results presented in Table 12.2 show clearly that Δ (w.r.t. Ni(II)) is not nearly such a useful criterion as it is in iron(II) complexes[48,57] for determining whether the analogous cobalt(II) complex of a given ligand will be high- or low-spin. Clearly, an "electron-rich" ligand cannot be a good electron acceptor, and in this context we note that although Mepy forms a low-spin iron(II) complex (Chapter 3, this work), the complex is markedly less stable towards oxidation and hydrolysis than most other low-spin iron(II) complexes of chelating ligands. This suggests that the high Δ value can force the electrons into the t_{2g} subset, but once they are there, they cannot form strong bonds with the ligand. Similar considerations

Table 12.2. The effect of Δ(w.r.t. Ni(II)) on the spin state of some cobalt(II) complexes.

Complex	Δ value of ligand (w.r.t.Ni(II)) cm^{-1}	spin state	ref.	
			Δ	spin state
$(py)_6Co^{2+}$	9850	high-spin	59	
$(NH_3)_6Co^{2+}$	10800	high-spin	48	
$(en)_3Co^{2+}$	11200	high-spin	55	
$(dipy)_3Co^{2+}$	12650	high-spin	55	60
$(BMI)_3CoI_2$	12660	spin-equilibrium	57	49
$(PMI)_3Co(BF_4)_2$	12670	spin-equilibrium	57	49
$(o\text{-}phen)_3Co^{2+}$	12700	high-spin	55	60
$(PAH)_3Co^{2+}$	12720	high-spin	57	61
$(BDH)_3Co^{2+}$	12800	spin-equilibrium	57	61
$(Mepy)_3Co^{2+}$	12800	high-spin (at 289 K)	Part One	
$(tripyam)_2Co^{2+}$	12800	spin-equilibrium	see text	
$(4\text{-}mpdpa)_2Co^{2+}$	13050	high spin ?	46	58

Abbreviations. py = pyridine; en = 1,2-diaminoethane; dipy = 2,2'-dipyridyl; BMI = diacetylbis(methylimine); PMI = pyridine-2-aldehyde methylimine; o-phen = 1,10-phenanthroline; PAH = pyridine-2-aldehyde hydrazone; BDH = diacetyldihydrazone; Mepy = O-methylpyridine-2-carboximidate; 4-mpdpa = 4-methyl-2-pyridyldi-2-pyridylamine.

may make the formation of low-spin cobalt(II) complexes of methyl-substituted derivatives of tripyam thermodynamically unfavourable. This situation appears to be carried to an extremity in the bis/‾tri(4-methyl-2-pyridyl)amine_/cobalt(II) ion: apparently, the preparative conditions favour the formation of a cobalt(III) derivative.[58]

To sum up, we suggest that there are four main factors which tend to favour spin-pairing in cobalt(II) complexes:-

1. Ligands having a very high Δ value (at least 12500 cm^{-1}).

2. Complexes in which the symmetry is such that the degeneracy of the ^2E_g state is lifted, or in which the ligands are sufficiently flexible to permit a tetragonal distortion,

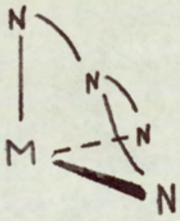
3. Crystal lattices which can accommodate tetragonal distortions and/or a slight shrinkage in the volume of the complex cation. This shrinkage will be less than in iron(II) and iron(III) crossover situations since an electron remains in the e_g orbitals in the low-spin cobalt(II) complexes, but not in the iron complexes.

4. Ligands having low-energy π orbitals available for overlap with the t_{2g} metal orbitals.

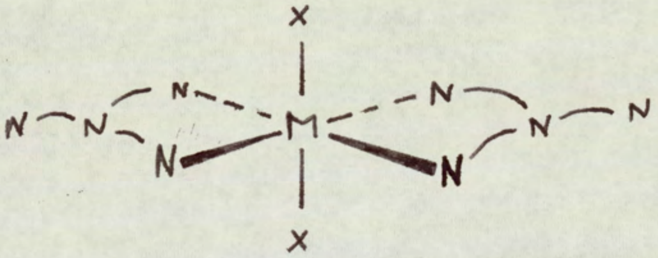
Whether or not a low-spin cobalt(II) complex is formed with a given ligand depends on the relative magnitudes of these four factors.

12.3. The nature of the bonding in complexes of tri(2-pyridyl)amine.

There are two features of the coordination behaviour of tri(2-pyridyl)amine which have aroused interest[1] and on which the present study may have some bearing. The first is the remarkably high ligand field strength of the terdentate ligand (I) and the second is that despite this very high Δ value, the ligand frequently forms diacidobis(bidentate) complexes (II).



I



II

Let us consider the equilibria

$$M^{2+}\text{(aq)*} + 2\,X^{-}\text{(aq)} + 2\,\text{tripyam(aq)} \overset{K_1}{\rightleftharpoons} \text{bis(tripyam)}M^{2+}\text{(aq)} + 2\,X^{-}\text{(aq)} \quad \text{— (A)}$$

$$M^{2+}\text{(aq)} + 2\,X^{-}\text{(aq)} + 2\,\text{tripyam(aq)} \overset{K_2}{\rightleftharpoons} \text{diaquobis(tripyam)}M^{2+}\text{(aq)} + 2\,X^{-}\text{(aq)} \quad \text{— (B)}$$

$$M^{2+}\text{(aq)} + 2\,X^{-}\text{(aq)} + 2\,\text{tripyam(aq)} \overset{K_3}{\rightleftharpoons} \text{di(X)bis(tripyam)}M^{2+}\text{(aq)} \quad \text{— (C)}$$

* The arguments which follow apply equally well to other solvent systems.

Since we are dealing with species which can be assumed to be kinetically labile under the conditions usually employed, the nature of the solid species formed in a particular situation will depend on the relative magnitudes of K_1, K_2, and K_3, unless they are nearly equal, in which case the solid with the highest lattice energy will be formed. In this context it is interesting that despite using a variety of solvents, very little more of the solid bis(terdentate) complexes was found to dissolve at the reflux temperature than at room temperature. It was also found that bis(tripyam)-copper(II) perchlorate isomerised to diperchloratobis(tripyam)-copper(II) on heating[2], and in preliminary studies made during the course of this work, it was found that samples of bis(tripyam)iron(II) perchlorate and bis(tripyam)iron(II) tetrafluoroborate sometimes exploded violently when placed in the He-Ne laser beam. Incidentally, this is another good reason for wearing safety goggles when adjusting the position of the sample in a laser Raman spectrometer. Taken together, these observations suggest that the lattice energies of the terdentate complexes are low, so that in situations where $K_1 \doteq K_2 \doteq K_3$, the solid product isolated is likely to contain bidentate ligands. Moreover, simple steric considerations indicate that in the bis(terdentate) complexes, the cations will be separated from the counter-ions by distances which are greater than in the complexes containing bidentate ligands.

Returning to the equilibria postulated above, K (in each case) is related to the enthalpy and entropy changes accompanying the formation of the appropriate complex by the usual expressions

$$\Delta G = -RT \ln K \quad \text{and} \quad \Delta G = \Delta H - T\Delta S$$

So far as translational entropy is concerned, equilibrium (A) is clearly favoured, since this results in the loss of translational entropy of only two particles: another approach would be to say that terdentate coordination of two tripyam molecules releases six solvent molecules from coordination sites around the metal, whereas (B) involves the loss of only four molecules. In (C), six solvent molecules are released, but the translational entropy of two anions is lost. This is the normal "chelate effect"[65]. It has been suggested that the conformational entropy of the ligands may be greater when they are bidentate[1], but the equilibrium position of the ligand has since been found to favor the terdentate mode.

Enthalpy changes on coordination are more difficult to assess. It has been shown that the basicity of the third pyridyl nitrogen atom in tripyam is lowered when the other rings are quaternised. Thus, it is only possible to methylate two pyridyl groups of tripyam, but all three can be methylated in the analogous phosphine and arsine.[62] It has been suggested that this may be due to some conjugative effect in tripyam, and that the reduced basicity of the third nitrogen atom accounts for the formation of so many complexes in which the ligand is bidentate.[1,46] However, the third base dissociation constant of trifunctional ligands is invariably lower than the first and second ones, because of the difficulty of attaching a third positive charge to a species which already carries two. On this basis, the difference between the amine and the arsine and phosphine can be accounted for by the greater distances between the pyridyl nitrogen atoms in the phosphine and the arsine, and by the ability of their pyridyl rings to rotate about the central atom so as to minimise the repulsion between the positive charges on the quaternised compounds: the spectroscopic data for the tri(2-pyridyl) compounds (Sections 8.3.3 and 8.4.3) offer clear support for this hypothesis. Moreover, the spectra of tripyam indicate (Section 8.2.2) that the molecule has C_{3v} symmetry in the solid and in chloroform solution. This would appear to rule out any conjugative effect involving the central nitrogen atom, since the lone pair must be orthogonal to the ring orbitals. There is therefore nothing peculiar about tripyam as a terdentate ligand in this respect, so the reduced basicity argument, if applicable in tripyam, should apply to any other terdentate ligand. Since other terdentate ligands invariably form complexes in which the ligands are, in fact, terdentate, it is doubtful whether enhanced basicity is a major factor in the ease of formation of tripyam complexes in which the ligand is bidentate. However, to the extent to which ion pairing and/or solvation effects are important in the preparative conditions used, an enthalpy effect may favour the formation of bidentate complexes, since work must be done in order to remove attached species from the metal ion before the coordination of each donor atom in a tripyam molecule can take place.

The Mössbauer spectrum of bis(tripyam)iron(II) perchlorate exhibits a negligible quadrupole splitting (ΔEq = 0.00 mm sec^{-1})[4], which shows that in this low-spin complex, the terdentate ligands are producing an effectively octahedral ligand field.[66] Although it has been shown that the iron(II), cobalt(II) (^{4}T), nickel(II) and copper(II) complexes in this series are isomorphous,[2,5] this does not neccessarily mean that they are isostructural, since minor distortions of the metal-ligand framework need not be apparent in X-ray powder photographs. It has been shown [51,63] that metal-ligand bond shortening occurs in low-spin complexes of iron(II). This has been attributed to the vacancy of the e_g orbitals[52]; alternatively, it can be argued that a close approach is enforced by the π-bonding which stabilises the low-spin state. It follows that some distortion of the cubic metal-ligand framework must occur in the high-spin tripyam complexes. That the stability of the bis(terdentate) tripyam complexes is strongly dependent on the radius of the metal ion is demonstrated by the fact that bis(terdentate) complexes of chromium(III)[3] and cadmium(II) (this work) could not be prepared. The distortion postulated could take one (or more) of three different forms:-

(a). Octahedral geometry involving orbital misdirection. This would involve some bending of the ligands about the pyridyl-nitrogen bonds: energy would be required to do this, but the octahedral geometry which maximises the L.F.S.E. would be preserved, even though the actual value might be reduced by less effective σ-overlap. It is interesting to note that a distortion of this type would not reduce π-overlap: indeed, it might increase it, since a σ orbital which no longer points directly at the metal ion must acquire some p character. A detailed ligand-field treatment of the bonding in these complexes is beyond the scope of this work: however, simple symmetry considerations show that in these complexes, only two out of the three t_{2g} orbitals <u>can</u> overlap with the π orbitals on the pyridyl rings. A similar situation occurs in the tris-complexes of 2,2'-dipyridyl and 1,10-phenanthroline.

(b). Octahedral geometry retaining maximum σ-overlap. This is most unlikely since it would involve stretching of bonds in the ligand.

(c) True D_{3d} geometry in which the ligands retreat from the metal ion along the C_3 axis. This need involve no distortion of the ligand, but it would cause a significant reduction in the L.F.S.E., and should give rise to trigonal splittings in the crystal field spectra of the cations. This is unlikely since no such trigonal splittings were detected, either in tripyam complexes or in bis-complexes of cis,cis-triaminocyclohexane [64,67,68], hydrotris(1-pyrazolyl)borate[69], tris(1-pyrazolyl)methane[69], or 1,3-diamino-2-aminomethylpropane[70], all of which are of D_{3d} symmetry.

It therefore seems likely that distortions of the type (a) occur in these complexes. They will be formed in preference to bis(bidentate) complexes only when the L.F.S.E. gained in an octahedral ligand field is more than sufficient to compensate for the factors opposing terdentate coordination, which must include the energy required to produce the distortion in the ligand. Among the complexes studied to date, this will only apply to low-spin iron(II) and to complexes of cobalt(II) and nickel(II) containing anions which are poor donors. Although Cu(II) has a fairly high L.F.S.E., it needs to undergo a tetragonal distortion in order to conform to the requirements of the Jahn-Teller theorem. It therefore takes advantage of the built-in tetragonality of the bis(bidentate) system whenever suitable donors are available to fill the axial positions. With all other metals the ligand evidently prefers to adopt the bidentate configuration in which the six-membered chelate ring is flexible enough to accommodate either distorted octahedral (tetragonal, approximately D_{4h}) geometry, or tetrahedral configurations with ions such as Zn(II), Mn(II) and Co(II) in the presence of halide ions. Thus, the hypothesis outlined in (a) affords an explanation of the coordination behaviour of tripyam which is in accord with most of the known chemistry of the ligand.

It is possible that the orbital misdirection referred to, with the consequent development of some p character in the nitrogen lone pairs, may account for the ability of this ligand to stabilise the ^1A and ^2E states in its iron(II) and cobalt(II) complexes, respectively: an effect of this type was invoked in an explanation of the observation of charge-transfer transitions of unusually low energy in the bis(cis,cis-triaminocyclohexane)cobalt(II) ion[68]. It is possible that the resulting increased $p\pi - d\pi$ overlap might compensate for the lack of extensive conjugation in this ligand, and in other non-conjugated ligands containing 2-pyridyl groups.[48]

There remains the question of why terdentate tri(2-pyridyl)-amine exerts such a high value of Δ. Although it is widely realised[65] that chelation increases the stability of complexes by an entropy effect, it is less generally known that chelation also increases the stability of complexes to a small but nevertheless significant extent by an enthalpy effect[71]. Let us consider a metal ion being approached by six unidentate ligands, each carrying a fractional negative charge. Work must be done to bring these charges together and to make them point in the right direction for the formation of an octahedral complex. This effect causes an inter-ligand repulsion which tends to reduce the metal-ligand bond distances and hence the bond strength. Moreover, the value of Δ is inversely proportional to the fifth power of the metal-ligand bond distances.[72] If, on the other hand, two terdentate ligands carrying the same donor groups are brought together near a metal ion, a large part of this repulsive energy is already built into the ligands: indeed, it makes a contribution to the enthalpy of formation of the complex, since an opportunity is thereby provided for some delocalisation of the negative charges. This enthalpy gain on chelation has been found to be particularly small in complexes of non-transition metal ions, presumably because the ligand electrons are not delocalised on complex formation[71].

Another effect has been briefly mentioned by Busch[67] in connection with the unusually high value of Δ [w.r.t.Ni(II)] produced by cis,cis-triaminocyclohexane. It was suggested that the rigidity of this terdentate ligand might enforce a strong octahedral field. The effect on orbital overlap of skeletal vibrations of metal-ligand systems offers support for this idea. Let us consider a twisting vibration such as

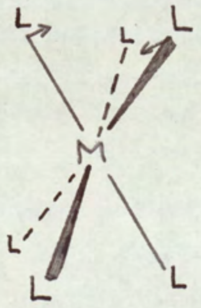


Table 12.3. Δ values [w.r.t. Ni(II)] produced by unidentate, bidentate, and terdentate ligands containing similar coordinating groups.

group	unidentate complex	cm^{-1}	ref.	bidentate complex	cm^{-1}	ref.	terdentate complex	cm^{-1}	ref.
$-NH_2$	$(NH_3)_6Ni^{2+}$	10800	55	$(en)_3Ni^{2+}$	11200	55	$(cis,cis\text{-}tach)_2Ni^{2+}$	11550	67
							$(pmtn)_2Ni^{2+}$	12050*	70
-py	$(py)_6Ni^{2+}$	9850	59	$(dipyam)_3Ni^{2+}$	11100	73	$(tripyam)_2Ni^{2+}$	12800	2

* the higher Δ value produced by this ligand is probably due to its ability to encapsulate the nickel(II) ion more effectively than cis,cis-tach.

Abbreviations py = pyridine; en = 1,2-diaminoethane; cis,cis-tach = cis,cis-triaminocyclohexane; pmtn = 1,3-diamino-2-aminomethylpropane; dipyam = di(2-pyridyl)amine; tripyam = tri(2-pyridyl)amine

In complexes of tripyam and related terdentate ligands, each set of three L groups are "tied together", so that if effective σ (or π) overlap at one metal-ligand bond is to be reduced, then either the ligand must undergo some deformation or else <u>both</u> of the ligand orbitals must simultaneously move out of effective overlap with the metal orbitals. In a complex of bidentate ligands, the constraints are much less, and no constraint at all exists in complexes containing unidentate L groups. The net result of this"enforced covalency" effect is to increase the amount of time which a ligand orbital spends in effective overlap with a metal orbital. Like the repulsion effect discussed above, this effect will be most pronounced in complexes of metal ions having high L.F.S.E. values, and will be of no significance in complexes of non-transition metals, since in these complexes there is no overlap of ligand orbitals with metal orbitals. The results produced by the "repulsion effect" and the "enforced covalency effect" are illustrated in Table 12.3.

To sum up, there is clearly nothing mysterious about the effect of chelation on Δ values. It is certainly not neccessary to invoke the transmission of electronic effects through chelate ring systems containing fully saturated groups.[48]

12.4. Conclusions.

1. The vibrational spectra of bis[tri(2-pyridyl)amine] complexes indicate that they possess D_{3d} symmetry in solution. Although the solid-state spectra are more complicated, no gross departure from this symmetry is indicated. However, splittings in some metal-sensitive ligand vibrations in the copper(II) and low-spin cobalt(II) complexes are consistent

with a tetragonal distortion of the electron distribution around the metal ions in these complexes.

2. Inter-ligand vibrational coupling is only significant when the metal ion is in a low-spin state. In nearly all other cases the g and u vibrations are accidentally degenerate. This is consistent with the stronger bonding expected in the low-spin complexes.

3. The assignments of metal-ligand stretching vibrations are in good agreement with recent work on similar complexes. In particular, there is a marked decrease in frequency with decreasing L.F.S.E., which confirms the importance of covalent bonding in these complexes.

4. The variation of the vibrational spectra and magnetic susceptibility of bis[tri(2-pyridyl)amine]cobalt(II) perchlorate with temperature indicate that a $^4T \rightleftharpoons {}^2E$ equilibrium exists in this complex. The observation of superimposed spectra shows that the energy barrier between the two states is greater than the zero-point vibrational energy.

5. The unusually high Δ value produced by tri(2-pyridyl)amine when terdentate is attributed to

(a) its ability to enforce directionally effective covalent bonding without gross misalignment from its equilibrium position as a free ligand, and

(b) unusually efficient σ-bonding, promoted by the release of interelectronic repulsions between the nitrogen lone pairs in the ligand.

6. The ability of tri(2-pyridyl)amine to stabilise the ^1A and ^2E states in iron(II) and cobalt(II) respectively indicates that the ligand must retain some π-acceptor capability. It is suggested that the effect of orbital

misdirection, which produces some p character at the pyridyl nitrogen atoms, together with the "directional effectiveness" of the π-bonding, may compensate for the absence of extended conjugation in this ligand.

7. Some factors affecting the coordination behaviour of this ligand are discussed in the light of the proposals outlined in 5 and 6.

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