Studies in Aluminium Alkoxide Chemistry

Philip Michael Watts

Master of Philosophy

The University of Aston in Birmingham

March 1991

The University of Aston in Birmingham
Studies in Aluminium Alkoxide Chemistry
Philip Michael Watts
Master of Philosophy
1991

The original purpose of this research was to gain some insight into the mechanism of hydrolysis of aluminium isopropoxide and into the structures of the products obtained. In order to achieve this end I have firstly carried out a survey of the available literature on aluminium alkoxides and related compounds. Following this I have described several practical studies which I carried out in order to familiarise myself with this area of chemistry. Finally, I have included a section which outlines what information I have been able to deduce on the hydrolysis of aluminium isopropoxide.

To My Parents, Rob and Marion

Acknowledgements

I would like to thank Rhone-Poulenc Chemicals Ltd for financial support for my research. Also Prof. W R McWhinnie for his many helpful suggestions regarding the prosecution of my research and thesis, and Christine West for typing the thesis. I would also like to thank Dr P Monsef-Mirzai and Mr M Ali for assistance they have given me during this time.

Contents

Contents Continued...

Tables

Page

Chapter 3

Chapter 4

Appendix 1

Figures

Figures Continued...

Spectra

Page

Infrared Spectra

XPS Spectra

CHAPTER 1

INTRODUCTION

Synthesis

A) Aluminium Trisalkoxides

These materials have been prepared by a variety of different methods, several of which have been listed below:

(i) Reaction of the alcohol with aluminium metal. [1-5]

(ii) Alcohol exchange between the alcohol and an aluminium alkoxide. [2-5]

(iii) Alcohol exchange between the ester and an aluminium alkoxide. [5,6]

(iv) Oxidation or hydrolysis of the aluminium alkyl [1,3,4,7-9]

(v) Reaction of the alcohol with the aluminium alkyl [2,5,10]

(vi) Reaction of the alcohol with aluminium chloride [1,3] or sulphide [11,12]

(vii) Miscellaneous reactions [2,13].

The first method has received widespread use in the preparation of low molecular weight alkoxides [14,15], although Ayres et al [16] claim it to be the only method of preparing tribenzyloxyaluminium. The procedure involves adding aluminium metal to an excess of the alcohol, followed by refluxing the mixture with a suitable catalyst until the aluminium has dissolved. The reaction mixture is then worked up to produce the desired product.Several factors must be kept in mind while carrying out the reaction:

(a) Exclusion of moisture from the reaction vessel. Water will hydrolyse aluminium alkoxides and so stringent precautions should be taken to exclude all moisture from the reaction [17]. Possible techniques include working under an inert atmosphere, using calcium chloride drying tubes and sealed apparatus, and adding a moisture trap to the reaction mixture, eg anhydrous aluminium chloride [4].

(b) Choice of catalyst. A variety of catalysts have been used, including mercury (amalgamated with the aluminium [16,18]), iodine [5,19-21], mercury (II) chloride [2,5,14,15,19,22-25] (or acetate [1,26,27]), a small amount of the desired alkoxide [19,28], hydrogen chloride [1] and carbon tetrachloride [14,15]. All these catalysts are believed to act by cleaning the oxide layer off the surface of the aluminium [12,29] after which the reaction proceeds exothermically.

(c) Recovering the product on completion of the reaction. After completion of the reaction the product will be mixed in with various impurities, including finely divided aluminium and the remnants of the catalyst. Several methods of removing the impurities have been suggested, including damp ether and centrifuging off the precipitate [28], and recrystallisation techniques [16]. However, the preferred method is to purify the product by subliming or distilling it off at reduced pressure [24, 30,31].

Examples of this method are the preparation of the methoxide by McElvain and Venerable [25], the ethoxide by Wilhoit et al [23], the isopropoxide by Fieggen and Gerding [26], the phenoxide by Lukasiak et al [12] and various aryl oxides by Ayres et al [16] and Oliver and Worrall [29].

The second method is used for preparing the alkoxides of higher boiling point alcohols. Aluminium isopropoxide is virtually always used as the starting alkoxide (due to its ease of manufacture and low cost), though any alkoxide of a low boiling point alcohol could be used [4,5]. The procedure involves refluxing the starting alkoxide in a mixture of the other alcohol and some other solvent (usually an aromatic hydrocarbon [32-34]), followed by azeotroping off the lower boiling alcohol with the solvent until reaction is complete.

The reaction is a stepwise equilibrium,

$$Al(OR)_3 + R'OH \rightleftharpoons Al(OR)_2(OR') + ROH$$

$$Al(OR)_2(OR') + R'OH \rightleftharpoons Al(OR)(OR')_2 + ROH$$

$$Al(OR)(OR')_2 + R'OH \rightleftharpoons Al(OR')_3 + ROH$$

and therefore can be manipulated to produce mixed alkoxides [5,34] by controlling the amount of alcohol (R'OH) added to the reaction mixture. Steric effects will also affect the reaction, making it difficult [32,35] or impossible [33] to obtain complete exchange of alcohols on the aluminium atom.

Examples of this method are the preparation of the butoxides and pentoxides by Mehrotra [32,36], the tertiary butoxides and pentoxides by Bains [34,35], the phenoxide by David et al [33] and Berny and Berrest [37], several mono-isopropoxide bis-alkyl phenoxides by David et al [33] and the 2-chloroethoxide by Paul et al [38].

The third method is used as an alternative to the second method. The procedure is similar to the second method, but the aluminium alkoxide is dissolved in the ester instead. The ester alcohol is exchanged for the alcohol attached to the aluminium.

$Al(OR)_3+R''COOR' \rightleftharpoons Al(OR)_2(OR')+R''COOR$

The reaction is again a stepwise equilibrium and so is driven to the right by distilling off the lower boiling ester (R"COOR). It can also be halted before complete exchange has taken place, either by choice or because of steric effects.

Examples of this method are the preparation of several butoxides (including the tertiary butoxide) by Baker [6] and Mehrotra [5] and the n-hexadecyloxide and allyloxide by Baker [6].

The fourth method is a general method for the production of alkoxides from their corresponding aluminium alkyls. The procedure involves synthesizing the aluminium alkyl (from the alkene, hydrogen and aluminium metal), followed by either passing a stream of dry oxygen [8] through a solution of the aluminium alkyl or carefull and homogeneous addition of a calculated amount of water [4] to the solution. The second part of the reaction should be thermostated [8] and monitored carefully, since the reaction is very exothermic.

Examples of this method are the prepartion of the 2-methyl pentoxide and the 2-ethylhexoxide by Sladkov et al. [8].

The fifth method is a modification of the second method. The alkyl group attached to the aluminium is always a low molecular weight alkane (usually ethane [39,40]), so that when it is replaced it will evaporate off.

$AlR_3+3R'OH \rightarrow Al(OR')_3+3RH\uparrow$

The procedure involves the slow addition of the aluminium alkyl to a mixture of the alcohol and an inert solvent (eg diethyl ether [39]) at a very low temperature. The reaction is allowed to warm gradually until it reaches room temperature, after which it is refluxed for a few hours. The solvent is then removed and the product collected. The initial cooling is necessary to control the exothermic reaction which initially takes place. Examples of this method are the preparation of the 2,2,2-trifluoroethoxide by Ueshima et al [39] and several chloroalkoxides by Ueshima et al [39] and Saegusa and Ueshima [40].

The sixth method has been used to prepare several aryloxides of aluminium. Lukasiak et al [12] used both aluminium chloride and aluminium sulphide in the preparation of the triphenoxide, refluxing each reagent with phenol in xylene for several hours. They found that though the sulphide produced a pure product, the chloride produced a compound which retained some of its chlorine. Repeating the reaction with aluminium chloride in anisole, and refluxing for fifty hours, still did not effect complete replacement of the chlorine. Malhotra et al [11] repeated these experiments on phenol, o-nitrophenol and o-chlorophenol, claiming to produce the trisaryloxide in every case. However, no evidence was given to justify their claims.

Other methods used to synthesise aluminium alkoxides include the reaction of an alcohol with aluminium hydride [2] or isopropyl iminoalane [2] and a modification of the Meerwein Ponndorf-Verley reaction [9,13]. The latter was used to produce the 2,2,2-trichloroethoxide of aluminium from the aldehyde (2,2,2-trichlorethanal) and aluminium ethoxide in ethanol. The procedure involved heating the mixture to 135°C under an inert atmosphere and fractionating off the acetaldehyde produced until the reaction has ceased (see ref. 13 for test). The ethanol was then distilled off.

$$CCl_3CHO + Al(OCH_2CH_3)_3 \rightleftharpoons Al(OCH_2CH_3)_2(OCH_2CCl_3) + CH_3CHO$$

In conclusion, the most convenient method for preparing aluminium alkoxides is the method of alcohol interchange between the aluminium alkoxide and free alcohol. However, the reactions of aluminium metal [26,31], aluminium sulphide [12] and aluminium alkyls [39] with alcohols have been shown to be excellent methods of producing pure aluminium alkoxides.

B) Chelating Compounds of Aluminium

This set of compounds can be split into the following groups:

(i) The carboxylates of aluminium, including the dicarboxylates and ∝-hydroxy carboxylates.

(ii) The ß-diketonates of aluminium, and also the ∝-diketonates and "pseudo" ß-diketonates of aluminium.

(iii) The glycoxides of aluminium.

(iv) The alkoxyalkoxides of aluminium.

(v) The N,O-chelates of aluminium.

(vi) The S,O-chelates of aluminium.

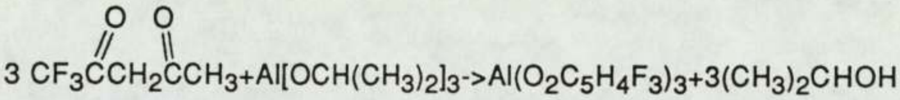
The carboxylates of aluminium were first investigated in the 1920s, when Burrows and Wark [41a] published an article on the preparation of aluminosalicyclic acid. Initially, workers were doubtful that the tricarboxylates of aluminium could be produced [41b - 45]. However, later work [46-48] showed that the formation of the tricarboxylates is possible under anhydrous conditions.

All the early synthetic work on aluminium carboxylates involved reacting a metal carboxylate with an inorganic salt of aluminium (eg the nitrate [49], sulphate [41,50] or chloride [51]). In each case only the mono-or biscarboxylates were produced, except for the preparation of aluminium succinate by Duval et al [49]. Later workers either used a modification of the alcohol interchange reaction (reacting the carboxylic acid with an aluminium alkoxide [14,47,52]), or reacted the carboxylic acid with aluminium chloride [53,54], or reacted the acid anhydride with an aluminium alkoxide [55,56] (or chloride[57]).

Examples of the second set of reactions include the preparation of the trilaurate, trimyristate, tripalmitate and tristearate by Mehrotra and Pande [55], the trioleate by Gilmour et al [58], the salicylates by Rai et al [54], the tri-acetate, tri-propionate and tri-butyrate by Pande and Mehrotra [56] and the furoates and thenoates by Singh et al [59]. (Several miscellaneous reactions have also been used to synthesise the tri-formate [57], the trilactate [60], the trilaurate [61,62], the dihydroxymonolaurate [63] and aluminosalicyclic acid [41a].)

The diketonates of aluminium have been prepared by seven different methods:

(a) The reaction of an aluminium alkoxide with the ß-diketone (or "pseudo" ß-diketone). The procedure is similar to the one used to exchange alcohols attached to the aluminium atom. It has been used to prepare the tris acetylacetonate by Case and Pinnavaia [64], the trisethyl acetoacetate by Kugler [65] and Charles et al [66], the tris-(1,1,1-trifluoro-2,4-pentanedionate) by Fay and Piper [67],



$$3\,CF_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3+Al[OCH(CH_3)_2]_3 \rightarrow Al(O_2C_5H_4F_3)_3+3(CH_3)_2CHOH$$

the tris-(1-phenyl-1,1-butanedionate) by Fay and Piper [68], the tri-salicylaldehyde derivative by Mehrotra and Mehrotra [69] and a variety of mixed alkoxide (or siloxide) diketonates [69-75].

(b) The reaction of an inorganic aluminium salt with the diketone. The salts used have been the sulphate [1, 76-78], the halide [1, 78-85], the nitrate [86-91] and the hydroxide [92]. The procedure varies depending on the diketone being used, but the principle of the reaction is to create a set of conditions under which a significant amount of the diketone exists in the enol form. For instance, acetyl acetone should be dissolved in a basic solution (eg add ammonia [77] or sodium hydroxide [88] to a mixture of one of the reactants and water), whereas the fluoro-substituted ß-diketones can be dissolved in a polar organic solvent (eg ethanol [86] or carbon tetrachloride [81]). A short reflux may be necessary to precipitate the product.

This is the preferred method for making many of the tris-diketonates of aluminium. For example, it has been used to prepare the trisacetylacetonate by Young [77], the hexafluoro analog ($CF_3COCHCOCF_3$) by Morris et al [81] the diphenyl analog ($C_6H_5COCHCOC_6H_5$) by Pinnavaia et al [83], the tris derivatives of tropolone (by Muetterties and Wright [80]) and maltol (by Finnegan et al [87]) and various fluoro substituted tris-ß-diketonates by Das et al [86].

(c) The reaction between aluminium metal and the ß-diketone. The procedure is similar to that used in the preparation of aluminium alkoxides from aluminium metal and the alcohol (see section A, method 1). Fernelius and Bryant [82] have used this method to prepare the trisacetyl acetonate, while Sievers et al [93] have used it to prepare the tris-(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate).

(d) The reaction between an aluminium alkyl and a metal diketonate. Only one example of this reaction is cited in the literature and that is the reaction between trimethyl aluminium and tris (acetylacetonato)cobalt(III) [94]. The reaction was carried out in the presence of 2,2'-dipyridyl, using benzene as a solvent and keeping the reaction mixture at 6°C for nearly one hour. The trimethyl aluminium was added to the reaction mixture slowly (over 20 minutes), and the mixture was stirred thoroughly while it warmed up at the end of the reaction.

(e) The double decomposition of two tris ß-diketonates of aluminium. This reaction was carried out by Patterson et al. [71] using a 1:2 (molar ratio) mixture of tris(acetylacetonato)aluminium and tris(ethylacetoacetato)aluminium. The mixture was heated and then distilled under vacuum to yield the product (bis(ethylacetoacetato), mono-(acetylacetonato)aluminium). Case and Pinnavaia [64] have also used this method to prepare several mixed ß-diketones of aluminium.

(f) The reaction between a tetraalkylaluminoxane and a ß-diketone. The only examples of this reaction in the literature are those carried out by Pietrzykowski et al [95] to produce tris-(acetylacetonato)aluminium. The procedure involved mixing the tetraalkylaluminoxane (R_4AlO) in diethylether at -70°C. Acetylacetone in diethylether was slowly added and then the reaction mixture was allowed to slowly warm up to room temperature. Distilling off the diethylether precipitated the product.

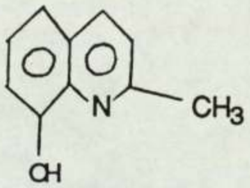
(g) Tris-(acetyl acetonato)aluminium is frequently produced as a by-product of the reaction between sodium acetylacetonato and aluminosiloxanes [96,97]. These reactions can be modified to produce tris-(acetylacetonato)aluminium as the major product [98].

The glycoxides of aluminium have received less attention than the carboxylates and diketonates of aluminium. Two methods of preparation have been used, the transesterification reaction (see section A, Method 3) and the alcohol exchange reaction [99] (using the glycol and aluminium isopropoxide; see section A, method 2). Both of these methods have been described elsewhere.
Examples of these reactions involving glycols are the preparation of the ethylene glycoxide by Baker [6] and the butylene glycoxides hexylene glycoxides and catechollates by Mehrotra and Mehrotra [99].

The alkoxyalkoxides of aluminium have also received little attention, with only the methoxy ethoxide being cited in the literature [71,100, 101]. The trimethoxyethoxide [100,101] was prepared by reaction of the alcohol with aluminium metal in the presence of mercury (II) chloride.

The N,O-chelates of aluminium can be split into five groups, the 8-hydroxyquinolines (8-quinolinol and its derivatives), the alkanol amines, the lactams, the nitrilophenols and the alkylenediamino-tetraacetates.

Attempts at preparing the tris 2-methyl-8-quinolinol derivative of aluminium have been made by Fernando and co-workers [102-105].

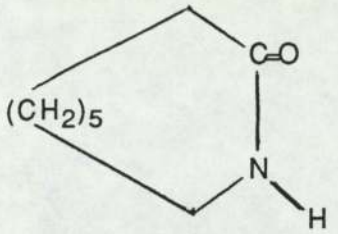


2-methyl-8-quinolinol

Reacting anhydrous aluminium chloride with 2-methyl-8-quinolinol in dry alcohol-free chloroform under anhydrous conditions (dry nitrogen atmosphere and diethylamine proton scavenger [105] produces bis(2-methyl-8-quinolinato)aluminium(III)-μ-oxo-bis (2-methyl-8-quinolinato)aluminium(III) [103-105] (complexed to chloroform under certain conditions). Repeating the action in dimethyl sulfoxide (DMSO) produces the adduct of DMSO and tris(2-methyl-8-quinolinato)aluminium(III) [105]. The tris-(5-fluoro-8-quinolinato) complex of aluminium has been prepared (by Hollingshead [106]) by reactiong ammonium alum with 5-fluoro-8-hydroxyquinoline in acidic solution.

Mehrotra and co-workers [107,108] have prepared various alkanolamine derivatives of aluminium. They were produced by reacting the alkanolamine with aluminium isopropoxide in benzene, the method used being similar to section A, method 2. Examples of the compounds which they have prepared are the tris(aminoethoxide) [107], the tris [(methylamino)ethoxide] [108], the tris [(dimethylamino)-propoxide] [108] and the bis-(p-aminophenylethoxide)monoisopropoxide [108]. On the other hand, Machacek et al. [109] prepared tris [(dimethylamino)ethoxy] aluminium (III) from aluminium metal and (dimethylamino) ethanol in the presence of mercury (II) chloride. The reaction mixture was refluxed and the product distilled off at 156-160°C/0.4 Torr.

Aluminium caprolactamate has been prepared by Kriz and Casensky [110]. The method used was to react isopropyliminoalane $HAl{=}NCH(CH_3)_2$ with caprolactam in benzene.



caprolactam

The reaction mixture was cooled until it finished evolving hydrogen and isopropylamine, at which point it was refluxed for two hours and the solvent removed. Kriz and co-workers [111] have also prepared the isopropoxy caprolactamates using either aluminium isopropoxide or isopropyliminoalane and isopropanol as the starting material.

Aluminium complexes of 2,2'2"-nitrilotriphenol (NTP) have been prepared by Muller and Burgi [112]. Initially they added a solution of NTP in dry pyridine (py) to a solution of aluminium isopropoxide in dry benzene. The mixture was refluxed for five minutes and on cooling produced Al[NTP(-3H)] (py). Heating this compound to over 110°C removed the pyridine and produced the dimeric compound $\{Al[NTP(-3H)]\}_2$. Repeating the initial procedure, but replacing the pyridine with quinuclidine (quin), the benzene with DMSO and mixing the solutions at 100°C, followed by very slow cooling (-20°C per day), produces $\{H\ quin\}^+\ [Al[NTP(-3H)]\ (OH)\}^-$.

Pearson et al [113] have prepared the aluminium complex of R-(-)-1,2-propylene diaminetetra acetic acid (H_4-R(-)-PDTA). The method of preparation was simply to mix a standardised aluminium ion solution and Na_2H_2-R(-)-PDTA with a pH5.0 buffer. (The molar ratio of Al^{3+}:Na_2H_2-R(-)-PDTA was 1:1). Saito and Terry [114] have prepared the ethylenediamine tetra acetic acid (EDTA) amalog using a similar method.

The S,O-chelates of aluminium have received less attention than the N,O-chelates of aluminium, being restricted in the literature to a study of the thiosalicyclic acid derivatives of aluminium [115]. The method of preparation is similar to section A, method 2. In this case thioslicyclic acid is added to aluminium isopropoxide in benzene, the reaction mixture is refluxed and the isopropanol is azeotroped off.

C) Bimetallic (and Termetallic) Aluminium Alkoxides and Chelates

The bimetallic aluminium alkoxides and chelates can be split into eleven groups:

(i) Compounds containing Group IA metals.
(ii) Compounds containing Group IIA metals.
(iii) Compounds containing metals from the first row of the transition elements (Scandium to Copper, inclusive).
(iv) Compounds containing metals from the second and third rows of the transition elements (not including lanthanum).
(v) Compounds containing the lanthanide elements.
(vi) Compounds containing the actinide elements.
(vii) Compounds containing Group IIB metals.
(viii) Compounds containing Group IIIB elements.
(ix) Compounds containing Group IvB elements.
(x) Compounds containing Group vB elements.
(xi) Compounds containing Group VIB, Group VIIB and Group O elements.

Two general methods have been used to prepare the tetraalkoxyaluminates of the Group IA metals. The first method consists of reacting the metal aluminium hydride with the desired alcohol under anhydrous conditions [116-122],

$MAlH_4 + ROH \rightarrow MAlH_3(OR) + H_2\uparrow$

$MAlH_4 + 4ROH \rightarrow MAl(OR)_4 + 4H_2\uparrow$

The reaction is carried out by slowly adding the dry alcohol to a solution of metal aluminium hydride in a dry polar solvent (eg diethylether, THF or diglyme [117]), followed by recovering the precipitated product by centrifuging the solution. This method has been used to prepare the tetramethoxy, ethoxy, isopropoxy and tert-butoxy aluminates of lithium, sodium and caesium by Turova and co-workers [116,117,119] and the tetra tert-butoxy aluminate of potassium by the same authors [116,117].

The second method consists of reacting the metal alkoxide with the aluminium alkoxide [123-126]. Carrying out the reaction in a 1:1 molar ratio yields the metal tetra alkoxy aluminate.

$MOR + Al(OR)_3 \rightarrow MAl(OR)_4$

whereas carrying the reaction out in a 3:2 molar ratio yields the "pentametallic" compound $M_3[Al_2(OR)_9]$.

$3MOR + 2Al(OR)_3 \rightarrow M_3[Al_2(OR)_9]$

This method has been used to prepare the tetramethoxy, isopropoxy and tert-butoxyaluminates of lithium, sodium and potassium by Mehrotra and co-workers [123-125] and the pentametallic isopropoxides of the same metals by the same authors [123-125,127].

Other methods have been used to produce the metal aluminium chelates [41a, 76, 101, 109, 128-131]. For instance, Bailar and Jones [128] prepared hydrated potassium aluminium oxalate $[K_3[Al(C_2O_4)_3]\ 3H_2O]$ from freshly precipitated aluminium hydroxide, potassium oxalate and oxalic acid dihydrate in aqueous solution. Similarly, Dubey and Mehrotra [129] prepared several potassium aluminium catecholates from potash alum, catechol and potassium hydroxide in aqueous solution. Finally, Machacek and co-workers prepared sodium tetra [(dimethylamino)-ethoxy] aluminate [130] and sodium tetra (methoxyethoxy) aluminate [101] by reacting the "alcohol" with sodium and aluminium metal.

No bimetallic compounds of these types have been reported for rubidium or francium.

The Group IIA Metal tetraalkoxy aluminates (except Beryllium and Radium) can also be synthesized by one of three general methods. The first method involves reacting a mixture of both metals with the desired alcohol [132-134] in the presence of an iodine or mercury (II) chloride catalyst. The second method involves carrying out the reaction using the aluminium alkoxide [123,135,136] instead of aluminium metal. The third method involves carrying out the reaction using the metal alkoxide [125], as well as the aluminium alkoxide, instead of the metal itself (no catalyst is needed in this modification of the general reaction). The product obtained from these reactions is the metal bis-(tetra alkoxy aluminate).

$M + 2ROH \rightarrow M(OR)_2$

$Al + 3ROH \rightarrow Al(OR)_3$

$M(OR)_2 + 2Al(OR)_3 \rightarrow M[Al(OR)_4]_2$

However, if excess metal alkoxide is added to the product, the hexa alkoxy aluminate of the metal is produced [134].

$M[Al\ (OR)_4]_2 + 2M(OR)_2 \rightarrow M_3[Al(OR)_6]_2$

Examples of the synthesis of these bimetallic alkoxides are the preparation of the tetraethoxyaluminates by Kulpinski and Nord [132], Villani and Nord [133] and Govil and Mehrotra [135] the tetraisopropoxy aluminates by Mehrotra at al [136] and the hexaethoxy aluminate of barium by Turevskaya et al [134].

Beryllium aluminium isopropoxides have been prepared by Aggrawal et al [137] from beryllium chloride and potassium tetraisopropoxy aluminate in isopropanol. Other bimetallic alkoxides of beryllium have been prepared by alcohol exchange between the isopropoxide and the free alcohol [138]. No alkoxyaluminates of radium have been reported in the literature.

The preparations of two barium aluminium chelates have been reported. Barium tetrakis (1,2-ethanediolato) dialuminate (III) [139, 140] $Ba[Al_2(C_2H_4O_2)_4]$ has been prepared by mixing barium hydroxide, aluminium isopropoxide, water and ethylene glycol (molar ratio 1:2:9:40), and leaving it at 473K for two weeks. Barium aluminosalicylate [41a], $Ba[(C_7H_4O_3)_2Al(OH)(OH_2)]$ was prepared by gently heating the aqueous sodium salt with barium chloride.

The general method of preparing the first row transition metal alkoxyaluminates is to react the transition metal chloride with potassium tetraisopropoxyaluminate in isopropanol [123,141-143]. Other alkoxides (or chelates) may be prepared by using the alcohol interchange method [143] (section A, method 2). By the initial method, the tetraisopropoxyaluminates of scandium (III), chromium (III), iron (III), manganese (II), iron (II), cobalt (II), nickel (II) and copper (II) have been synthesised. Other tetraalkoxy aluminates of chromium (III) [143,144], iron (III) [143], cobalt (II) [145], nickel (II) [143,146] and copper (II) [143,147] have been synthesised, along with the acetylacetonate derivatives of all the previous elements, bar iron (III).

One other area of study has been the μ-oxoalkoxides of aluminium with several metals [148], including chromium (II), manganese (II), iron (II) and cobalt (II). Ouhadi et al [148] have used two different methods of producing these compounds:

(i) The thermal condensation reaction between aluminium trialkoxide and a metal (II) acetate [149].

(ii) The carefully controlled hydrolysis of a metal (II) tetraalkoxy aluminate (III) compound [150].

These produce a compound of the formula $(RO)_2AlOMOAl(OR)_2$.

The second row and third row transition metal alkoxyaluminates reported in the literature are confined to yttrium (see scandium [123,151]), zirconium, hafnium, niobium and tantalum. Otherwise, only the μ-oxoalkoxides of molybdenum and aluminium [148] (prepared in the same manner as the first row transition metal μ-oxoalkoxides), a trichelate of silver (I) and aluminium [152] and several isopropoxy aluminium chelates of zirconium [153] and molybdenum [154], are mentioned.

Zirconium and hafnium isopropoxyaluminates have been prepared [123,124,155] by reacting the metal isopropoxide with aluminium isopropoxide in isopropanol. Using 1:1 molar ratios of metal isopropoxide to aluminium isopropoxide produces the tris isopropoxymetal tetraisopropoxyaluminate,

$$M[OCH(CH_3)_2]_4 + Al[OCH(CH_3)_2]_3 \rightarrow [(CH_3)_2CHO]_3M\ [Al(OCH(CH_3)_2)_4]$$

while using a 2:1 molar ratio produces the bis-isopropoxymetal bis-(tetraisopropoxy) aluminate.

$$M[OCH(CH_3)_2]_4 + 2\ Al[OCH(CH_3)_2]_3 \rightarrow [(CH_3)_2CHO]_2M[Al(OCH(CH_3)_2)_4]_2$$

Further replacement of the isopropoxide groups attached to the metal atom will not occur.

Niobium and tantalum isopropoxyaluminates are prepared [123,156] by the same methods as their zirconium and hafnium analogs. The only difference in the products formed is that the metal ions in the niobium and tantalum bind to one more isopropoxide group eg

$Nb[OCH(CH_3)_2]_3\ [Al(OCH(CH_3)_2)_4]_2$ and $Ta\ [OCH\ (CH_3)_2]_4\ [Al(OCH(CH_3)_2)_4]$.

The trichelate of silver (I) and aluminium [152] is the tris [bis(triphenylphosphine) silver (I)] [tris(dithiooxalato-O,O') aluminate (III)]-bis- chloroform complex. It was prepared by extracting a solution of potassium [tris(dithiooxalato-O,O')aluminate (III)] in tetrahydrofuran (THF) with a solution of tris (triphenylphosphine) silver (I) chloride in dichloromethane. Pentane was added to the dichloromethane solution to precipitate the product, which was recrystallised from n-pentane and chloroform. A copper (I) analog [152] has been prepared by the same method.

The zirconium chelates have been prepared by Jain et al. [153] from tris isopropoxy zirconium tetraisopropoxyaluminate and a ß-diketone (in a 1:1 and 1:2 molar ratio). Trans-bis(μ-acetato-O,O')-bis [μ-(tetraisopropoxy)aluminate-O,O']dimolybdenum was prepared (by Lamotte et al[154]) by thermal condensation between aluminium isopropoxide and molybdenum (II) acetate in a 1:1 molar ratio.

The tetraisopropoxyaluminates of all the lanthanides, except for promethium, europium, terbium and thulium, have been synthesised by Mehrotra and co-workers [123,124,151,157-159]. Three methods of synthesis have been used,

(a) The reaction between the metal chloride and potassium tetraisopropoxy aluminate [151,157] (see this section, first row transition metals).

(b) The reaction between the metal chloride, aluminium chloride, potassium metal and isopropanol [151,157].

(c) The reaction between the metal isopropoxide and aluminium isopropoxide in isopropanol [151,157].

As usual, anhydrous conditions must be maintained throughout the reactions.The products formed from these reactions have the formula Ln(III) $[Al(OCH(CH_3)_2)_4]_3$.

The tetraalkoxy aluminates of the actinides are restricted in the literature to those of uranium and thorium. The tetraisopropoxy aluminate of thorium, Th $[Al(OCH(CH_3)_2)_4]_4$, was synthesised [123,124] in much the same way as the lanthanides, except that the sodium salt was used instead of the potassium salt.

However, when the ethoxides of aluminium and uranium underwent reaction [124,160], the product formed had the formula $Al[U(OCH_2CH_3)_6]_3$. Since uranium alkoxides are strong Lewis acids (much the same as aluminium alkoxides are), then it is possible to form compounds of this type.

The Group IIB metal tetraalkoxyaluminates have been prepared by Aggrawal and co-workers [137,161]. The method of preparation involved reacting the metal chloride with potassium tetraisopropoxy aluminate in isopropanol [137] (and ether in the case of mercury). This produced the metal tetraisopropoxyaluminates,

$$MCl_2 + 2K[Al(OCH(CH_3)_2)_4] \rightarrow M[Al(OCH(CH_3)_2)_4]_2 + 2KCl$$

which in the case of zinc [161] has been used to prepare other tetraalkoxyaluminates, by using the alcohol interchange method (see section A, method 2). (Meerwein and Bersin [162] also claim to have prepared the aluminium tris[trisisopropoxy zincate] from aluminium metal and zinc isopropoxide in isopropanol).

The μ-oxoalkoxides of aluminium and zinc have also been studied [148]. The original method of preparation was to react aluminium isopropoxide with zinc acetate in decalin at 200°C [149]. Other μ-oxoalkoxides (eg the n-butoxide) were then prepared by refluxing the μ-oxoisopropoxide with the desired alcohol and distilling off the isopropanol produced. A later method of preparation involved the controlled hydrolysis of zinc tetralkoxyaluminates [150].

$2Al(O\,i\text{-}Pr)_3 + Zn(OOCCH_3)_2 \rightarrow (i\text{-}PrO)_2AlOZnOAl(Oi\text{-}Pr)_2 + 2CH_3COOi\text{-}Pr$

$Zn[Al(On\text{-}Bu)_4]_2 + H_2O \rightarrow (n\text{-}BuO)_2AlOZnOAl(On\text{-}Bu)_2 + 4n\text{-}BuOH$

where: i-Pr = $(CH_3)_2CH$ and n-Bu = $CH_3(CH_2)_3$

The Group III B tetraalkoxyaluminates reported in the literature are confined to the indium [123,124,163] and gallium [123,163] tetraisopropoxy aluminates. They have been prepared by the same methods as were used to prepare the the lanthanides, ie the reactions between the metal chloride and potassium tetraisopropoxy aluminate, the metal chloride and aluminium chloride/potassium metal in isopropanol, and the metalisopropoxide and aluminium isopropoxide.

The only Group IVB tetraalkoxyaluminate reported in the literature is tin (IV) tetraisopropoxy aluminate (III) [164], $Sn[Al(Oi\text{-}Pr)_4]_4$. This compound was prepared by refluxing tin tetrachloride with sodium tetraisopropoxy aluminate in isopropanol and benzene. The product was filtered off and distilled under reduced pressure.

The Group VB tetraalkoxy aluminates have not been mentioned in the literature. However, one arsenic aluminium chelate [152] and one ammonium aluminium chelate [165,166] have been reported.

The arsenic compound, tris(tetraphenylarsonium) [tris(dithio-oxalato-O,O') aluminate (III)], was prepared in a similar manner to the silver salt (see this section, second row and third row transition metals). A solution of potassium [tris(dithiooxalato-O,O')aluminate (III)] in THF was extracted with a solution of tetraphenylarsonium chloride in dichloromethane. The product was precipitated by adding dry diethylether to the dichloromethane solution.

The ammonium compound, tetramethyl ammonium tris oxalato-aluminate (III) mono [165] (or tri[166]) hydrate, was prepared by Bulc. et al. from aluminium oxalate and ammonium oxalate in aqueous solution.

No Group VIB, Group VIIB or Group O aluminium alkoxides or chelates have been reported. A few termetallic alkoxides of aluminium with two other metals have been reported by Aggrawal and Mehrotra [167]. These have been prepared by the reaction of (isopropoxy beryllium) [tetra-isopropoxy aluminate (III)] [137] with the isopropoxides of titanium, zirconium, hafnium, niobium and tantalum, carried out by refluxing them in benzene. Titanium, zirconium and hafnium produce alkoxides of the formulae $MBeAl(Oi\text{-}Pr)_9$ and $MBe_2Al_2(Oi\text{-}Pr)_{14}$, the stoichiometry being dependent on the molar ration of the two reactants. Niobium and tantalum produce alkoxides of the formula $MBeAl(Oi\text{-}Pr)_{10}$.

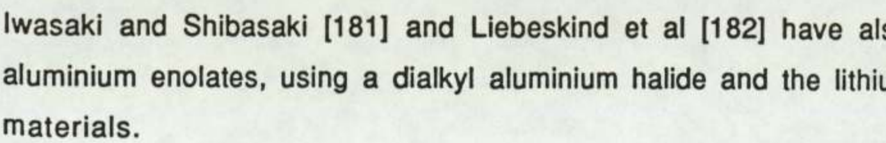
D) Organo-, Halo-, and Hydrido - Aluminium Alkoxides and Chelates

The organo aluminium alkoxides and chelates can be split into six groups:

(i) The mono- (and di-) alkoxides, phenoxides and alkenoxides.
(ii) The mono carboxylates.
(iii) The mono ß-diketonates and derivatives of the semiquinones.
(iv) The crown ether complexes.
(v) The isocyanates and other nitrogen-containing substituents.
(vi) The bimetallic alkyl aluminium alkoxides.

The organoaluminium alkoxides and phenoxides are generally prepared by mixing a 1:1 molar ratio of the aluminium alkyl and the alcohol (or ether [9, 168]) in an inert solvent (eg toluene [169,170] cyclopentane [170] or heptane [171-173]) at room temperature. Atwood et al [174] have prepared the methyl aluminium phenoxide ions, $[Al_2(CH_3)_6OC_6H_5]^-$ and $[Al(CH_3)_2(OC_6H_5)_2]^-$, by reacting trimethylaluminium with potassium phenoxide in the prescence of dibenzo-18-crown-6 and using toluene as a solvent. Mole and Jeffery [7], in their book on organoaluminium compounds, have suggested several other methods [9,10,175-177] of preparing organo aluminium compounds.

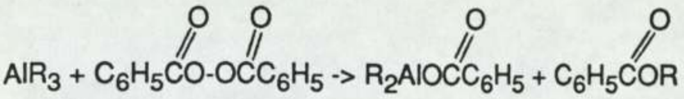
A few organo aluminium alkoxide halides have been prepared [172,178,179] by reacting the dialkyl aluminium halide with the alcohol in n-heptane and at low temperatures (-20^{o}C-O^{o}C). Also, a novel organoaluminiumalkenoxide, dimethylaluminium -4,4-dimethyl-pent -2-en-2-olate, has been synthesised by Jeffery et al [180]. It was prepared by slowly mixing trimethyl aluminium and mesityl oxide in diethyl ether, using bis(acetylacetonato) nickel as a catalyst and keeping the temperature at -50^{o}C. The reaction mixture was then very slowly warmed to room temperture and the solvent removed.



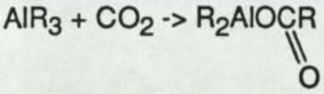
$$(CH_3)_2C = CH - \underset{CH_3}{\underset{|}{C}} = O + (CH_3)_3Al \rightarrow (CH_3)_3C\text{-}CH = \underset{CH_3}{\underset{|}{C}}\text{-}OAl(CH_3)_2$$

Iwasaki and Shibasaki [181] and Liebeskind et al [182] have also prepared several dialkyl aluminium enolates, using a dialkyl aluminium halide and the lithium enolate as their starting materials.

The organo aluminium carboxylates have been prepared by four different methods. The starting material is always an aluminium alkyl, but while Zakharin et al [183] reacted it with the carboxylic acid itself, Atwood et al. [184] used the ammonium salt, Stepovik, Razuvaev and co-workers [185-188] used the peroxide and Weidlein [189] and Lehmkuhl [190] used carbon dioxide. All the products were monocarboxylates.



$$AlR_3 + C_6H_5\overset{O}{\overset{/\!/}{C}}O\text{-}O\overset{O}{\overset{/\!/}{C}}C_6H_5 \rightarrow R_2AlO\overset{O}{\overset{/\!/}{C}}C_6H_5 + C_6H_5\overset{O}{\overset{/\!/}{C}}OR$$



$$AlR_3 + CO_2 \rightarrow R_2AlO\underset{O}{\underset{\backslash\!\backslash}{C}}R$$

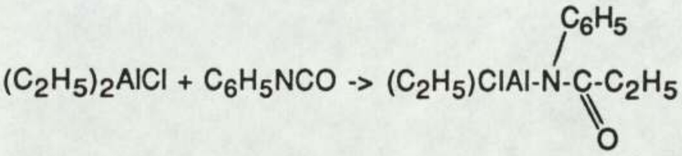
The organoaluminium ß-diketonates and semiquinones have been prepared by several different methods. Mole and Jeffery [7] suggested four methods of preparing the organoaluminium acetylacetonates, one of which was used by Pasynkiewicz and Dowbor [191]. It involved mixing trimethylaluminium with trisacetylacetonatoaluminium in toluene at room temperature. Pasynkiewicz and Pietrzykowski [94] modified this method by using trisacetylacetonato cobalt (III) in benzene, instead of the aluminium chelate. Another of Mole and Jeffery's methods was used by Roha et al. [192] and Kroll and Naegele [193], who prepared a similar compound from tri-isobutylaluminium and acetylacetone in methyl cyclopentane at -20°C. Davies et al [194] also used this method to prepare several diethylaluminium derivatives of the semiquinones.

Pietrzykowski et al [95] succeeded in preparing the tri-isobutyl acetylacetonatoaluminoxane, by slowly adding water to a solution of diisobutylaluminium acetylacetonate in diethylether at -40°C. After three to four hours, triisobutyl aluminium was slowly added to the solution and the reaction allowed to warm up to room temperature. The solvent was then distilled off and the product recovered.

Jeffery et al. [195] have also synthesized an unusual pair of organoaluminium ß-diketonates. Starting with dimethyl aluminium-4,4-dimethyl-pent-2-en-2-olate [180], they reacted this compound with either acetaldehyde or benzaldehyde, which resulted in a ß-diketonate containing three chiral centres (dimethyl aluminium 3-t-butyl-2,4-pentanedionate or the 2-t-butyl-2-phenyl-1,3-butanedionate analog).

The crown ether complexes of aluminium alkyls have been studied by Atwood and co-workers [196-198]. In all cases (except when using 12-crown-4) the crown ether was mixed with trimethyl aluminium in toluene and heated to 50-60°C for 1-24 hours, before allowing the reaction to cool. The number of trimethyl aluminium groups which attached to the crown ether seemed to depend on the length of the heating time rather than the molar ratio of the reactants. Trimethyl aluminium reacts much more exothermically with 12-crown-4 [198] and so in this case the reaction was carried out at 0°C. Atwood and co-workers [199-200] have also synthesised several complexes between trimethyl aluminium and the calixarenes.

The organo aluminium isocyanates have been studied by Jennings et al [201], Harada et al [202], Tani et al [203] and Horder and Lappert [204]. Hirabayashi et al [205] have also studied several similar reactions involving the reaction of diethyl(dimethylamino) aluminium with lactones and acid anhydrides. All of these reactions involve the insertion of the free substituent in between the aluminium atom and the amino group [205] or alkoxide group [202] (or alkyl group if neither of the previous is present [204]).



$$(C_2H_5)_2AlCl + C_6H_5NCO \rightarrow (C_2H_5)ClAl\text{-}\overset{C_6H_5}{N}\text{-}\underset{O}{\overset{\|}{C}}\text{-}C_2H_5$$

On the other hand, Higashi and Watabe [206] have prepared the dialkylaluminium alkanolamines by simply reacting the trialkylaluminium with the alkanolamine. Hurley et al. [207] have used the same reaction to produce the dialkylaluminium alkanolamines and dimethyl aluminium 8-quinolinolate, as have van Vliet et al [208] in preparing diethyl aluminium 2-pyridylmethanolate.

A few bimetallic alkyl aluminium alkoxides have been synthesized. Konomi and Tani [209] prepared sodium triethylaluminium ethoxide from an equimolar mixture of sodium tetraethylaluminate and ethanol in benzene. Lehmkuhl [177] prepared the same compound from diethylaluminium ethoxide, sodium hydride and ethylene. Atwood and Stucky [210] prepared magnesium bis[dimethyl dimethoxy aluminate (III)]-dioxan by partial oxidation of a solution of magnesium tetramethylaluminate in dioxan.

The haloaluminium alkoxides and chelates can be divided into the same groupings as their organo aluminium analogs. The alkoxy-and phenoxyaluminium halides have been prepared by several different methods. Flagg and Schmidt [211] prepared the bisisopropoxyaluminium fluoride by reacting a solution of diethylaluminium fluoride in heptane with a mixture of sodium metal and isopropanol at -70°C. Malhotra et al [11] prepared the phenoxy analogs by replacing the aluminium isopropoxide with phenol, which enabled them to reflux the reaction in benzene. This method was also used by Mehrotra and Mehrotra [212] and Funk and Rogler [213].

Two other methods deserve mention,

(a) the reaction between an aluminium alkoxide and acetyl chloride (or bromide) carried out by Mehrotra and Mehrotra [214,215] and Friberg and Hansson [216].

(b) the addition of carbon tetrachloride to a refluxing mixture of aluminium and alcohol (with a suitable catalyst) carried out by Simonyi and co-workers [217-219] and Foldesi [220].

The haloaluminium carboxylates [53,54,221,222] mentioned in the literature have all been prepared by the same method, with one exception, [222]. The carboxylic acid was added to the aluminium halide dissolved in a suitable solvent (eg ether) and refluxed for several hours [54]. Andrianov et al [222] used the sodium salt, instead of the free carboxylic acid.

The haloaluminium ß-diketonates have been synthesized by two different methods. Patterson et al [71] prepared the dichloroaluminiumacetylacetonate by refluxing aluminium chloride and acetylacetone in benzene, while Pasynkiwicz and Dowbor [191] prepared the same compound by mixing methyl aluminium dichloride with tris acetylacetonatoaluminium in toluene.

The dichloroaluminium derivatives of the semiquinones were prepared, by Davies et al. [194], by reacting the semiquinone with aluminium trichloride or ethylaluminium dichloride. The ethyl group is normally replaced in preference to the chlorine atom. The crown ether complexes of aluminium chloride were first prepared by Wada and Matsuda [223], from addition of the crown ether to a solution of aluminium chloride in ether. Atwood and co-workers [224,225] modified their procedure, using the ethyl aluminium dichloride and carrying the reaction out in toluene. The products were unlike their trimethyl aluminium analogs, in that they were 1:1 adducts.

Horder and Lappert [204] have prepared several isocyanate insertion products from the reactions of aluminium bromide, diethylaluminium chloride and ethyl aluminium dichloride with phenyl isocyanate and methyl isocyanate.

The hydridoaluminium alkoxides and chelates are restricted to the simple and bimetallic alkoxides, alkoxyalkoxides and aminoalkoxides.

The hydrido aluminiumisopropoxides have been prepared by Flagg and Schmidt [211] from aluminium hydride and aluminium isopropoxide in THF at $-70^{o}C$. Noth and Suchy [226] have prepared several hydridoaluminium alkoxides from aluminium hydride and the alcohol in THF, while Kriz and co-workers have prepared the alkoxides [227], alkoxyalkoxides [100] and aminoalkoxides [228] by the reaction of aluminium trichloride with sodium hydridoalkoxy-aluminates in benzene.

The bimetallic hydridoaluminium alkoxides have been prepared by Turova et al [117], Fusek et al [229], Zakharkin et al [122] and Brown and co workers [121,126,230], from the reaction of the group IA metal aluminium hydrides with alcohols.

$$LiAlH_4 + 3ROH \rightarrow LiAlH(OR)_3 + 3H_2\uparrow$$

Machacek and co-workers have prepared the bimetallic alkoxyalkoxides [101,131,227] and aminoalkoxides [109,130] from the reaction of two aluminium compounds, either of which will contain group IA metal ions, hydride ions and "alkoxide" ions,

eg $Na_3AlH_6 + 2Al(OR)_3 \rightarrow 3Na[AlH_2(OR)_2]$ [101]

$AlH_3 + NaAlH(OR)_3 \rightarrow Na[Al_2H_4(OR)_3]$ [109]

E) Miscellaneous Aluminium Compounds

This section includes the peroxides and siloxides of aluminium, as well as a few more unusual compounds [226,231].

The peroxides are generally encountered as unstable intermediates in the preparation of aluminium alkoxides from aluminium alkyls [8,232]. However, Dodonov et al [233] have prepared di(tert-butoxy)tert-butyl-peroxyaluminium by treating di(tert-butoxy) aluminium chloride with tert-butylhydroperoxide in diethylether (and in the presecence of diethylamine). Davies and Hall [234] have also carried out a similar reaction, using the aluminium alkoxide instead of the alkoxyaluminium chloride.

The siloxides are more easily obtained, Mehrotra and Pant [235] having prepared the tris(trimethyl siloxide) from aluminium isopropoxide and trimethylsilylacetate in cyclohexane. Wengrovius and co-workers [72,74] have prepared several mixed siloxide/ß-diketonates of aluminium, while Ercolani and co-workers [97,236] and Zhdanov and co-workers [237,238] have prepared several aluminosiloxane polymers and chloroaluminium siloxides.

Structure

A) Aluminium Trisalkoxides

Of all the aluminium alkoxides, aluminium isopropoxide has received the most attention in the literature. As early as 1933, Ulich and Nespital [239] proposed that aluminium isopropoxide had a tetrameric structure in the form of a ring (as did Robinson and Peak [240]) (Fig.1). Mehrotra expanded this work, proposing that aluminium isopropoxide could also exist in a trimeric form [32] and a dimeric form [36] (Fig.2). Bradley [241] continued this line of work, but disagreed with Robinson and Peak's structure for the tetrameric species, suggesting instead that one of the aluminium atoms should exist in a six co-ordinate state (Fig.3). Shiner et al [242] carried out some proton nuclear magnetic resonance studies on solid aluminium isopropoxide (as did Worrall and co-workers [243,244]) and found evidence to indicate that Bradley's suggestion for the structure of tetrameric aluminium was correct. Fieggen and Gerding's [26] studies of the infra-red and raman spectra of solid aluminium isopropoxide confirmed that the structure of the tetramer was that of Bradley [241] (Fig.3) and not Robinson and Peak [240] (Fig. 1).

On the other hand, Kleinschmidt and co-workers had turned their attention to the structure of trimeric aluminium isopropoxide [245] and the mechanism of interchange between the different forms of aluminium isopropoxide [31]. Proton nmr studies of liquid aluminium isopropoxide suggested (on integration of the peak heights) that trimeric aluminium isopropoxide contains a five co-ordinate aluminium atom (Fig.4). Fieggen and Gerding [26] were unable to confirm this from their infra-red and raman spectra of the low-boiling point aluminium isopropoxide (claimed to be a solid form of the trimer), but Kriz et al [2] have provided evidence in the form of aluminium-27 nmr studies for the existence of five co-ordinate aluminium in the trimer. Kleinschmidt and co-workers then expanded their proton nmr studies [31] to investigate the kinetics and the mechanism of interchange between the forms of aluminium isopropoxide, suggesting the possibility of the hexamer (Fig.5) existing as an intermediate in the mechanism. This would be in agreement with Daasch and Fales' [246] observations in the mass spectrum of aluminium isopropoxide (Fig. 6).

The only other work of note has been the confirmation of the tetrameric structure by Turova and co-workers [247,248] using X-ray crystallography [249] and the carbon-13 nmr studies (Fig.7) of Akitt and Duncan [250] showing the existence of two forms of the tetramer; mirror-images of each other.

Of less relevance on the subject of aluminium isopropoxide include infra-red studies by various workers [16,23,251-253], mass spectroscopy studies by Fieggen et al [27] and Brown and Masdiyasni [22], and gas chromatography studies by Brown and Masdiyasni [22].

A reasonable amount of work has been carried out on other aliphatic alkoxides of aluminium. However, except for the molecular weight determinations carried out by Mehrotra [32,36] and Bains [34], very little structural information has been gained from these studies.

Mehrotra found that the ethoxide [32], n-propoxide [32], n-butoxide [32] and less-branched pentoxides [36] were dimers. Bains obtained similar results when he found that the tertiary butoxides [34], pentoxides [34] and higher alkoxides [34] were dimers. Subsequent work by Bradley [24] on the methoxide, by Wilhoit et al [23] and Oliver and Worrall [254] on the ethoxide, by Oliver and Worrall [255] and Shiner et al [242] on the t-butoxides, and by

Guertin et al [251] on the s-butoxide and 2-pentoxide, have not clarified the picture. Amma [249] has gathered some data on the crystals of aluminium ethoxide, but no X-ray crystallographic analysis has been reported. Recently, Kriz et al [2] published a study of several aluminium alkoxides, using aluminium-27 nmr. However, some of the results may be suspect eg the ethoxide at 22°C. In this particular case, the authors suggest a structure containing both five and four coordinate aluminium (in a ration of 2.5:2 from the degree of association). However, the aluminium-27 nmr spectrum shows only one peak and the reference quoted for the degree of association [250] is concerned solely with the ispropoxide.

The aromatic alkoxides of aluminium have received even less attention than the aliphatic alkoxides of aluminium. However, useful information has been obtained on several of these compounds.

The first recorded work on the structure of the aromatic alkoxides was carried out by Ayres et al [16] on tribenzyloxyaluminium. On the basis of his molecular weight measurement and proton nmr studies, he proposed a cyclic trimeric structure (Fig 8). However, later work by Oliver and co-workers [29,256,257] using a 220MHz nmr spectrometer, rather than the 60MHz spectrometer used by Ayres et al, showed that tribenzyloxyaluminium (and tri-(4-chlorobenzyloxy)aluminium [29]) exists as a tetramer (Fig.9) in the solid state.

Lukasiak et al [12] have studied the structure of aluminium triphenoxide using infra-red spectroscopy and molecular weight measurements and have found it to be dimeric. On the other hand, David et al. [33] and Malhotra et al [11] claim that aluminium triphenoxide is trimeric, from their molecular weight measurements. The most recent work, by Kriz et al [2], claims that it exists in both forms.

B) Chelating Compounds of Aluminium

This set of compounds can be split into the same groups as have been used previously (see Synthesis, section B). Early workers [14] proposed polymeric structures for the biscarboxylates of aluminium (Fig.10), which is compatible with the formation of gels and high viscosity solutions observed [14,50]. Mehrotra and Rai [53] were able to calculate the molecular weights of some mono,-bis- and tris-carboxylates, calculating them to be dimers, dimers and monomers, respectively. However, as it has been pointed out by McRoberts and Schulman [47] and McBain and McClatchie [258] aluminium carboxylates gel on the addition of very small quantities of water. This fact would account for earlier observations.

A number of infra-red studies have been carried out on the formate [57,259] the furoate [59] and the thenoate [59]. These have been used to indicate that the carboxylate ion is a bidentate ligand when attached to the aluminium atom (Fig.11).Rinse [19] has studied the aluminium oxide stearate and proposed a hexameric structure from the molecular weight measurements and infra-red spectrum (Fig.12). Friberg has also carried out a similar set of studies [260-263].

The diketonates of aluminium are less sensitive to moisture than the carboxylates, and have therefore received more attention that the carboxylates.

The structure of aluminium trisacetylacetonate has been studied using several different analytical techniques, including carbon-13 nmr [264], raman spectroscopy [76,79], mass spectroscopy [265,266] and molecular weight measurements [267]. However, conclusive proof of the structure of the compound is available in the form of X-ray crystallographic studies [92, 268-274]. Hon and Pfluger [92] established the structure of a a-trisacetyl acetonatoaluminium as being a monomer containing octahedrally co-ordinated aluminium. McClelland [272] established the structure of γ-trisacetylacetonatoaluminium as being a racemic mixture of the two enantiomorphs of the monomer (Fig. 13).

The fluorinated analogs of aluminium trisacetylacetonate have also received much attention [270,275], particularly in the form of fluorine-19, carbon-13 and proton nmr studies [86,276-278]. Of more importance with regard to the structure of these compounds are the mass spectra [279], molecular weight determinations [267] and gas phase electron diffraction study [280] carried out on several of these compounds. The mass spectra and molecular weight determinations of tris(hexfluoroacetylacetonato)aluminium [279] tris- (trifluoroacetylacetonato)aluminium [267,269] and tris(trifluoropivaloylacetonato) aluminium [267] show that all three species are monomeric, while the gas phase electron diffraction study of tris (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) aluminium shows it to have an octahedral structure similar to aluminium tris acetylacetonate. This suggests that the ß-diketonates of aluminium all have very similar structures to the acetylacetonate.

On the other hand, the mixed alkoxide (or siloxide)/ ß-diketonates of aluminium have been shown by Garbauskas and co-workers to be dimeric [72-74], or trimeric [72,74] in some cases, by analysis of their crystal structures.

Two "α-diketonates" of aluminium have also been analysed by X-ray crystallography. Tris(tropolonato) aluminium [281] exists as a monomer containing six co-ordinate aluminium with the ligands arranged in a trigonal prismatic arrangement (Fig.14). the maltol derivative of aluminium [87] exists as a monomer with the aluminium - oxygen bonds forming a distorted octahedron.

The structures of the glycoxides of aluminium have received very little attention, the only work reported being that of Mehrotra and Mehrotra [99]. They succeeded in establishing, from molecular weight determinations, that aluminium glycoxides and monoisopropoxide monoglycoxides are oligomeric in nature (the compounds tested were hexameric/pentameric and tetrameric).

Similarly, the catechollates have received very little attention, with regards to their structures. Meijer [282] has studied the bis (acetylacetonato) aluminium catechollate, proposing its structure to be dimeric, with the catechollate ligands in the bridging positions.

Again, very little work has been reported on the alkoxyalkoxides of aluminium. Kriz et al [100] have studied aluminium 2-methoxy ethoxide using proton nmr and molecular weight measurements. From their results they propose a tetrameric structure containing four six co-ordinate aluminium atoms. (Fig. 15).

All the N,O-Chelates of aluminium mentioned in the synthetic section have structural analyses carried out on them.

The 2-methyl-8-quinolinato complexes of aluminium have been studied by X-ray crystallography (the oxo-bridged complex) [103,104] and various other analytical techniques [105,283] (mixed ligand species). Kushi and Fernando [103,104] established that the oxo-bridged complex was a dimer containing five co-ordinate aluminium atoms (Fig.16). Scherer and Fernando [105] proposed structures for the compounds obtained in chloroform or DMSO. Both are monomers containing six co-ordinate aluminium.

Mehrotra and co-workers [107,108] have calculated the molecular weights of a number of alkanolamine complexes of aluminium. They found that the (mono-alkanol)amines and mixed alkoxide/(mono-alkanol)amines were tetramers [108], while compounds containing the (di-tri-alkanol)amines tended towards higher oligomers [107].

Kriz and Casensky [110] have studied the structure of aluminium caprolactamate using proton nmr, infra-red spectroscopy and molecular weight measurements. From their results, they deduce that the compound exists as either a monomer, a dimer or both, depending on the solvent used, the concentration of caprolactamate and the temperature. The aluminium atoms could exist in a five co-ordinate state in both forms (Fig.17). Kriz and co-workers [111] have also studied the structures of the mixed isopropoxide/caprolactamates, finding that the monocaprolactamate is dimeric with 5 co-ordinate aluminium and bridging isopropoxide groups, and the bis-caprolactamate is similar in structure except that the aluminium atom may be six co-ordinate.

Muller and Burgi [112] have studied the crystal structures of the 2,2',2" - nitrilotriphenolate of aluminium in its dimeric form, and its monomeric forms (when bonded to another nucleophile as well). The dimer contains two penta co-ordinated aluminium atoms, positioned in the centre of a distorted trigonal bipyramid of four oxygen atoms and one nitrogen atom. The monomers contain one pentaco-ordinated aluminium atom, positioned in the centre of a more regular trigonal bipyramid (Fig.18).

The R(-)-PDTA complex of aluminium [113] has been studied by Pearson et al. They suggest a monomeric structure for the complex, with the aluminium atom octahedrally bound to four oxygen and two nitrogen atoms.

No structural analysis has been reported on the S,O-chelates of aluminium.

C) Bimetallic (and Termetallic) Aluminium Alkoxides and Chelates

The bimetallic aluminium alkoxides and chelates can be split into the same groups as were used previously (see Synthesis, section C).

The structures of the Group IA metal alkoxyaluminates have been studied using X-ray powder diffraction, infra-red spectroscopy, aluminium-27 nmr, mass spectroscopy and conductivity measurements [116]. The aluminium-27 nmr spectra indicate that the aluminium exists in a four co-ordinate state, and infra-red studies carried out on the alcohol solution of these compounds suggest that the compounds are monomeric and ionic in structure, $M^+[Al(OR)_4]^-$. However, infra-red spectra and conductivity measurements taken in THF indicate that the structure is no longer monomeric. Mass spectroscopy studies also indicate the existence of dimeric, trimeric or tetrameric species in the gas phase. X-ray powder diffraction studies have also served to indicate that the compounds are not isostructural in the solid phase (with the exception of the t-butoxides), and therefore exist as oligomers in many cases.

Studies on the analogous chelates of group IA metal and aluminium are restricted to the raman spectra [76] and crystal structures [284-287] of the oxalates, and the crystal structure [288] of the EDTA complex. Both Taylor [285], working on the potassium oxalate, have found the structure to be monomeric, with the aluminium in a slightly distorted octahedral geometry (Fig.19). Two enantiomorphs of this structure exist [287]. Polynova et al [288] have studied the potassium aluminium EDTA complex, finding that the aluminium atom is six co-ordinate with four oxygen atoms and two nitrogen atoms bonded to the aluminium atom.

Studies of the Group IIA Metal alkoxyaluminates have been carried out by Mehrotra and co-workers [135-137, 289, 290]. The central elements of the group (magnesium to barium) [135,136,289] have been shown by molecular weight measurements, to be compounds with an empirical formula of $M[Al(OR)_4]_2$ which are monomeric, dimeric or trimeric. Generally magnesium tends towards being monomeric and barium tends towards being trimeric, while calcium and strontium will occupy a form between the two. Infra-red spectroscopy and nmr studies [136] suggest that the bonding in these compounds is more covalent in character than that of the group IA alkoxyaluminates. Barium has also been shown, by Turova et al. [134], to form a crystalline alkoxyaluminate with the formula $Ba_3[Al(OCH_2CH_3)_6]_2$.

Beryllium behaves slightly differently to the other group IIA metals. The beryllium isopropoxyaluminate [137] exists either in the standard form, $Be[Al(Oi\text{-}Pr)_4]_2$, or as the 1:1 adduct, $i\text{-}PrOBe[Al(Oi\text{-}Pr)_4]$. Both species are monomeric, but the latter slowly dimerizes with age [290].

One barium aluminium chelate has been studied. Cruickshank and Dent Glasser [139,140] have investigated the crystal structure of barium aluminium ethyleneglycoxide, $Ba[Al_2(C_2H_4O_2)_4]$. They found that the aluminium exists in a penta co-ordinate state (Fig.20).

Molecular weight measurements and elemental analysis of the first row transition metal alkoxyaluminates [141-143] (and acetyl-acetonatoaluminates) show that they are generally monomeric with the formula $M[Al(OR)_4]_n$, where n is equal to the oxidation state of the metal 'M'. Further studies, carried out by Mehrotra and co-workers, have shown that the trivalent metals (scandium [123,151,291], chromium [142,143] and iron [142,143]) have structures similar to tetrameric aluminium isopropoxide, with the transition metal occupying the six co-ordinate position (Fig. 21). On the other hand , the divalent metals exist in two different forms [142,143]. Earlier members of the series (manganese [142,143] and iron [142,143] exist with the transition metal in a four co-ordinate state (Fig. 22), while later members of the series (cobalt[145], nickel [146] and copper [147]) prefer to have the transition metal in a six co-ordinate state (Fig. 22).

Ouhadi et al [148] have carried out some studies on the structures of the μ-oxoalkoxides of chromium (II), iron (II) and cobalt (II) with aluminium. Their results show that while the chromium (II) and iron (II) compounds generally exist as monomers in benzene, the same compounds in cyclohexane mostly exist as dimers (and in one case a tetramer). The cobalt (II) compounds have been found to be dimers, trimers, tetramers or hexamers. Further spectroscopic studies have simply indicated the complex nature of the compounds.

Of the second and third row transition metal alkoxyaluminates, structural studies have beein carried out on the Yttrium (see Scandium [123,151,291), Zirconium [123,124], Hafnium [123,155], Niobium [123,156], Tantalum [156] and Molybdenum [148,154] compounds.

Mehrotra and co-workers [123,155] have shown, from elemental analysis, infra-red spectroscopy and proton nmr studies, that the zirconium and hafnium alkoxyaluminates exist in two forms, $(RO)_2M(IV)[Al(OR)_4]_2$ (Fig.23) and $[(\mu\text{-}RO)(RO)_2M(IV)\{Al(OR)_4\}]_2$ (Fig.24), both of which contain the metal in a six co-ordinate geometry. Similar studies by the same authors [123,156] on the niobium and tantalum alkoxyaluminates have shown that they form similar structures to their zirconium and hafnium counterparts, only in their case both compounds are monomeric, $(RO)_3M(V)[Al(OR)_4]_2$ and $(RO)_4M(V)[Al(OR)_4]$, the first of which contains the metal in a seven coordinate geometry [156].

Ouhadi et al [146] have studied two μ-oxoalkoxides of molybdenum and aluminium. Molecular weight measurement show that the isopropoxide is monomeric in benzene and dimeric in cyclohexane, while the n-butoxide is trimeric in benzene. The electronic adsorption spectra (and colours) indicate some interaction between the alkoxide groups and molybdenum, as does the complexity of the carbon-13 nmr spectrum of the isopropoxide in benzene. Obviously (as in the case of chromium, iron and cobalt analogs) the structure of these compounds is more complex than the simple formula $(RO)_2Al\text{-}O\text{-}M\text{-}O\text{-}Al(OR)_2$ suggests, but no concrete conclusions could be reached on the basis of this work.

On the other hand, Lamotte et al [154] were able to produce crystals of trans-bis (μ-acetato-O,O')-bis[μ-(tetraisopropoxy)-aluminate-O,O']dimolybdenum and by means of X-ray crystallographic studies have calculated its structure (Fig. 25).

Of the other transition metal aluminium chelates, structural studies have only been carried out on tris[bis(triphenylphosphine)silver(1)] [tris(dithiooxalate-O,O')aluminate(III)] [152,292] and its copper (I) analog aluminium atom to be in a six co-ordinate state, while the silver atom was in a four co-ordinate state (Fig.26).

The structures of the lanthanon alkoxyaluminates have been reported extensively by Mehrotra and co-workers [123,124,151,157,158,293] and Oliver and Worrall [255]. Mehrotra and Agrawal [158] originally suggested a structure similar to that of tetrameric aluminium isopropoxide, with the lanthanon occupying the six-coordinate position (cf scandium, Fig.21). Later work by Oliver and Worrall [255] on Lanthanum, Holmium, Ytterbium and Lutecium confirmed that this structure applied in general to all the trivalent lanthanon tetraalkoxy-aluminates.

No structural work has been reported on the alkoxyaluminates (or chelates) of the actinide elements.

Structural analyses of the Group IIB metal alkoxyaluminates, carried out by Mehrotra and co-workers [137,162], have shown that they have similar structures to their groupIIA counterparts, $M[Al(OR)_4]_2$. Molecular weight measurements indicated that all the compounds investigated were monomeric. Other work, carried out by Ouhadi et al [148], on the μ-oxoalkoxides of zinc and aluminium has shown that they have similarly complex structures to their transition metal counterparts.

Likewise, infra-red and proton nmr studies carried out by Mehrotra and Mehrotra [163,291,293] on the Group IIIB metal isopropoxyaluminates have shown that the indium compound has a structure similar to the lanthanon alkoxyaluminates (cf Scandium, Fig.21).

Gallium isopropoxyaluminate, $GaAl_3(Oi\text{-}Pr)_{12}$, and aluminium isopropoxygallate, $AlGa_3(Oi\text{-}Pr)_{12}$, have similar structures, except that the six coordinate position may be occupied by either aluminium or gallium in both compounds.

No structural work has been reported on the Group IVB element alkoxyaluminates (or chelates) The only work reported on the structures of the Group V element alkoxyaluminates (or chelates) is that of Bulc et al. [165,166], Coucouvanis and Piltingsrad [152], Hoard et al [294] and Dwyer and Mellor [295]. Bulc et al havew analysed the crystal structures of ammonium tris(oxalato)aluminate (III) trihydrate [166] and tetramethylammonium tris(oxalato) aluminate (III) monohydrate [165], finding the aluminium to be hexa co-ordinate in both cases [cf the sodium analog, Fig. 19]. Hoard et al. [294] have calculated the lattice parameters for the ammonium salt of the EDTA complex of aluminium, while Dwyer and Mellor [295] have suggested a six co-ordinate structure for this complex, (similar to the R(-)-PDTA complex, see previous section). Coucouvanis and Piltingsrad studied the structure of tris (tetraphenylarsonium) [tris(dithiooxalato-O,O') aluminate (III)] [152], finding that it had a structure similar to the bis(triphenylphosphine) silver (I) analog (cf Fig.26).

No information is available on the Group VI B, VII B or O elements alkoxyaluminates (or chelates).

The termetallic alkoxides of aluminium, beryllium and either titanium, zirconium, hafnium, niobium or tantalum have been analysed by Aggrawal and Mehrotra [167]. The titanium beryllium aluminium isopropoxides, $(i\text{-}PrO)_3Ti(\mu\text{-}Oi\text{-}Pr)_2Be(\mu\text{-}Oi\text{-}Pr)_2Al(Oi\text{-}Pr)_2$ and $(i\text{-}PrO)_2\ Ti[(\mu\text{-}Oi\text{-}Pr)_2\ Be(\mu\text{-}Oi\text{-}Pr)_2Al(Oi\text{-}Pr)_2]_2$, are both monomeric in benzene (Fig. 27), while the zirconium and hafnium analogs are dimeric and monomeric respectively (Fig. 27). Niobium and tantalum form isopropoxides, $(i\text{-}PrO)_4Nb(\mu\text{-}Oi\text{-}Pr)_2Be(\mu\text{-}Oi\text{-}Pr)_2$ $\text{-}Al(Oi\text{-}Pr)_2$, with a similar monomeric structure to titanium.

D) Organo-, Halo- and Hydrido-Aluminium Alkoxides and Chelates

The structural work that has been reported on these compounds can be divided into eight groups:

(i) The alkoxyaluminium halides.

(ii) The organoaluminium alkoxides.

(iii) The crown ether complexes of organo- and halo- aluminium compounds.

(iv) The organo- and halo- aluminium isocyanates.

(v) The ionic organoaluminium carboxylates and alkoxides.

(vi) Other organoaluminium compounds.

(vii) Other haloaluminium compounds.

(viii) The hydrido aluminium compounds.

Structural work has been carried out on a variety of different alkoxyaluminium halides. Flagg and Schmidt [211] carried out molecular weight studies of the isopropoxyaluminium fluorides and chlorides, finding that they were oligomeric in nature (dimeric, trimeric, hexameric or short chain polymers). Further studies using infra-red spectroscopy and proton/fluorine-19 nmr spectroscopy enabled them to suggest some structures for the fluorides (Fig. 28). Yanovskii et al [296] carried out X-ray crystallography and powder diffraction, mass spectroscopy and molecular weight determination studies on two isopropoxyaluminium chlorides. The first compound, $AlCl(Oi\text{-}Pr)_2$, was prepared in two different forms, one of which was discovered to be trimeric and the other to be polymeric. The second compound, $Al_3Cl_5(Oi\text{-}Pr)_4$, was also a trimer, the structure being elucidated by X-ray crystallography (Fig. 29) and containing penta co-ordinated aluminium.

Other work has included the determination of the molecular weights of the phenoxyaluminium chlorides (both monomeric)by Malhotra et al [11] and the studies by Pasynkiewicz and co-workers [172,178] of some alkoxyaluminium halides. The latter were found to be trimeric in the case of the methylmethoxy compounds [178] and dimeric in the case of the methyl [2,6-dimethylphenoxy) compounds [172] (Fig.30), both sets of compounds existing as cis and trans isomers.

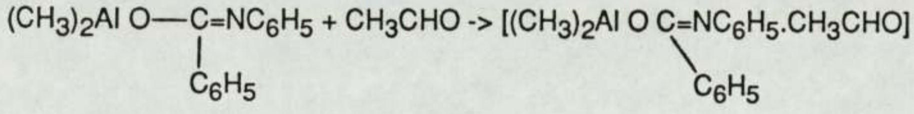
A similar amount of work has been reported on the structures of the organoaluminium alkoxides. Molecular weight calculations have been carried out by several authors [9, 297-302], all of whom agree that in general the alkylaluminium alkoxides are dimeric or trimeric (in the case of the smaller alkyl and alkoxide groups [297,300]). Otherwise, Drew et al [303] carried out a gas phase electron diffraction study of the dimethyl aluminium methoxide, finding it to be a cyclic trimer with the methoxide groups forming the bridging ligands. Tarao [300] has carried out some infra-red and raman spectroscopy studies on the same compound (and two others), coming to the same conclusions.

The first structural study on the crown ether complexes of aluminium trichloride was carried out by Wada and Matsuda [223]. Molecular weight measurements and proton nmr spectra of the benzo-15-crown-5 complex indicated that it was monomeric with the aluminium atom bound to all five of the oxygen atoms. Later studies by Atwood et al [224] showed that the aluminium atom actually occupies a position inside the ring, while losing one chlorine atom (Fig. 31). Atwood and co-workers have also analysed the crystal structures of two other aluminium chloride complexes and five trimethylaluminium complexes. In the other two aluminium chloride complexes [225] the aluminium atom binds to only four oxygen atoms in the crown ether (while losing one chlorine atom) and occupies a position above the ring with the two remaining chlorine atoms in a cis configuration. In the trimethylaluminium complexes [196-198], the aluminium atom binds to only one oxygen atom and loses no methyl groups. Each complex contains two or more attached trimethylaluminium groups. Atwood et al have also analysed the structures of several trimethylaluminium: calixarene complexes [199,200].

Evidence for the structures of the organo- and halo- aluminium isocyanates has been collected by several groups [201, 202, 204, 237, 304]. Using a number of different analytical techniques they have calculated that the isocyanate group inserts itself into an aluminium ligand linkage [202, 204] and generally forms a dimeric cyclic structure [237,304], (Fig.32). The order of preference for insertion into the linkage is,

Al-OR>Al-R>Al-X(halide)

Kai et al [305] have also looked at the crystal structure of the reaction intermediate in the polymerisation of aldehydes by these compounds,



$$(CH_3)_2Al\ O\text{—}\underset{\substack{|\\ C_6H_5}}{C}{=}NC_6H_5 + CH_3CHO \text{ -> } [(CH_3)_2Al\ O\ \underset{\substack{\diagdown\\ C_6H_5}}{C}{=}NC_6H_5.CH_3CHO]$$

They found that the aldehyde inserted into the aluminium-nitrogen bond to form a "ß-diketonate".

Atwood and co-workers have studied the structures of the ionic organoaluminium alkoxides and carboxylates using X-ray crystallography. Generally these compounds exist as monomeric ions [174,184,306,307], but in one reported case [210] the compound was crystallised with its solvent, forming a chain-like structure (Fig. 33).

Other organoaluminium compounds which have been studied include the carboxylates by Weidlein [189], the aminoalkoxides by Sato et al [308] and Hurley et al [207], the semiquinones by Davies et al [194], the acetylacetonates by Pietrzykowski et al [95] and Kroll and Naegele [193], the lactones and acid anhydrides by Hirabayashi et al [205], the 8-quinolinolates by Sen et al [309] and Hurley et al [207] and the 2-pyridylmethanolates by van Vliet et al [208]. The most unusual of these compounds are the alkylacetylacetonato aluminoxanes [95] ($R_3acacAl_2O$ and $R_2(acac)_2Al_2O$). The structure proposed for the trialkyl species is a dimer containing two bridging oxygen atoms (Fig. 34). The dialkyl species is probably monomeric.

The aminoalkoxides [308] are cyclic dimers (similar to the isocyanates, see Fig. 32), while the lactones and acid anhydrides [205] form insertion compounds (cf the isocyanates) which may have cyclic structures. Van Vliet et al [208] have shown that the dialkylaluminium 2-pyridylmethanolates are dimers, with the two methanolate groups acting as bridging ligands (ie the aluminium atom is pentaco-ordinate).

The semiquinones [194] of trisalkyl aluminium compounds and haloaluminium compounds exist as monomers containing aluminium in a four co-ordinate state. In a non-coordinating solvent (eg toluene) the semiquinone acts as a chelating ligand, but in a weakly co-ordinating solvent (eg diethylether) breaks the chelation by binding to the aluminium itself.

The hydridoaluminium "alkoxides" have been studied by Kriz and co-workers [100,228]. Aluminium sesqui (2-methoxyethoxy) hydride [100] has been shown to have the same tetrameric structure as aluminium 2-methoxyethoxide (Fig. 15), but with the six terminal 2-methoxyethoxide groups exchanged for hydrogen atoms. Aluminium sesqui (2-dimethylaminoethoxy)-hydride [228], $Al_2H_3[OCH_2CH_2N(CH_3)_2]_3$, also has a similar tetrameric structure except that the nitrogen atoms do not bind to the aluminium atoms, making the outer aluminium atoms tetrahedral in geometry.

E) Miscellaneous Aluminium Alkoxides

All the structural work in this section has been done on the aluminium siloxides.

Garbauskas and co-workers [72,74] have worked out the crystal structures of several ß-diketonatoaluminium siloxides. The trimethylsiloxides were dimeric, while the triphenylsiloxides were monomeric.

Wheatley [310] studied the X-ray diffraction analysis of tetramethyl stibonium tetrakis trimethylsiloxyaluminate, $[(CH_3)_3Sb][Al(OSi(CH_3)_3)_4]$. The anion turned out to be monomeric and a regular tetrahedron.

Bonamico and Dessy [311-313] and Ercolani et al [96,97,236] have studied the structures of several halogenated aluminosiloxanes, ranging from oligomers to long-chain polymeric species. X-ray crystallography has indicated that the compound $C_8H_{24}Al_3Br_5O_6Si_4$ contains a pentaco-ordinated aluminium atom [313], and that the molecules crystallise in long helical chains [311] (Fig.35).

Physical Properties

A) Melting Point/Boiling Point

The melting points and boiling points of a number of aluminium alkoxides, chelates and related compounds are listed in tables I-VII(Appendix 1).

B) Colour

Most aluminium alkoxides and related compounds are colourless [7,12,55,91,116,314]. In the other cases, the colour is determined by the nature of one of the groups attached to the aluminium compound, eg the bimetallic alkoxides of the transition metals [143] or the 2-methyl-8-quinolinol complexes [105].

C) Solubility

From the work carried out by Shiner et al [242] aluminium isopropoxide seems to be soluble in most organic solvents. However, it is more soluble in non-polar solvents than in polar solvents.

Studies of the methoxide, ethoxide and tertiary butoxide [315] have shown that while the tertiary butoxide is also soluble in most organic solvents, the ethoxide is only soluble in hot organic solvents and the methoxide is insoluble in organic solvents.

On the other hand, the phenoxides are more soluble in polar solvents than in non-polar solvents. The phenoxide itself [12,316] is only soluble in polar organic solvents and hot aromatic solvents, while the benzyloxide [16] is soluble in polar and non-polar organic solvents, though only in warm hydrocarbons, not cold hydrocarbons.

The carboxylates of aluminium [58] are very soluble in non-polar organic solvents, but not in polar organic solvents. The acetylacetonate [77] and 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate [81] are both soluble in organic solvents (though the former is more soluble), but insoluble in water.

The bimetallic isopropoxides of aluminium [123,142] are generally soluble in most organic solvents, though the group IA tetraisopropoxyaluminates have been shown to be insoluble in the case of lithium [123,126] and sodium [123]. The solubilities of the group IIA tetraethoxyaluminates have also been studied [134,135] and it was found that they are more soluble that the aluminium ethoxide [315]. The same can be said for zinc tetramethoxyaluminate [161] which is soluble in polar organic solvents. On the other hand, the lithium alkoxyaluminates seem to be insoluble in most solvents [126], though the methoxide and ethoxide are soluble in their alcohols.

The isopropoxyaluminium halides have been studied by several workers [211,217,317]. In general, they found that the compounds were soluble in polar organic solvents, moderately soluble in aromatic and halogenated organic solvents, and insoluble in aliphatic hydrocarbons.

D) <u>Viscosity</u>

Very little work has been reported on the viscosities of aluminium alkoxides and their related compounds. Casensky et al [101] have made a study of the variation of viscosity with temperature and concentration for sodium bis(2-methoxyethoxy)aluminium hydride in benzene.

Fieggen and Gerding [318,319] carried out two studies on the effect of aging and temperature on the viscosity of liquid aluminium isopropoxide. They also used Vogel's equation [319],

$\ln h = B + A/(T-C)$ where: A,B,C= constants h = viscosity

T= temperature

to calculate the viscosity at different temperatures. The calculated values were in good agreement ($\pm$2.5%) with the experimentally determined values for the viscosity.

In addition to this, Weiss [320] has made a study of the effect of adding aluminium alkoxides to fatty acids and oils, with respect to their viscosity.

E) <u>Density, Refractive Index, Dielectric Constant and Dipole Moment</u>

Two studies of interest have been carried out, one by Fieggen and Gerding on liquid aluminium isopropoxide [318], and the other by Lukasiak et al on aluminium phenoxide [12].

Fieggen and Gerding [318] measured the density of liquid aluminium isopropoxide* at 25^{o}C, when freshly distilled and over a period of aging for 350 hours. The value gradually increased from 0.964 to 0.975. Similar work was carried out on the refractive index and dielectric constant measurements. The dipole moment (μ) of freshly distilled liquid aluminium isopropoxide was then calculated as being 1.23 $\sqrt{n}$ Debyes, where n=molecular association (probably between two and four in value, ie μ= 1.7-2.5D).

Similar work on solid aluminium phenoxide [12], and calculating the dielectic constant in benzene, gave values of 1.25g/cm^3 for the density and 1.65± 0.1D for the dipole moment.

* Aluminium isopropoxide remains in a supercooled liquid state for long periods of time before solidifying.

Kinetics and Thermodynamics

A number of studies have been made on the kinetics and thermodynamics of processes involving the aluminium alkoxides and related compounds. These studies can be split into four groups:

(i) Kinetic and thermodynamic studies of processes involving the aluminium alkoxides.
(ii) Kinetic studies of the racemization processes of aluminium ß-diketonates and carboxylates.
(iii) Kinetic studies of ligand exchange reactions involving aluminium (III) species.
(iv) Other kinetic and thermodynamic studies.

A) Aluminium Alkoxides

The first study of interest is that of Wilson [321], who has calculated the heat of formation of aluminium isopropoxide. To do this, he used the heats of reaction of aluminium isopropoxide (solid and liquid), aluminium chloride (solid) and isopropanol (liquid) in excess hydrochloric acid solution, and the known values for the heats of formation of aluminium chloride (solid), isopropanol (liquid) and hydrochloric acid (aqueous solution). The result obtained indicated a heat of formation (ΔH_f) for the gaseous (dimeric) aluminium isopropoxide was calculated as -2446.9 kJmol^{-1}. The author did not quote a value for the heat of formation of liquid (trimeric) aluminium isopropoxide, since in his view the liquid was probably an equilibrium mixture of several different structures.

Kleinschmidt et al [31]have studied the rates of interconversion between the different forms of aluminium isopropoxide. They followed the change in concentration of the tetramer by integrating the methyl proton region of its proton nmr spectrum. These results were fitted into a computer simulation of the interconversion process, and rates for the trimer/(tetramer + dimer) equilibrium and dimer/tetramer equilibrium were calculated. Results indicated that a hexameric intermediate was present in the former equilibrium, rather than the monomer being present.

An earlier set of studies were carried out by several workers [322-325] on the kinetics of the reactions of aldehydes and ketones with aluminium alkoxides (Meerwein-Ponndorf-Verley reaction [326-328]). These kinetic studies have been valuable in determining the mechanism of this reaction.

Other work which has been reported is the measurement of some enthalpies and entropies of vaporisation by Wilhoit [314] and Mehrotra [5,32]. However, the two authors disagree considerably (±20-25%) on the values for these parameters. Bleyerveld et al [329] have also calculated the enthalpy and entropy of vaporisation for aluminium isopropoxide, obtaining values roughly half those obtained by Mehrotra and Wilhoit. (Otherwise, Kozunov and Turova's [330] studies on the kinetics of dissolution of aluminium isopropoxide in isopropanol is the only other work reported).

B) The Racemization of Aluminium ß-Diketonates and Carboxylates

The most comprehensively studied member of this group of compounds is tris(trifluoro-2,4-pentanedionato)aluminium (III). The original work was carried out by Fay and Piper [67,278] who used fluorine-19 and proton nmr spectroscopy to determine the equilibrium constant for the cis-trans isomerism reaction at various temperatures [67]. These results were used to calculate the enthalpy, entropy and free energy of isomerisation [67], while the work was later expanded to determine the activation energy and predict the mechanism involved [278]. Further studies by Haworth and co-workers [86,277,331] using carbon-13 and proton nmr spectroscopy confirmed the conclusions reached by Fay and Piper [278].

Other kinetic studies carried out include those of Pickering et al [276] on the 1,1,1,5,5,5-hexafluoro-2,4-pentanodionates and dibenzoylmethanates, those of Holm and co-workers [332,333] on the 1-phenyl-5-methylhexane-2,4-dionate and two substituted tropolonates, and those of Gillard et al [287] on the oxalate.

C) Ligand Exchange Reactions Involving Aluminium (III) Species

One of the first kinetic studies of the complexation reactions of aluminium with oxygen containing species was made by Dubey and Mehrotra [129]. They carried out potentiometric studies of the aluminium nitrate/potassium hydroxide/catechol system, calculating the values of the equilibrium constants for the three equilibria:

$Al^{3+} + A^{2-} \rightleftharpoons AlA^{+}$ where: A=catechollate ion

$AlA^{+} + A^{2-} \rightleftharpoons AlA_2^{-}$

$AlA_2^{-} + A^{2-} \rightleftharpoons AlA_3^{3-}$

Similar studies were carried out by Ohman and Sjoberg on the aluminium chloride/sodium hydroxide/catechol system [334] and identical systems with the catechol replaced by either citric acid [335], oxalic acid [336], salicyclic acid [337], gallic acid [338,339] or 1,2-dihydroxynaphthalene-4-sulfonic acid [340]. In the case of catechol, they were able to calculate the equilibrium constants for the formation of the three major species AlA^{+}, $AlA_2^{-}$and AlA_3^{3-}, as well as for two minor species $Al_3(OH)_3A_3$ and $Al(OH)A_2^{2-}$. Thus they could construct distribution diagrams indicating the percentage of each species at different pHs (at fixed concentrations of aluminium and ligand). Similar results were obtained for the other acids.

Motekaitis and Martell have carried out a similar study using several hydroxycarboxylic acids [341] as the ligand. They have also studied the system using N-phosphonomethylglycine as the ligand [342].

Likewise, Hancock and co-workers [343-345] have carried out studies of equilibria involving various dihydroxy compounds (including dihydroxy carboxylic acids and suphonic acids), tetra- and hexa-hydroxy compounds [345] and also acetylacetone [344].

On the other hand, Hidaka and co-workers [346-349] have gone a step further, calculating both the equilibrium constants and the activation energies for the ligand exchange reactions involving the sulfonic acids of hydroxyquinoline and several azo compounds (Fig.36).

Two other studies by Murakami [350] and Kosenko and Andriyuk [351] are concerned with the rate of complexation of aluminium with semi-xylenol orange [350] and semimethylthymol blue [350], and the rate of exchange of the latter ligand with ethylenediamine tetra-acetate (EDTA) [351]. The reasoning behind using these ligands is based on the coloured nature of the ligands and species produced.

A number of other workers have also carried out equilibrium studies of various aluminium (III)/chelate systems [60,353-370], and Gut [371] has studied the equilibria involving aluminium chloride/alkoxide ions.

D) Other Kinetic and Thermodynamic Studies

Irving and da Silva [372] have calculated the enthalpies of formation for two of the aluminium ß-diketonates, while Berg and Truemper [90,91], Sievers and co-workers [373,374] and Igumenov et al [267] have measured the vapour pressures of the aluminium ß-diketonates (using them to calculated the enthalpies, entropies and free energies of vaporisation).

Otherwise, the only other kinetic or thermodynamic studies reported are those carried out by Jefferey and Mole [299] and Davidson and Brown [375] on the dialkyl aluminium alkoxides.

Mechanistic Chemistry

The major areas of study into the mechanisms of production and reaction of the aluminium alkoxides (and related species) are:

(i) The mechanism of the catalytic action of aluminium alkoxides in the Meerwein-Ponndorf-Verley reaction [326-328] and Tischtschenko reaction [173,376]

(ii) The mechanism of insertion into the aluminium oxygen bond [202] and also the aluminium-halide [204], alkyl [204] and nitrogen [205] bonds.

(iii) The mechanism of reaction of aluminium alkyls with oxygen [232] and peroxides [185].

(iv) The mechanism of the catalytic action of aluminium alkoxides in the ortho-alkylation reactions of phenols [377] and related species [378].

(v) The mechanism of stereoisomerism of the ß-diketonates of aluminium [379-382].

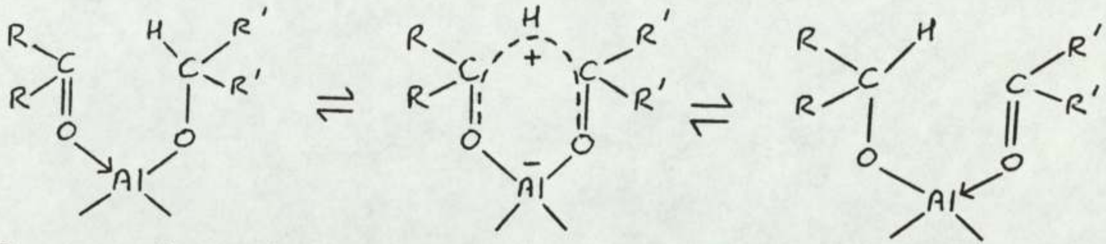
A) Meerwein-Ponndorf-Verley Reaction (MPV Reaction)

Since the MPV reaction and Tischtschenko reaction have the same starting point [173,328,376], their mechanisms have been considered side-by-side in order to determine which reaction will predominate under certain conditions.

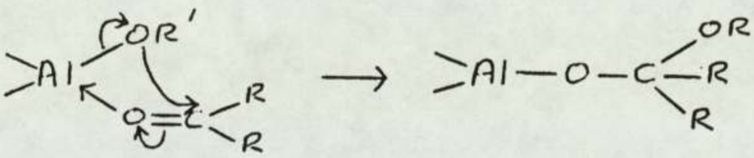
Initial mechanisms proposed [328] involved rather unlikely steps such as transfer of the [-OAl(OCH_2CH_3)$_2$] group between carbon atoms (unlikely because of the high specificity of the reaction [322]). Meerwein [383,384] was the first to propose that the mechanism involved the nucleophilic attack by an aldehyde or ketone onto the aluminium atom, followed by transfer of a hydrogen atom. This mechanism was adopted by later workers [385], including Jackman and co-workers [322,386,387], who used a kinetic study [322] of the racemization of

±aluminium but-2-oxide and ±aluminium octyl-2-oxide to establish the feasibility of this mechanism:

$R_2C{=}O + Al(OCHR'_2)_3 = R_2C{=}O{\rightarrow}Al(OCHR'_2)_3$



Saegusa and co-workers [173,376] proposed that the Tischtschenko reaction followed a similar route involving the nucleophilic attack of the aldehyde or ketone. This would be followed by further nucleophilic attack by a neighbouring alkoxide group onto the carbonyl group carbon atom, and finally a repetition of the MPV reaction, in order to produce the ester.



As can be seen from this illustration, The Tischtschenko reaction can be viewed as either a form of insertion reaction or as the preliminary step of a polymerisation reaction.

These two reaction mechanisms have since been established as the correct mechanisms [325,388,389], with only one or two modifications [323,324,390]. Bains and Bradley [323] first noted that the kinetics of the MPV reaction [322] at low temperatures did not agree with the proposition that the hydrogen atom transfer was the rate-determining step. Thus they proposed that the mechanism was more complex than had previously been believed. This was confirmed by Shiner and Whittaker [324,390], who showed that the nucleophile attack takes placed on the oligomeric form of the aluminium alkoxide, rather than on the monomeric form (as had previously been believed).

Other work carried out on these mechanisms includes that of Foldesi [220] on the effect of chlorine substituents on the rate and mechanism of reaction, and that of Gal et al [391] on the effect of an adjacent oxime group on the reaction yield. McElvain and co-workers [25,315] have also carried out some work on the mechanism of the conversion of ortho esters to ketene acetals, which is similar to the above reactions.

B) Insertion Reactions

As was previously mentioned [173,376], the Tischtschenko reaction is an insertion reaction and it seems probable that other insertion reactions follow a similar mechanism [392,393]. Mechanistic studies of the co-polymerization of phenyl isocyanate and ethylene oxide in the presence of diethylaluminium ethoxide [202] have shown this to be the case, as has the crystal structure of the complex initially formed between dimethyl aluminium oxybenzylideneaniline, $Me_2AlOC(C_6H_5)=NC_6H_5$, and acetaldehyde [305,394].

If aluminium compounds containing two or more different substituents are used, it has been established that insertion occurs preferentially into an aluminium-oxygen [169,202,205], (nitrogen carbon bond), However, Lappert and co-workers [204,395] established that insertion occurs preferentially in an aluminium-carbon bond, rather than an aluminium-halogen bond.

C) Reaction of Aluminium Alkyls with Oxygen or Peroxides

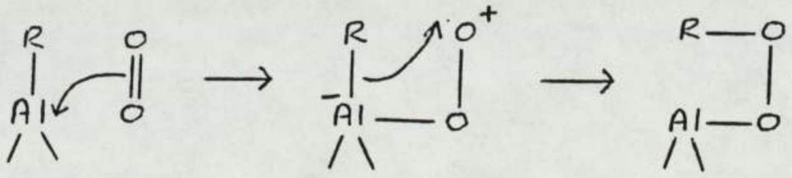
The reaction between aluminium alkyls and oxygen is a very complex reaction. Razuvaev et al [232] have studied the reaction mechanism of triethylaluminium with oxygen and have concluded that the mechanism is a stepwise conversion of alkyl groups into alkoxide groups, via the peroxides.

$Al(C_2H_5)_3 + O_2 \rightarrow Al(C_2H_5)_2\ (OOC_2H_5)$

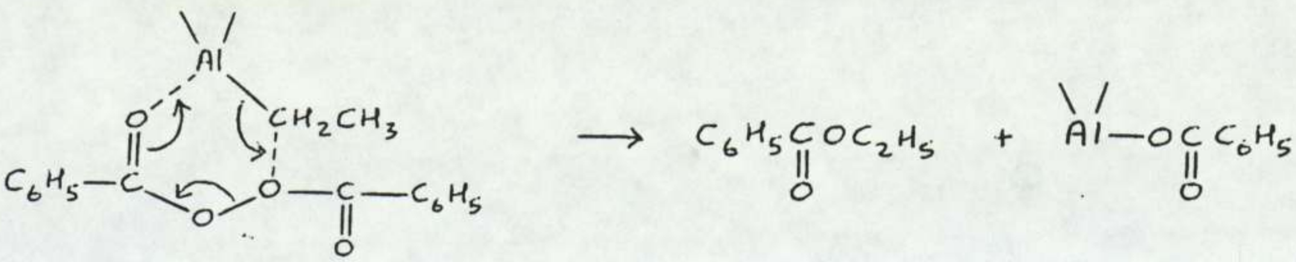
$Al(C_2H_5)_2(OOC_2H_5) + Al(C_2H_5)_3 \rightarrow 2Al(C_2H_5)_2(OC_2H_5)$ etc.

This is in agreement with the earlier observations of Sladkov et al [8]. However, Razuvaev et al [232] also point out that many side reactions can, and do, occur in this process.

Davies and Roberts [396] elaborated on this work, showing that the mechanism is actually an insertion mechanism.

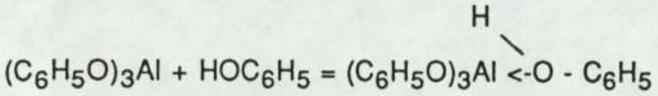


Stepovik et al [185] and Razuvaev and co-workers [186-188] have studied the reaction of triethylaluminium with benzoylperoxide, which forms diethylaluminium benzoate. The reaction proceeds using two mechanisms, a free radical mechanism and a form of nucleophilic attack, with the latter mechanism dominating. The latter mechanism involves the formation of a six-membered ring in the intermediate which breaks up to form the products.



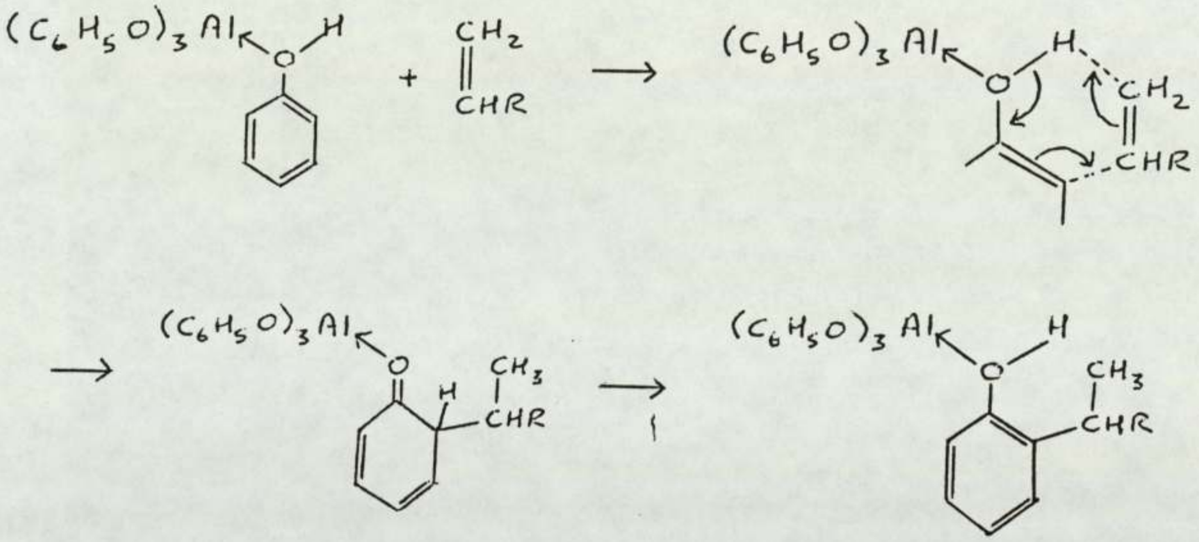
D) Orthoalkylation Reactions

Aluminium phenoxide was first used as a catalyst for the orthoalkylation reactions of phenol by Kolka et al. [397,398] who proposed that the reaction was initiated by the formation of a complex involving the aluminium phenoxide and phenol,



$$(C_6H_5O)_3Al + HOC_6H_5 = (C_6H_5O)_3Al \leftarrow \overset{H}{O} - C_6H_5$$

and proceeds via a six-membered transition state.



This leads to selective ortho-(and ortho/para-) alkylation.

Kozlikovskii and co-workers have expanded on this work to include other aryl alcohols [378,399] and other alkenes [377,400,401]. They have also deminstrated that the orthoalkylation of phenol using alcohols [402], aldehydes [403,404] or ketones [405,406] uses a similar mechanism.

E) Stereoisomerism of the Aluminium ß-Diketonates

The original work on the mechanism of stereoisomerism of the aluminium ß-diketonates was carried out by Fay and Piper [278] on tris(1,1,1-trifluoro-2,4-pentanedionato) aluminium(III), (abbrev. Al $(tfac)_3$). From their kinetic studies, they were able to gather enough evidence to suggest that the stereoisomerism took place via a bond rupture mechanism (Fig.37), rather than a rhombic or trigonal twist mechanism (Fig.38) or dissociation mechanism.

However, later work by Pickering et al. [276] indicated that Fay and Piper's work [278] was only applicable to aluminium ß-diketonates containing fluorocarbon substituents. From their studies, they determined that aluminium ß-diketonates containing only alkyl or aryl substituents used the rhombic twist mechanism (Fig. 37).

On the other hand, Muetterties and co-workers [85,333] studies of the a-isopropenyl and

a-isopropyltropolonates showed that these compounds used a trigonal twist mechanism (Fig.38).

Further studies by Haworth and co-workers [86,277,331,] have confirmed the conclusions of Fay and Piper [278]. Fay et al [407] also carried out a study of the isomerism of mono(-2,4-pentanedionato-)bis (1,1,1-trifluoro-2,4-pentanedionato) aluminium (III), and concluded that it probably used the bond rupture mechanism as well.

A study of the mixed isopropoxide/acetylacetonate of aluminium has been carried out by Wengrovius et al [74]. In their investigation of the isomerism of that compound, they concluded that the mechanism must involve bond rupture since any twist mechanism would merely result in the starting material.

F) Other Mechanistic Studies

Three other areas of the chemistry of aluminium alkoxides have received some attention.

Ueshima et al [39] have looked at the polymerisation of cyclic ethers by aluminium haloalcoholates. Their results have shown that the mechanism involved is cationic polymerisation, as opposed to the anionic mechanism associated with the polymerisation and insertion reactions previously mentioned [376] (see Mechanistic Chemistry, section A+B).

This is due to the electron-withdrawing effect of the halogens on the oxygen atom of the haloalcoholate group, causing it to be a weaker nucleophile and thus allowing cationic polymerisation to be initiated.

Kleinschmidt et al [31] have studied the mechanism involved in the interconversion of aluminium isopropoxide oligomers. Using their kinetic studies, they have postulated mechanisms for the conversion of dimer into tetramer, trimer into hexamer and hexamer into dimer and tetramer. Although the mechanism is not proven, it is consistent with the data available.

The other area of study is the thermal decomposition of the aluminium alkoxides. Both Malhotra et al [11]and Lukasiak et al [12] have studied the thermal decomposition of aluminium phenoxide, with differing results. However, the results of Malhotra et al [11] seem to be overly simplistic and somewhat dubious in nature. Lukasiak et al [12] discovered that the initial decomposition takes place from about 100°C up to about 250°C with the loss of a quantity of diphenylether (or similar compounds) to produce a compound containing a reduced number of phenoxide groups plus a large number of oxygen bridges, with a possible formula of

$Al_6O_7(OC_6H_5)_4$. Later decomposition at about 400°C probably involves hydrolytic decomposition by moisture in the air,

$$Al_6O_7(OC_6H_5)_4 + 4H_2O \rightarrow 4C_6H_5OH + Al_6O_7(OH)_4$$

followed by final decomposition into aluminium oxide and water vapour.

Other thermal decomposition studies include these of Child and Atkins [408] on the ethoxide, Piekos [409] on several of the alkoxides, Friberg [410] on the hydroxy aluminium biscarboxylates, Eisentraut and Sievers [411] on several of the ß-diketonates, and Karpovskaya et al [412] on the lithium and sodium tetramethoxyaluminates. The latter study [412] is of interest because it appears the compound loses alkoxide groups (in the form of ethers etc), but not the group IA metal (as had been previously supposed).

G) Conclusions

Since aluminium alkoxides are strong Lewis acids, they are very susceptible to nucleophilic attack. This is followed by loss of either the attacking nucleophile or some other group attached to the aluminium atom, and thus the combined reaction can be viewed as a typical nucleophilic substitution.

However, in the preceding sections it has been shown that, given the right circumstances, other reactions may take place in between the addition and release of groups on the aluminium atom.

For instance, given a suitably positive centre on the attacking nucleophile (cf the MPV reaction [376]), then hydride ion transfer can take place. Alternatively, nucleophilic attack may take place at this positive centre, involving either an adjacent alkoxide group on the aluminium atom (cf the Tischtschenko/insertion reactions [202,376]) or a free nucleophile (cf cationic polymerisation [39]).

Alternatively, given a suitably negative centre on the attacking nucleophile (cf orthoalkylation reactions [403,405]), then electrophilic attack may take place at this negative centre.

Therefore, it is important to consider the nature of the attacking nucleophile before predicting the products of the reaction.

Applications

Aluminium alkoxides (and related compounds) have found many applications, primarily in the fields of catalysis and modification of the physical and chemical properties of various compounds.

A) Catalysis

In order to appreciate why aluminium alkoxides (and related compounds) act as catalysts for certain reactions, it is useful to look back at their mechanisms of reaction. Thus it can be seen that they will catalyse three types of reaction:

(i) Polymerisation using an anionic co-ordination mechanism [202] (insertion mechanism). This is a stereospecific method of polymerisation [237,304,413] which produces high molecular weight, regular (crystalline) polymers [376] and alternating co-polymers [202]. The one requirement for the polymer monomer is that it should contain a polar group, eg a carbonyl group [169,202,376], thiocarbonyl group [414] or alkylene oxide group [202,415].

Examples include the polymerisation of lactones using zinc (or cobalt (II)) μ-oxyaluminium alkoxides [416], of isocyanates using aluminium butylate [417], of alkylene oxides using aluminium alkoxides [415,418] or alkoxyaluminium halides [419], of aldehydes using aluminium alkoxides [376] and the copolymerisation of phenylisocyanate and ethylene oxide using diethylaluminium ethoxide [202].

(ii) MPV reactions - using the mechanism previously described (see Mechanistic Chemistry, section A). This is a method for the selective reduction of carbonyl groups [420] in the presence of other easily reducable groups, eg carbon-carbon double bonds.
Generally, either aluminium isopropoxide [1,15,322,376, 386,421-424] or an isopropoxyaluminium chloride [217,218,220,391,424,425] is used as the catalyst, though Bersin [426], Yager and Hancock [325] and Jackman et al [427] have used other aluminium alkoxides.

(iii) Orthoalkylation reactions [428,429]- using the mechanism previously described (see Mechanistic Chemistry, section D). This is a method for the selective ortho- (and ortho/para-) alkylation of aryl alcohols using either alkenes [377,397,430], compounds containing carbonyl groups [403,405, 431-433] or alcohols [402].

The catalyst used is always aluminium phenoxide.

Other applications of the aluminium alkoxides (and related compounds) in this field have included:

(a) The use of diisobutyl aluminium 2,6-di-t-butyl-4-methylphenoxide in the synthesis of prostaglandins [434], germacrene [435] and other natural products [4, 35].

(b) The use of lithium alkoxyaluminium hydrides as mild reducing agents [117,436-438] for the preparation of germane from germanium tetrachloride [439] and the reduction of acid chlorides [126,230,440], aldehydes [126,441], ketones [126,441-443], nitriles [121,444] and amides [445,446]. Sodium bis(2-methoxyethoxy) aluminium hydride has also been used for the latter purpose [447,453].

(c) The use of an aluminium alkoxide [421,454] or alkoxyaluminium hydroperoxide [23] in the oxidation of alcohols to aldehydes and ketones. (This is the back reaction of the MPV reaction, known as the Oppenhauer oxidation [455]).

(d) The use of aluminium methoxide [25] or t-butoxide [30,315] in the conversion of orthoesters into ketene acetals.

(e) The use of an aluminium alkoxide [1,328,376,456,457] or magnesium tetralkoxyaluminate [132] as a catalyst in the Tischtschenko reaction.

(f) The use of the aluminium haloalcoholates [39] in the cationic polymerisation of alkylene oxides. This method produces lower molecular weight polymners than the anionic co-ordination mechanism [202].

(g) The use of an aluminium alkoxide [458,459], dialkyl aluminium alkoxide [192,460] or dialkylaluminium carboxylate [460] as an ingredient in the catalysts used for the oligomerisation [458] or polymerisation [459,460] of alkenes.

(h) The use of aluminium alkoxides [461,462] and glycoxides [463] as precursors in the formation of catalyst supports (and aluminium oxide films [464,465]).

(i) The use of dialkylaluminium enolates [181,182,466,467] in the stereoselective condensation of imines.

B) Modification of Physical and Chemical Properties

Aluminium alkoxides (and related compounds) have found many applications in this area. A detailed description of these applications can be gained from the work of Harwood [1,4], Schlenker [468-471], Rinse [19,472] and Royle [473].

The major applications of most interest have included the following:

(i) The use of aluminium alkoxide, phenoxide and carboxylate derivatives [474-478] as drying agents for surface coatings (eg paints and varnishes). Their hydrolysis products [476,479] are also used for this purpose.

(ii) The use of similar compounds as thickening and gelling agents in paints and oils [44,476,479-482].

(iii) The use of aluminium alkoxides [481,483-485] (and their hydrolysis products [479]) in the waterproofing of fabrics.

(iv) The use of aluminium alkoxides in water-absorbent resins [486] (as the water-absorption agent [1]).

(v) The use of aluminium phenoxides [487a], and polymeric species [1,4,19,48,487b,488] formed by heating or hydrolysis of aluminium alkoxides and carboxylates, as fuel and lubricant additives. The aluminium compound increases the lifetime of the fuel (or lubricant) and engine by retarding corrosion of the engine [4,19] and deterioration of the fuel (or lubricant) [487].

(vi) The use of various aluminium compounds as additives in resins [1,7,489,490] and organosilicon rubbers [1]. For instance, aluminium phenoxides and phenoxide/aldehyde resins improve the hardening characteristics of epoxy resins [490]. On the other hand, aluminium alkoxide, phenoxide, carboxylate and hydroxide derivatives (and their condensation products) soften and toughen polyvinylidene resin binders [491].

(vii) The use of aluminium phenoxides [1,492] as anti-bacterial agents.

(viii) The use of aluminium carboxylates [493] and oxyaluminium carboxylates [494] in pharmaceutical products. The aluminium atom acts as a carrier for the "active" carboxylic acids, and enable the recipient to take larger doses of the acid [493]. It also has other beneficial effects [473], such as masking unpleasant tastes and acting as a slow release agent.

(ix) The use of various aluminium alkoxides [1] and oxyaluminium carboxylates [494] in the cosmetics industry.

CHAPTER 2

EXPERIMENTAL

Synthetic Techniques

A) Preparation of Aluminium Isopropoxide

To dry isopropanol (100cm^3) was added aluminium turnings (or powder) (13.5g, 0.5 mole) together with a catalyst (iodine or mercury (II) chloride) (0.5g). The mixture was heated under reflux under an inert (N_2) atmosphere for 4 hours. The reaction mixture was filtered hot to remove the catalyst ($HgCl_2$) and unreacted aluminium; the filtrate was set aside to cool and the solidifed aluminium isopropoxide was separated.

B) Preparation of Other Aluminium Alkoxides

To dry toluene (100cm^3) was added aluminium isopropoxide (2.75g, 0.0625 mole) together with the appropriate alcohol (0.1875 mole). The mixture was heated under reflux under an inert (N_2) atmosphere for 2 hours. The isopropanol was distilled off as an azeotrope with toluene at 90^{o}C. When the temperature of the distillate started to rise, the remainder of the toluene was removed under vacuum and the resulting solid was collected.

C) Preparation of Hydrolysed Aluminium Isopropoxide

To dry isopropanol (200cm^3) was added aluminium isopropoxide (20.4g, 0.1 mole). The mixture was heated under reflux for 20 minutes, during which a mixture of distilled water (1.8cm^3, 0.1 mole) and isopropanol (50cm^3) was added dropwise. The isopropanol was distilled off under vacuum and the resulting gel dried at 120^{o}C for 2 hours, to give sample C1.

D) Preparation of Hydrolysed Aluminium Isopropoxide (Method 2)

To dry isopropanol (1000cm^3) was added aluminium isopropoxide (204g, 1 mole). Aliquots of this solution were taken and treated with water such that the mole rations, $Al(Oi\text{-}Pr)_3:H_2O$ were 1:0.25; 1:0.5, 1:0.75 and 1:1. The mixtures (samples D1, D2, D3 and D4) were centrifuged and ^{27}Al nmr spectra were measured immediately. A second preparation of the 1:0.75 mixture (Sample D3H) was refluxed for 105 hours , cooled centrifuged and subjected to ^{27}Al nmr analysis.

E) Preparation of Hydrolysed Aluminium Isopropoxide (Method 3)

Aluminium Isopropoxide (128.5g, 0.63 mole) and isopropanol ($125cm^3$) were heated to reflux when an isopropanol ($105cm^3$)/water ($10.8cm^3$, 0.6mole) mixture was added at $2cm^3min^{-1}$ via a vapouriser set to 170°C. On completion of the addition, the vapouriser and peristaltic pump were washed through with isopropanol ($6cm^3$). A sample of the cloudy solution was taken for ^{27}Al nmr analysis (sample E1). The cloudy solution was distilled at 95°C to afford a solid product which was further treated at 90°C under reduced pressure to give sample E2.

F) Preparation of Hydrolysed Aluminium Isopropoxide (Method 4)

A Solution of aluminium isopropoxide (61.2g, 0.3mole) in isopropoanol ($75cm^3$) was heated to reflux. A mixture of isopropanol ($150cm^3$) and water ($5.4cm^3$, 0.3mole) was prepared and added cold to the refluxing solution at a rate of 1.8 cm^3min^{-1}. On completion of the addition the pump was washed with isopropanol ($15cm^3$). The reaction mixture was treated on a rotatory evaporator (40°C, reduced pressure) for 1 hour, after which solid sample F1 was taken.

G) Preparation of Hydrolysed Aluminium Isopropoxide (Method 5)

A solution of aluminium isopropoxide (61.2g, 0.3mole) in isopropanol ($60cm^3$) was heated to and maintained at 30°C. Isopropanol ($250cm^3$) and water ($5.4cm^3$, 0.3 mole) were mixed and added cold at a rate of $1.4cm^3min^{-1}$. On completion of the addition the pump was washed with isopropanol ($6cm^3$) and a sample of the precipitated solid was taken (sample G1).

H) Preparation of Hydrolysed Aluminium Isopropoxide (Method 6)

This method attempts to simulate as closely as possible the industrial procedure.Aluminium isopropoxide (148.9g, 0.73 mole) was dissolved in isopropanol ($140cm^3$) and heated to reflux. A mixture of isopropanol ($130cm^3$) and water ($12.6cm^3$, 0.7 mole) was added to the refluxing solution via a vapouriser set at 180°C at a rate of $1.8cm^3 min^{-1}$. On completion of the addition the pump was washed through with isopropanol ($6cm^3$) and sample H1 was taken. The reaction mixture was distilled at 84°C to remove the bulk of the isopropanol ($276cm^3$), sample H2 was then taken. Solvent 260/290 was added and after 10 minutes mixing, sample H3 was taken. The reaction mixture was further distilled, the temperature rising to 180°C at which point it was held constant for 1 hour.

For comparative purposes a further sample H4M was acquired from the industrial process.

I) Preparation of Aluminium Oxalate

To a solution of oxalic acid dihydrate (18.9g, 0.15 mole) in distilled water (50cm^3) was added a solution of aluminium chloride hexahydrate (12.075g, 0.05mole) in distilled water (50cm^3). The precipitate was filtered off and washed with a little distilled water.

J) Preparation of Strontium Aluminium Oxalate

To a solution of strontium oxalate dihydrate (31.44g, 0.15 mole) in distilled water (100cm^3) was added a solution of aluminium chloride hexahydrate (12.075g, 0.05 mole) in distilled water (50cm^3). The precipitate was filtered off, washed with distilled water and dried at 120°C.

K) Preparation of Barium Aluminium Oxalate

To a solution of barium carbonate (14.8125g, 0.075 mole) in distilled water (50cm^3) was slowly added a solution of 50% (by volume) nitric acid until carbon dioxide ceased to be evolved. The reaction mixture was filtered to remove any remaining solid and to the filtrate was added oxalic acid dihydrate (9.45g, 0.075 mole). When the oxalic acid had dissolved, a solution of aluminium chloride hexahydrate (6.0375g, 0.025 mole) in distilled water (50cm^3) was added. The reaction mixture was filtered and the solid washed thoroughly with distilled water to remove any traces of oxalic acid or aluminium oxalate.

L) Preparation of Aluminium Acetylacetonate

To a solution of ammonium alum (2.65g, 0.05 mole) in distilled water (100cm^3) was added acetylacetone (15ml). 2M ammonia solution was added dropwise until the reaction mixture turned alkaline. The reaction mixture was cooled in ice until a precipitate formed. The precipitate was filtered off and dried at 70°C, then recrystallised from chloroform.

M) Preparation of Aluminium 8-Hydroxyquinolinate

To dry chloroform (200cm^3) was added 8-hydroxyquinoline (21.75g, 0.15mole) and anhydrous aluminium chloride (6.675g, 0.05mole). The precipitate was filtered off, washed with a little chloroform and dried at 50°C.

N) Preparation of the Aluminium EDTA Complex

To a solution of ammonium alum (2.65g, 0.05mole) in distilled water (100cm^3) was added the disodium EDTA complex (16.8g, 0.05 mole). The reaction mixture was left to stand and the crystals collected as they formed.

O) Preparation of Lithium Aluminium Isopropoxide

A dispersion of lithium in nujol was prepared by heating lithium metal in nujol up to 180^{o}C (in a silicone oil bath) and shaking the molten mixture vigorously. The dispersion was set aside to cool and the nujol separated off. To dry isopropanol (200cm^3) was added dispersed lithium (1.4g, 0.2 mole). The reaction mixture was stirred and warmed gently until the lithium dissolved; aluminium isopropoxide (40.8g, 0.2mole) was added and the reaction mixture was heated under reflux under an inert (N_2) atmosphere for 4 hours. The reaction mixture was set aside to cool and the solidified product was separated.

P) Preparation of Other Metal Aluminium Isopropoxides

The sodium and calcium analogs of the lithium salt were prepared by the same method, but without initially producing the dispersed metal. However, the calcium analog required the metal to be refluxed in the dry isopropanol for 8 hours, before the aluminium isopropoxide was added.

Analytical Techniques

A) Nuclear Magnetic Resonance Spectroscopy

Nmr spectra were obtained with a Bruker AC-E 300 MHz spectrometer, equipped with multinuclear and MAS solid state probes. The "magic angle" was set with KBr and Delrin rotor spinning rates were 5kHz. The frequencies were 78.206 MHz (^{27}Al) and 44.168MHz (^{6}Li). For some of the spectral lines, linewidths at half-height were measured in order to determine the asymmetry of the environment around the aluminium atom.

B) Infra-red Spectroscopy

Infra-red spectra were obtained with a Perkin-Elmer 1710 FTIR spectrometer. Samples were prepared either as KBr discs or as a nujol mull between two KBr plates.

C) X-Ray Diffraction Studies

Samples of the hydrated aluminium isopropoxide were heated to 200°C, 400°C, 600°C and 800°C in a muffle furnace. The resulting powders (samples C2, C4, C6 and C8) were then analysed with a Phillips X-ray diffractometer using Co-K radiation with a typical scan speed of $1^{\circ} 2\theta \text{ min}^{-1}$.

D) Chlorine Determination

A sample of the strontium aluminium oxalate was fused with sodium carbonate at 1000°C for 2 hours. The resulting solid and crucible were cooled and placed in a beaker, into which was added 100cm^3 of conc. nitric acid. The solution was stirred and diluted to 400cm^3 with distilled water.

Addition of a small quantity of silver nitrate solution revealed the presence of chlorine by forming a white suspension of silver chloride.

CHAPTER 3

The following work was intended to be a study of how small changes in environment around the aluminium nucleus affected the ^{27}Al nmr spectra. A series of syntheses were carried out with the intention of producting a number of 6 co-ordinate aluminium species and a number of 4 co-ordinate aluminium species.

Unfortunately, the products obtained did not fall neatly into the categories which I had hoped they would. Therefore, I have dealt with each synthesis separately, rather than in two groups.

Some Model Aluminium Compounds

Nine aluminium chelates and bimetallic aluminium isopropoxides were synthesised using the methods described in Chapter 2. Analyses were carried out on the reaction products and are summarised below.

Compound	^{27}Al nmr (solution)		^{27}Al MASnmr		^{6}Li MAS nmr
	δ (ppm)	Linewidth (Hz)	δ (ppm)	Linewidth (Hz)	δ (ppm)
Aluminium Oxalate	11.98	600	-0.28	47	
	16.52	800	(asymmetric)		
	62.82	4300			
Strontium Aluminium oxalate			9.54	1200	
Barium Aluminium oxalate	12.28	600	0.01	47	
	16.48	800	(asymmetric)		
	64.21	3700			
Aluminium Acetylacetonate	-1.02	110	-5.88	375	
			(asymmetric)		
Aluminium 8-hydroxyquinolinolate	30.68	1550	29.08	1250	
	62.64	3000			
Aluminium EDTA complex			-0.92	810	
Calcium Aluminium isopropoxide			7.68	1850	
			76.62	1500	
Lithium Aluminium isopropoxide			80.10	750	0.589
(Lithium isopropoxide					0.344)
Sodium Aluminium isopropoxide			61.87	470	

Aluminium oxalate and Barium Aluminium oxalate were dissolved in deuterium oxide.

Aluminium acetylacetonate and Aluminium 8-hydroxyquinolinate were dissolved in deuterated chloroform.

Compound	CHN Analysis				IR Spectrum (KBr disc) (see Appendix 2)
	%C	%H	%N	(% Cl)	
Aluminium oxalate	18.86	4.54			√
$Al_2(C_2O_4)_3$-calc.	22.64	-			
$Al_2(C_2O_4)_3.9H_2O$-calc.	15.00	3.75			
$H_3Al(C_2O_4)_3$ -calc.	24.49	1.02			
$H_3Al(C_2O_4)_3.7H_2O$-calc.	17.14	4.05			
Strontium Aluminium oxalate	10.86	1.12		(~10)	√
$Sr[Al (C_2O_4)_2Cl(H_2O)]$ $1.5H_2O$-calc.	12.94	1.35		(9.57)	
$Sr[Al (C_2O_4)_2Cl(H_2O)]$ $1.5H_2O$+X-calc.	10.86	1.13		(8.03)	
Barium Aluminium oxalate	17.31	3.96			√
$Ba_3[Al (C_2O_4)_3]_2$-calc.	14.49	-			
$H_3Al(C_2O_4)_3.7H_2O$-calc.	17.14	4.05			
Aluminium Acetyl acetonate	55.68	6.69			√
$Al(C_5H_7O_2)_3$-calc.	55.56	6.48			
Aluminium 8-hydroxy -quinolinate	63.96	3.84	8.61		√
$Al(C_9H_6NO)_3$-calc.	70.59	3.92	9.15		
$Al(C_9H_6NO)_2OH$-calc.	65.06	3.92	8.43		
$Al(C_9H_6NO)_2Cl$-calc.	61.63	3.42	7.99		
Aluminium EDTA complex	0.28	5.97	2.79		√
(Ammonium alum -calc.)	0	6.18	3.09		
Lithium Aluminium isopropoxide	3.51	3.07			√
$Li[Al(OC_3H_7)_4]$-calc.	53.33	10.37			
Sodium Aluminium isopropoxide	4.61	1.99			√
$Na[Al(OC_3H_7)_4]$-calc.	50.35	9.79			

XPS analyses (see Appendix 2) were also obtained for Aluminium oxalate, Strontium Aluminium oxalate and Aluminium Acetylacetonate, a chlorine analysis was carried out on Strontium Aluminium oxalate. (Result 10% by mass).

Aluminium Oxalate

Examining the nmr of the solid sample, a chemical shift (δ) of -0.28ppm indicates that the aluminium atom exists within a regular octahedral arrangement of oxygen atoms. The very narrow linewidth confirms the highly symmetrical arrangement of the oxygen atoms.

The asymmetry of this peak however, may indicate that the the presence of a small second order quadrupole effect ie the symmetry may not be precisely oxtahedral.

Examining the CHN analysis indicates that the species present cannot be represented by the empirical formula $H_3Al_2(C_2O_4)_3$, since there is insufficient carbon and too much hydrogen present in the analysis. The infrared spectrum has a broad peak at 3300cm^{-1}, indicating that hydrogen-bonded -OH groups are present in the compound. Therefore, we must assume that some water molecules are present (~7) some of which may be hydrogen-bonded to the aluminium complex in the solid form.

Investigating the nmr of the solution, it is obvious that the compound has undergone some kind of dissociation. The species present contain aluminium in the four coordinate state and in two different unsymmetrical six coordinate states.

Strontium Aluminium Oxalate

Examining the nmr of the solid sample, a chemical shift (δ) of 9.54ppm and linewidth of 1200Hz indicates that the aluminium atom exists within an unsymmetrical arrangement of six donor atoms. In this case, the aluminium atom may not be entirely surrounded by oxygen, since the XPS spectrum and chlorine analysis indicate that some chlorine is present. (The XPS spectrum also indicates the presence of Strontium in the compound).

Examining the CHN analysis indicates that, as with Aluminium Oxalate, there must be some water molecules attached to the complex. The infrared spectrum has two peaks at 3500cm^{-1} and 3300cm^{-1}, indicating that there are two types of water molecule attached to the complex.

One method of explaining these observations would be to assume an empirical formula of $[SrAl(C_2O_4)_2\ Cl(H_2O)].1.5\ H_2O$ for the complex. Thus the complex would contain the aluminium atom in an unsymmetrical arrangement of six donor atoms (four oxygen atoms from the two oxalate ions, one oxygen atom from the water molecule and one chlorine atom), two different water molecules, a carbon to hydrogen ratio roughly in agreement with the CHN analysis and a chlorine percentage (9.57) which agrees with the chlorine analysis result of 10% by mass.

An nmr of this complex in solution was not obtained since the complex appears to be insoluble in all commonly available solvents.

Barium Aluminium Oxalate

Examining the nmr spectra of both the solid sample and the solution and comparing them with the equivalent nmr spectra of Aluminium Oxalate shows remarkable similarities. Further examination of the CHN analyses and infrared spectra confirm these similarities.

This suggests that the compound is almost certainly Aluminium Oxalate and not Barium Aluminium Oxalate.

Aluminium Acetylacetonate

Examining the nmr of the solid sample, a chemical shift (δ) of -5.88ppm and the linewidth of 375Hz indicates that the aluminium atom exists within an irregular octahedral arrangement of oxygen atoms. The asymmetry of the peak indicates that, as with Aluminium Oxalate, the presence of a second order quadrupole effect.

The CHN analysis and infrared spectrum indicate that unlike the oxalates, Aluminium Acetylacetonate has no water molecules attached. The nmr of the solution contains a narrower peak than the nmr of the solid sample, located at -1.02ppm. This is due to the greater freedom of movement of the molecule in solution averaging out the quadrupole effect seen in the nmr of the solid.

Aluminium 8-Hydroxyquinolinolate

Examining the nmr of the solid sample, a chemical shift (δ) of 29.08ppm indicates that the aluminium atom exists within an arrangement of five donor atoms. The linewidth of 1250Hz indicates that the arrangement is unsymmetrical, partly due to the fact that some of the donor atoms are nitrogen atoms rather than oxygen atoms.

Examining the CHN analysis indicates that an empirical formula of $Al(C_9H_6NO)_2$ OH is more likely than $Al(C_9H_6NO)_3$ or $Al(C_9H_6NO)_2Cl$. This is confirmed by the infrared spectrum which has a small, broad peak at $3400cm^{-1}$. This is also in agreement with observations made by Fernando and co-workers on the 2-methyl-8-quinolinol analogue [102-105].

The nmr of the solution shows two peaks at 30.68ppm and 62.64ppm. The former is due to the five coordinate aluminium complex, while the latter is due to a four coordinate aluminium complex probably produced by dissociation of one of the aluminium nitrogen bonds.

Aluminium EDTA Complex

Examining the nmr of the solid sample, a chemical shift (δ) of -0.92ppm indicates that the aluminium atom exists with an arrangement of six donor atoms, as might be expected with an EDTA complex. However, the CHN analysis indicates that there is little or no carbon in the complex, with effectively eliminates that possibility of the compound containing EDTA. A comparison of the CHN analysis with the theoretical analysis expected for Ammonium Alum shows close agreement, ie the preparation simply recrystallised the Ammonium Alum out of solution.

Metal Aluminium Isopropoxides

From what has been reported in the literature by Turova and co-workers [116,117] and Mehrotra and co-workers [123, 136], Group IA and IIA Metal Aluminium Isopropoxides normally contain aluminium in a four coordinate environment. The only exceptions to these observations are that the Group IA Metals form a complex with the formula $M_3Al_2(OiPr)_9$[123], while Turova et al [134] have reported a Barium complex with the formula $Ba_3[Al(OCH_2CH_3)_6]_2$ where the aluminium atom is in a six coordinate environment.

Examining the nmr of the solid calcium complex, there are two peaks at 76.62ppm and 7.68ppm. The peak at 76.62ppm corresponds to four coordinate aluminium in the species $Ca[Al(OiPr)_4]_2$. However, the peak 7.68ppm corresponds to six coordinate aluminium, which indicates that a complex similar to that of the Barium salt reported by Turova et al [134] has been produced (with a formula $Ca_3[Al(OiPr)_6]_2$).

The nmr spectra of the solid lithium and sodium complexes, both show a peak in the 60ppm to 90ppm region, indicating that in both cases the aluminium atoms exist in four coordinate environments. The difference in peak position could be due to a greater degree of oligomerisation in the lithium complex.

All these complexes hydrolyse easily, as can be seen from the large -OH peaks on their infrared spectra, and so by the time the CHN analyses were carried out most of the complex had been hydrolysed and the isopropoxide ions lost.

CHAPTER 4

The following work was carried out for my industrial sponsors in order to investigate the mechanism involved in the hydrolysis of aluminium isopropoxide. This reaction is a major industrial process on their site.

Attempts were made to simulate the industrial process as closely as possible (methods 3-6), to heat the hydrolysis product (method 1) in order to determine it's structure by XRD, and to vary the ratio of water to aluminium isopropoxide (method 2).

Finally, some reactions between sterically hindered phenols and aluminium isopropoxide were used to try and isolate intermediates in the reaction between aluminium isopropoxide and oxygen donating species.

Observations on the Reaction of Aluminium Isopropoxide with Limited Quantities of Water and with Ortho-Substituted Phenols.

Results

Table I

^{27}Al nmr data relating to the hydrolysis of aluminium isopropoxide by methods 3-5 (experimental section E-G).

Sample	**δ (ppm) vs $[Al(H_2O)_6]^{3+}$**
Sample E1 (C_6H_6/C_6D_6 solution)[a]	0.62 (sharp) 5.10 (broad) 38.20 (shoulder) 66.20 (broad)
Sample E2 (MAS NMR)	0.63 31.95 59.01
Sample F1 (MAS NMR)	2.88 30.60 64.89
Sample G1 (C_6H_6/C_6D_6 solution)	64.50 (broad)

[a] Addition of benzene evented a clear solution.

Table II

Batch hydrolysis of aluminium iospropoxide - ^{27}Al nmr of solutions obtained on addition of indicated molar quantity of water to IM aluminium iospropoxide in isopropanol (experimental section D, method 2).

Nature of substrate	^{27}Al nmr data (vs. $[Al(H_2O)_6]^{3+}$), δ.ppm		
	6 co-ord	5 co-ord	4 co-ord
Al $(Oi\text{-}Pr)_3$, IM in isopropanol	9.52		66.7 (broad)
(D) at 70°C	9.17		
	6.60	45.4	66.7 (broad)
Al $(Oi\text{-}Pr)_3$, IM in dmso-D_6 at 70°C	5.09	38.8 (broad)	61.2 (broad)
(D) + 0.25 mole H_2O	9.12		65.4
Sample D1 at 70°C	6.51	~43.0 (broad)	65.4
(D) + 0.5 mole H_2O	9.10		64.8
Sample D2 at 70°C	6.60	46.2	64.8
(D) + 0.75 mole H_2O	9.11		61.7
Sample D3 at 70°C	6.60	42.9	61.7
(D) + 0.75 mole H_2O, 1.5hr reflux	9.10		69.7
Sample D3H at 70°C	6.80	43.1	69.7
(D) + 1.0 mole H_2O	9.54		~68.0 (broad)
Sample D4 at 70°C	9.20		
	6.62	~43	~68.0 (broad)
(D) + 1.0 mole H_2O SOLID PHASE (MAS NMR)	~3		62.1
$Al(O\ i\text{-}Pr)_3$ in benzene solution at room temp.	0.67		60.26

Table III

^{27}Al nmr data for sample produced by method 6 (experimental section H). This method attempts to simulate the industrial process.

Sample in C_6H_6/C_6D_6 solution	**δ (ppm) vs $[Al(H_2O)_6]^{3+}$**
Sample H1	7.16 (weak) 6.87 ~41. (shoulder)
Sample H2	~5. (weak) 67.5 (assymetric)
Sample H3	~5. (weak) 67.7 (asymmetric)
Sample H4M	~8. (v. weak) 71.6

Table IV

^{27}Al nmr date for product of 1:1 hydrolysis of aluminium isopropoxide (experimental section C, method 1) and of the products of heating the material to the indicated temperatures.

Sample	**δ (ppm) vs $[Al(H_2O)_6]^{3+}$**
Hydrolysis product in C_6H_6/C_6D_6 solution. Sample C1	62.8
Solid, as above, heated to 200°C (MAS NMR) Sample C2	60.9
Heated to 400°C (MAS NMR) Sample C4	60.9 ~36.
Heated to 600°C (MAS NMR) Sample C6	61.7 36.1
Heated to 800°C (MAS NMR) Sample C8	29.6 (overlap of SSB with $\delta \simeq 0$?)

Table V

Solid reaction products of phenols with aluminium isopropoxide.

Phenol	Product	Analysis (calculated)	^{27}Al MAS NMR data δ(ppm) vs $[Al(H_2O)_6]^{3+}$
2,6-dimethyl phenol C_8H_9OH	$(C_8H_9O)Al(Oi\text{-}Pr)_2.4H_2O$	C,49.2;H,5.9 (C, 49.7;H,9.1)	55.7 (4 co-ord) 28.6 (5 co-ord) 1.28 (6 co-ord)
2-t-butyl-4-methylphenol $C_{10}H_{15}OH$	$(C_8H_9O)Al(Oi\text{-}Pr)_2 3H_2O$	C,54.9;H,7.8 (C, 54.8;H,10.0)	62.7 (4 co-ord) 4.7 (6 co-ord)
2,6-di-t-butyl phenol $C_{14}H_{21}OH$	$(C_{14}H_{21}O)Al(Oi\text{-}Pr)_2.H_2O$	C,65.5;H,9.0 (C,65.2;H,10.0)	65.3 (4 co-ord) 36.6 (5 co-ord) 1.04 (6 co-ord)
2,6-diphenyl phenol $C_{18}H_{13}OH$	$(C_{18}H_{13}O)Al(Oi\text{-}Pr)(OH)$ (phenol:ALISO^b=2:1)	C, 74.8; H,5.44 (C, 72.4; H,6.0) IR 3517cm^{-1}, sharp	62.9 (4 co-ord) 31.1 (5 co-ord) 3.47 (6 co-ord)
	$(C_{18}H_{13}O)_2Al(OH)$ (phenol:ALISO=3:1)	C,79.9;H,5.6 (C,80.8;H,5.0) IR 3517cm^{-1},sharp	58.4 (4 co-ord) 36.6 (5 co-ord) 5.09 (6 co-ord)
2-phenylphenol $C_{12}H_9OH$	$(C_{12}H_9O)Al(Oi\text{-}Pr)_2.1.5$ i-PrOH	C,66.79;H,8.69 (C,66.83;H,8.66)	57.97 (4 co-ord) 32.32 (5 co-ord) ~3. (6 co-ord)
	$(C_{12}H_9O)_2Al(Oi\text{-}Pr).3i\text{-}PrOH$	C, 71.79;H,8.02 (C, 71.52;H,8.11)	~58. (4 co-ord) ~28. (5 co-ord) ~8. (6 co-ord)

^{b}ALISO = $Al(Oi\text{-}Pr)_3$

Kriz et al [2] have reported δ(octahedral) =

3.2ppm and δ(tetrahedral) = 58.5ppm at 52.31 MHz for tetrameric aluminium isopropoxide. Working at 78.206 MHz, we observed resonances in benzene solution at 0.67ppm (Octahedral) and 60.26ppm (tetrahedral) (see table II).

Methods 3-5 were designed to add the requisite quantity of water to a solution of aluminium isopropoxide in isopropanol to produce a product mixture which was as homogeneous as possible. In practice, the final solution was, at best, cloudy. The method differed in the temperatures of both additive and bulk solution. The relevant nmr data are gather into table I. Sample E1 (solution phase) shows four resolved resonances. One sharp band occurs at 0.62ppm, close to that observed for the octahedral resonance of $[Al(Oi\text{-}Pr)_3]_4$. A new broad band is seen in the octahedral region (5.10ppm) together with a very broad tetrahedral resonance at 66.2ppm, possibly arising from the overlap of two resonances, which shows a distinct shoulder at 38.2ppm. It is probable that at least two species were present, one probably unreacted $[Al(Oi\text{-}Pr)_3]_4$, the other a new material with three aluminium environments. The solid E2, obtained by removal of solvent, also shows three aluminium environments. Method 4 was similar to method 3 but differed in the precise conditions used to isolate solid F1. This material also shows 3 aluminium environments, but absolute peak maxima differ from those observed for E2. Method 5 involved adding the isopropanol/water mixture to a cooler solution of aluminium isopropoxide in isopropanol. The precipitated solid G1 was examined in benzene solution and gave a ^{27}Al nmr spectrum with a single broad resonance in the tetrahedral region at 64.5ppm.

Method 2 studied the effect of adding different molar quantities of water. All solutions were maintained at 70°C (for nmr measurements also). The data are recorded in table II. All solutions became cloudy on addition of water, the solid phase became more apparent as the $[Al(Oi\text{-}Pr)_3]:H_2O$ ration approached 1:1. The data in table II are largely for solution phases (at 70°C) after centrifugation. The spectra are complex and when the $Al(Oi\text{-}Pr)_3:H_2O$ ration is greater than 1, octahedral, pentaco-ordinate and tetrahedral aluminium sites are located. When the ratio becomes 1:1, the pentaco-ordinate environment is lost from the solid phase.

Method 6 (table III), although in many respects similar to method 3-5, is closer to the actual industrial process in terms of work up following hydrolysis of the $Al(Oi\text{-}Pr)_3$. The sample H1, taken immediately following hydrolysis showed three aluminium environments, but further work up (samples H2 and H3) produce specimens which lack evidence of a 5 co-ordinate aluminium site and are very similar to the spectrum of sample H4M obtained directly from the manufacturing process.

Method 1, (table IV) involved the more dilute addition of water to isopropoxide in isopropanol in a 1:1 molar ration. The solid product shows a single resonance associated with tetrahedral aluminium when dissolved in benzene solution. The product was heated successively to 200°C, 400°C, 600°C and 800°C. Changes were monitored by ^{27}Al MAS NMR and XRD. Perhaps surprisingly all the specimens appeared X-ray amorphous, no evidence for crystalline aluminium oxides was obtained for specimens heated to higher temperatures. The spectra of the heated speciments were broad with many spinning side bands. The major feature of note is the steady development of a resonance located in the 36-29ppm region which is attributable to 5 co-ordinate aluminium; tetrahedral resonances are discernable in the specimens heated to 400°C and 600°C. The spinning sidebands in the 800°C specimen spectrum are so dominant that they may hide a resonance at $\delta \sim$ O (octahedral) and the possibility that a tetrahedral resonance is still present could not be entirely dismissed.

Table V gathers data obtained on products of reactions carried out between various ortho substituted phenols and aluminium isopropoxide in a 1:1 mole ration (2:1 and 3:1 in the case of 2,6-diphenylphenol and 1:1 and 2:1 in the case of 2-phenylphenol). 2,6-Disubstituted phenols gave products of the form (RO)Al(Oi-Pr)$_2$.xH_2O (where R=2, 6-dimethyl- or 2,6-di-t-butylphenol) which contain 4,5 and 6 co-ordinate aluminium whereas the product from 2-t-butyl-4-methylphenol shows only 4 and 6 coordination for the metal. With 2,6-diphenylphenol the behaviour was different. Greater ratios of the phenol were necessary to obtain products and hydrolysis of Al-Oi-Pr linkages was a competing reaction. The products (RO)Al(Oi-Pr)(OH) and (RO)$_2$Al(OH) contain 4,5 and 6 coordinate aluminium and also show a very sharp asymmetric band in the IR at 3517cm^{-1}. This is assigned to a bridging hydroxyl group. 2-phenylphenol gave products of the form (RO)Al(Oi-Pr)$_2$:Xi-PrOH and (RO)$_2$Al(Oi-Pr).Xi-PrOH which, as with the 2,6 disubstitued phenols, contain 4, 5 and 6 coordinate aluminium.

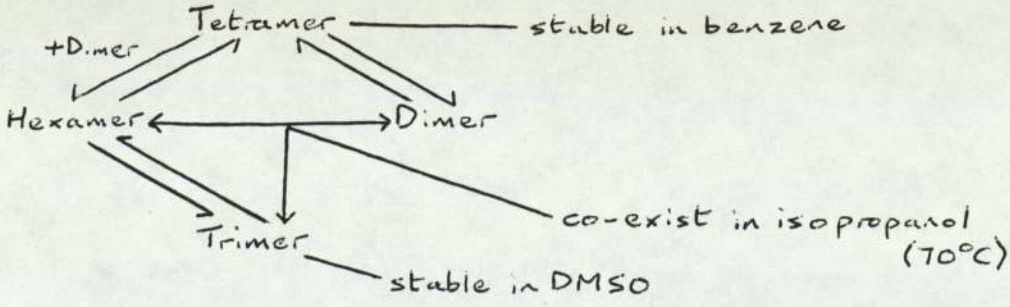
Discussion

^{27}Al is a quadrupolar nucleus (I=5/2) and spinning at the magic angle will not average to zero the second order quadrupole effects that will be present in a non-cubic lattice. Under these circumstances the maximum of the observed1/2 <->-1/2 transition does not correspond to the isotropic chemical shift. Nor, when comparing solid state spectra, do significant differences in peak maxima necessarily imply differences in shielding [499-501]. Despite these problems it is fortunate that the "apparent chemical shifts" obtained from peak maxima do reflect quite well the coordination number of aluminium. Thus resonances with maxima close to δ=O (relative to $[Al(H_2O)_6]^{3+}$) reflect octahedral environments whereas the range 50-80ppm implies tetrahedral coordination. Also there is evidence that the intermediate range (~25-40ppm) is attributable to 5 coordination about aluminium [2,502]. Some caution is required for MAS NMR spectra since spinning side bands associated with other resonances may occur in the "pentacoordinate region".

It is clear that solution phase E1 associated with hydrolysis method 3 (table I) contains a new species which is generated by the addition of slightly less than one molar equivalent of water to the isopropanol solution of aluminium isopropoxide, also there is spectral evidence for the presence of the tetrametic alkoxide, eg δ=0.62ppm, but the addition of benzene prior to analysis may be influential here (see below). The solid E2 isolated from E1 contains three aluminium environments. The data are qualitatively similar to those of Kriz et al [2] for trimeric aluminium isopropoxide at 70°C (3.2, 33.1,. 61.1ppm) and strongly suggest that the initial hydrolysis product has a structure based on that of $[Al(Oi\text{-}Pr)_3]_3$, and, therefore, that it is the trimeric form of the alkoxide that it is the reactive intermediate. It is also clear that the precise conditions used to isolate a solid product can influence the aluminium environment, thus sample G1 for example contains only tetrahedral aluminium.

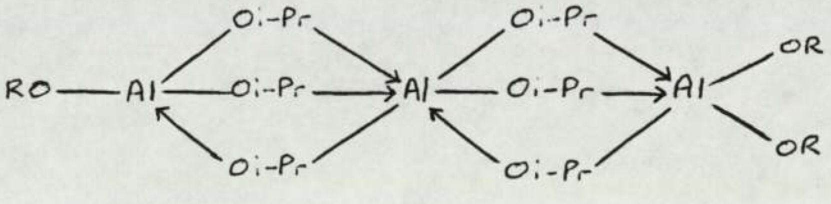
Further support for the view that a trimer is the reactive intermediate comes from the experiments described under hydrolysis method 2 (table II). Even IM aluminium isopropoxide in isopropanol at 70°C shows a complex spectrum with the co-existence of several species. The strongly co-ordinating solvent dmso gives a more simple spectrum showing three aluminium environments. Although close to 9ppm in IM aluminium isopropoxide in isopropanol it arises from another isomeric form of the alkoxide (hexamers and/or dimers) and that this octahedral resonance is probably twinned with a tetrahedral resonance which overlaps that from a second species, a solvated trimer contributing additional resonances at 6.60 and 45.4ppm. Solvation by dmso stabilises the trimer and by contrast the tetramer is the sole species in benzene solution. As water is added the two species initially present in isopropanol solution persist, differing in detailed solvation environment as the solvent composition changes. However, when the $Al(Oi\text{-}Pr)_3$:H_2O ratio reaches 1:1, the five coordinate aluminium environment is lost in the solid phase isolated from this mixture.

Under the conditions of methods 2-5 it is proposed that the dominant reactive species is the trimer of the alkoxide and that, when water is added is a single aliquot rather than gradually some evidence of either hexamer and/or dimer [31] is seen (such species being present in isopropanol solution at 70°C - see below).



The data from hydrolysis method 6, which simulates most closely the industrial process, do not conflict with the above argument, but demonstrate that when solids are finally isolated their spectra are dominated by tetrahedral aluminium resonances. The observed maximum of the resonance fluctuates over a range of some 12.6 ppm as conditions of precipitation, phase of spectral measurement, and solvent are changed (tables I, III and IV). Heating the hydrolysis product (Al $(Oi\text{-}Pr)_3:H_2O$ =1:1) (table IV) failed to produce a crystalline material at temperatures up to 800°C. However, heating did cause dramatic changes in the ^{27}Al MAS NMR spectrum. In particular the growth of a broad resonance characteristic of 5 coordinate aluminium centred 29.6ppm (800°C speciment table IV) was noted. A six coordinate site almost certainly coexists in this amorphous phase which probably represents a transition during thermolysis from the essentially 4 coordinate aluminium in the hydrolysis product to the six coordination present in the ultimate product, Al_2O_3. Since the materials are all X-ray amorphous it is difficult to speculate further as to their nature.

If indeed the trimeric form of the alkoxide is the reaction intermediate, reaction with a material that might arrest the reaction at an earlier stage would provide support for, even if not confirmation of, the hypothesis. Accordingly, the reaction between aluminium isopropoxide and various ortho-substituted phenols was considered. Reaction of aluminium isopropoxide with 2-t-butyl-4-methylphenol (ROH) in a 1:1 molar ratio afforded a product $(RO)Al(Oi\text{-}Pr)_2.3H_2O$ (table V) which, like some of the solids obtained from hydrolysis reactions, contains only 4 and 6 coordinate aluminium. However, 2,6-dimethyl-,2,6-di-butyl and 2-phenylphenol give 1:1 products which show the presence of 4,5 and 6 coordinate aluminium and give spectra similar to those attributed to the trimeric alkoxide species discussed previously. Thus sterically hindered phenols stabilise the trimer and, by so doing, lend support to the view that it is indeed an important intermediate in reactions of $Al(Oi\text{-}Pr)_3$ with both HOH and ROH. A possible structure for trimeric $(RO)Al(Oi\text{-}Pr)_2$ is:



Reaction with 2,6-diphenylphenol (R'OH) was slower and required a 2:1 mole ratio (phenol-alkoxide) to give a 1:1 product, $(R'O)Al(Oi\text{-}Pr)(OH)$. Some hydrolysis also occurred, the moisture probably being of atmospheric origin. A 3:1 mole ratio of reactants afforded $(R'O)_2Al(OH)$. Sharp IR bands at 3517cm^{-1} imply bridging OH groups and given the great similarities of the ^{27}Al MAS NMR spectra with those of the derivatives of other 2,6-disubstituted phenols, structures similar to the above may be postulated. Indeed, the ingress of moisture suggests that initial stages of hydrolysis of the alkoxide may involve replacement of (Oi-Pr) bridges with (OH) bridges in the trimer.

The balance of evidence suggests the reactive intermediate in the hydrolysis of aluminium isopropoxide to be a trimeric isomer, $[Al(Oi\text{-}Pr)_3]_3$, containing 4,5 and 6 coordinate aluminium atoms when present in coordinating solvents.

REFERENCES

REFERENCES

1) Industrial Applications of the Organometallic Compounds , 239-257, 351-354,(Chapman and Hall, London.1963) J H Harwood.

2) J Magn. Res. 60, 375-381 (1984) O Kriz, B Casensky, A Lycka, J Fusek and S Hermanek.

3) Chem. Ind., 39-40, (1961) B K Davison.

4) Chem. Process Eng., 48, (6), 100-102, (1967) J H Harwood.

5) Inorg. Chim. Acta Rev. 1, 99-112, (1967) R C Mehrotra.

6) J. Amer. Chem. Soc., 60, 2673-2675, (1938) R H Baker.

7) Organoaluminium Compounds, 205-228, (Elsevier, 1972) T Mole and E A Jefferey.

8) Dokl. Acad. Nauk SSSR Ser. Khim. 119, 1159-1161, (1958 A M Sladkov, V A Markevich, I A Iavich, L K Luneva, V N Chernov).

9) Adv. Inorg. Chem. Radiochem. 7, 263-348, (1965) R Koster and P Binger.

10) Chem. Ber. 88, 7420763, (1955) E Bonitz.

11) J. Indian Chem. Soc. 62, 494-497, (1985) K C Malhotra, A J Kaur, and J M K Kalra.

12) Rocz. Chem. 44, 1675-1683, (1970) J Lukasiak, L A May, I Ya Strauss and R Piekos.

13) Org. Synth. 15, 80-84, (1935) W Chalmers.

14) Proc. Roy. Soc. London (A) 200, 136-148, (1950) T S McRoberts & J H Schulman.

15) J. Chem. Soc. 2468-2470 (1954) S Coffey & V Boyd.

16) J. Chem. Soc B 1385-1389 (1967) D C Ayres, M Barnard & M R Chambers

17) Adv. Inorg. Chem. Radiochem. 15, 259-322, (1972) D C Bradley.

18) J. Amer. Chem. Soc. 60, 1151-1159 (1938) J Rinse.

19) Ind. Eng. Chem. 56(5), 42-50, (1964) J Rinse.

20) J. Chem. Soc. 29, 158-162, (1876) J H Gladstone and A Tribe.

21) J. Chem. Soc., 39, 1-12, (1881) J H Gladstone and A Tribe.

22) Anal. Chem. 41, 1243-1250, (1969) L M Brown and K S Mazdiyasni.

23) J. Inorg. Nucl. Chem. 24, 851-861, (1962) R C Wilhoit, J R Burton, F-T Kup, S-R Huang & A Viquesnel.

24) Nature 184, 55-546, (1959) D C Bradley & M M Faktor.

25) J. Amer. Chem. Soc. 72, 1661-1669, (1950) S M McElvain & J T Venerable.

26) Rec. Trav. Chim., 90, 410-422, (1971) W Fieggen & H Gerding.

27) Rec. Trav. Chim. ,87, 377-383, (1968) W Fieeggen, H Gerding & N M M Nibbering.

28) Org. Synth., 21, 8-10, (1941) W Wayne and H Adkins.

29) J. Chem. Soc. A, 1389-1391, (1970) J G Oliver, & I J Worrall.

30) J. Amer. Chem. Soc. 77, 4571-4577, (1955) S M McElvain and R E Starn Jnr..

31) J. Org. Chem. 38, 3334-3337, (1973) D C Kleinschmidt, V J Shiner Jnr., & D Whittaker.

32) J. Indian. Chem. Soc., 30, 585-591, (1953) R C Mehrotra.

33) Cienc. Cult. (Sao Paulo), 27, 50-53, (1975) P G David, F David & V J Shiner Jnr..

34) J. Indian Chem. Soc., 54, 586-590, (1977) M S Bains.

35) Can. J. Chem., 40, 381-383, (1962) M S Bains.

36) J. Indian Chem. Soc. 31, 85-90, (1954) R C Mehrotra.

37) Bull. Soc. Chim. France 4709-4711, (1968) M F Berny & M O Berrest.

38) Chem. Ind. , 829-830, (1970) R C Paul, H S Makhni & S L Chadha.

39) Bull. Chem. Soc. Japan, 41, 1194-1200, (1968) T. Veshima, S Tomita, and T Saegusa.

40) Inorg. Chem. 6, 1679-1681, (1967) T Saegusa and T Veshima.

41a) J. Chem. Soc., 222-229, (1928) G J Burrows, and I W Wark.

41b) J. Amer. Chem. Soc. 54, 3266-3268, (1932) W McBain & W L McClatchie.

42) Trans. Farady Soc., 34, 660-677, (1938) A S C Lawrence.

43) Anal. Chem. 24, 635-638, (1952) W W Harple, S E Wiberley & W H Bauer.

44) J. Phys. & Colloid Chem. 53, 23-39, (1949) V R Gray & A E Alexander.

45) J. Oil Colour Chem. Ass. 37, 378-382, (1954) A E Alexander.

46) Nature, 172, 74, (1953) R C Mehrotra.

47) Nature, 162, 101-102, (1948) T S McRoberts, and J K Schulman.

48) J. Inst. Pet. 31. 303-314, (1945) A S C Lawrence.

49) Ann. Phys., 17, 1-71, (1942) C Duval, J Lecomte & F Douville.

50) J. Phys. Chem. 58, 61-64, (1954) F A Scott, J. Goldenson, S E Wiberley, W H Bauer.

51) J. Amer. Chem. Soc., 70, 1053-1054,
(1948) G H Smith, H H Pomeroy, C G McGee, K J Mysels.

52) J. Inorg. Nucl. Chem. 24, 961-966, (1962) K C Pande & R C Mehrotra.

53) J. Inorg. Nucl. Chem., 24, 961-966, (1962) R C Mehrotra & A K Rai.

54) J. Prakt. Chem., 20, 105-112, (1963) A K Rai, R K Mehrotra & R C Mehrotra.

55) J. Inorg. Nucl. Chem., 2, 60-65, (1956) R C Mehrotra and K C Pande.

56) Z. Anorg. Allg. Chem. 286, 291-295 (1956) K C Pande & R C Mehrotra.

57) Zh. Neorg. Khim. 14, 102-105, (1969) E G Pogodilova, A I Grigor'ev, A V Novoselov.

58) J. Chem. Soc. 1972-1976, (1956) A Gilmour, A Jobling & S M Nelson.

59) Inorg. Chim. Acta, 34, 25-27, (1979) M Singh, B L Mathur, A Kachhawaha.

60) Inorg. Chem., 22, 525-529, (1983) S J Karlik, E Tarien, G A Elgarish, G L Eichhorn.

61) Can. J. Chem., 35, 799-816, (1957) A E Leger, R L Haines, C E Hubley, J C Hyde, H Sheffer.

62) J. Chem. Soc., 2082-2083, (1950) J Glazer, T S McRoberts, J H Schulman.

63) J. Amer. Chem. Soc., 71, 278-282, (1949) C G McGee.

64) Inorg. Chem. 10, 482-486, (1971) D A Case and T J Pinnavaia.

65) J. Polym. Sci., 29, 637-645, (1958) V. Kugler.

66) 9, 25-27, (1967) R G Charles, N C Peterson, G H Franke.

67) J. Amer. Chem. Soc. 85, 500-504, (1963) R C Fay, T S Piper.

68) J. Amer. Chem. Soc., 84, 2303-2308, (1962) R C Fay, T S Piper.

69) Indian. J. Chem., 2, 386-388, (1964) R C Mehrotra, R K Mehrotra.

70) Can. J. Chem., 39,795-798, (1961) R K Mehrotra, R C Mehrotra.

71) J. Amer. Chem. Soc., 81, 4213-4217, (1959) T R Patterson, F J Pavlik, A A Baldoni, R L Frank.

72) Acta Cryst., 1536-1540, C40, (1984) M F Garbauskas, J H Wengrovius, R C Going, J S Kasper.

73) Acta Cryst., C43, 2441-2442, (1987) M F Garbauskas, J H Wemgrovius,.

74) J. Amer. Chem. Soc. 108, 982-989, (1986) J H Wengrovius, M F Garbauskas, E A Williams, R C Going, P E Donahue, J F Smith.

75) Z Naturforsch, (B) 27, 1145-1148, (1972) U B Saxena, A K Rai, R C Mehrotra.

76) Inorg. Chem., 3, 513-517, (1964) R E Hester, R A Plane.

77) Inorg. Synth., 2, 25-26, (1946) R C Young.

78) Inorg. Chem., 2, 73-76, (1963) G S Hammond, D C Nonhebel, C S Wu.

79) Spectrochim. Acta, (A), 40, 233-239, (1984) B A Kolesov, I K Igumenov.

80) J. Amer. Chem. Soc.,86, 5132-5137, (1964) E L Muetterties, C M Wright.

81) Inorg. Synth., 9, 28-30, (1967) M L Morris, R W Moshier, R E Sievers.

82) Inorg. Synth., 5, 105-113, (1957) W C Fernelius, B E Bryant.

83) Inorg. Chem., 12, 763-768, (1973) T J Pinnavaia, M T Mocella, B A Averill, J T Woodard.

84) Inorg. Chem., 6, 2022-2029, (1967) J J Fortman, R E Sievers.

85) J. Amer. Chem. Soc. 91, 4420-4425, (1969) E L Muetterties, C W Alegranti.

86) Inorg. Chim. Acta, 49, 17-20, (1981) M Das, D T Haworth, J W Beery.

87) J. Amer. Chem. Soc., 108, 5033-5035, (1986) M M Finnegan, S J Rettig, C Orvig.

88) J. Amer. Chem. Soc. 81, 3188-3189, (1959) M M Jones.

89) J. Amer. Chem. Soc., 75, 3784-3786, (1953) B E Bryant, W C Fernelius, B E Douglas.

90) Anal. Chim. Acta, 32, 245-252, (1965) E W Berg, J T Truemper.

91) J. Phys. Chem., 64, 487-490, (1960) E W Berg, J T Truemper.

92) J. Coord. Chem., 3, 67-76, (1973) P K Hon, C E Pfluger.

93) J. Gas. Chromatogr. 5, 241-247, (1967) R E Sievers, J W Connolly, W D Ross.

94) J. Organometal. Chem., 142, 205-210, (1977) S Pasynkiewicz, A Pietrzykowski.

95) J. Organometal. Chem., 201, 89-96, (1980) A Pietrzykowski, S Pasynkiewicz, A Wolinska.

96) J. Chem. Soc., A, 603-605, (1966) C Ercolani, A Camilli, G Sartori.

97) J. Chem. Soc., A, 608-611, (1966) C Ercolani, A Camilli, L de Luca, G Sartori.

98) Izv. Akad. Nauk SSSR Ser. Khim. 10, 1261-1266, (1961) A A Zhdanov, K A Audrianov, A A Bogdanova.

99) J. Indian. Chem. Soc., 39, 635-640, (1962) R C Mehrotra, R K Mehrotra.

100) Collect. Czech. Chem. Commun., 39, 2559-2566, (1974) O Kriz, P Trska, B Casensky.

101) Collect. Czech. Chem. Commun., 36, 2648-2657, (1971) B Casensky, J Machacek, K Abraham.

102) Chem. Communs., 1107-1109, (1967) P R Scherer, Q Fernando.

103) J. Amer. Chem. Soc., 92, 91-96, (1970) Y Kushi, Q Fernando.

104) Chem. Communs., 555-556, (1969) Y Kushi, Q Fernando.

105) Anal. Chem. 40, 1938-1945, (1968) P R Scherer, Q Fernando.

106) Chem. Ind., 344-346, (1954) R G W Hollingshead.

107) J. Indian. Chem. Soc., 39, 677-682, (1962) R C Mehrotra, R K Mehrotra.

108) Inorg. Chim. Acta., 98, 121-124, (1985) R Duggal, R C Mehrotra.

109) Collect. Czech. Chem. Commun., 38, 343-349, (1973) J Machacek, B Casensky, K Abraham.

110) Collect. Czech. Chem. Commun., 44, 2772-2779 (1979) O Kriz, B Casensky, J Machacek.

111) Collect. Czech. Chem. Commun., 45, 1336-1342, (1980) O Kriz, B Casensky, J Machacek.

112) Helv. Chim. Acta., 70, 520-533, (1987) E Muller, H B Burgi.

113) J. Coord. Chem., 7, 203-212, (1978) K J Pearson, R J Palma Sr., J R Baker.

114) J. Chem. Soc., 4701-4704, (1956) K Saito, J Terrey.

115) Aust. J. Chem., 21, 1651-1652, (1968) M Hasan, B S Sankhla, R N Kapoor.

116) Koord. Khim., 3, 1299-1308, (1977) N. Ya. Turova, M I Karpovskaya, a V Novoselova, g A Kirakosyan, V P Tarasov, N I Kozlova.

117) Inorg. Chim. Acta., 21, 157-161, (1977) N Ya Turova, M I Karpovskaya, A V Novoselova, S I Bakum .

118) Anal. Chem., 22, 534-538, (1950) C J Lintner, R H Schleif, T Higuchi.

119) Zh. Obshch. Khim. 47, 1338-1346, (1977) N Ya Turova, M I Karpovskaya, A V Novoselova.

120) Izv. Akad. Nauk SSSR Ser. Khim., 28, 1273-1277, (1979) V V Gavrilenko, M I Vinnikova, V A Antonovich, L I Zakharkin.

121) J. Amer. Chem. Soc., 86, 1079-1085, (1964) H C Brown, C J Shoaf.

122) Zh. Obshch.Khim., 36, 200-206, (1966) L I Zakharkin, D N Maslin, V V Gavrilenko.

123) J. Indian Chem. Soc., 54, 109-116, (1977) R C Mehrotra, J Singh .

124) Inorg. Chim. Acta Rev., 5, 127-136, (1971) R C Mehrotra, A Mehrotra.

125) Coord. Chem. Rev. 14, 1-27, (1974) P N Kapoor, R C Mehrotra.

126) J. Amer. Chem. Soc. 80, 5372-5376, (1958) H C Brown and R F McFarlin.

127) Proc. 9th Int. Conf. Coord. Chem. 253-255, (1966) R C Mehrotra, M M Agarwal, P N Kapoor.

128) Inorg. Synth. 1, 35-38, (1939) J C Bailar, E M Jones.

129) J. Inorg. Nucl. Chem., 26,1543-1550, (1964) S N Dubey, R C Mehrotra.

130) Collect. Czech. Chem. Commun. 37, 2175-2182, (1972) O Kriz, J Machacek.

131) Collect. Czech. Chem. Commun., 37, 2537-2543, (1972) B Casensky, J Machacek, K Abrham.

132) J. Org. Chem. 8, 256-270, (1943)M S Kulpinski, F F Nord.

133) J. Amer. Chem. Soc. 69, 2605-2607, (1947) F J Villani, F F Nord.

134) Zh. Neorg. Khim. 24, 1815-1820, (1979). E P Turevskaya, N Ya Turova, M I Yanovskaya, A V Novoselova

135) Synth. React. Inorg. Met. - Org. Chem. 5 (1975) 267-277 S. Govil and R C Mehtrotra

136) Inorg. Chim. Acta 29 (1978) 131-136, R C Mehrotra, S Goel, A B Goel, R B King and K C Nainan.

137) Synth. React. Inorg. Met.-Org. Chem. 13 (1983) 571-583, M Aggrawal, C K Sharma and R C Mehrotra.

138) Synth. React. Inorg. Met.-Org. Chem. 14 (1984) 139-150, M Aggrawal and R C Mehrotra.

139) Acta Cryst. C41, (1985) 1014-1017 M C Cruickshank and L S Dent Glasser.

140) J. Chem. Soc. Chem. Commun. (1985) 84-85 M C Cruickshank and L S Dent Glasser.

141) Synth. React. Inorg. Met.-Org. Chem. 9 (1979) 79-88 J V Singh, N C Jain and R C Mehrotra.

142) J. Indian. Chem. Soc. 59 (1982) 715-722 R C Mehrotra

143) Coordination Chemistry - 21 (1981) 113-125 R C Mehrotra

144) Inorg. Chem. 23 (1984) 1046-1048 R C Mehrotra and J Singh.

145) J. Coord. Chem. 13 (1984) 273-279 R C Mehrotra and J V Singh.

146) Can. J. Chem. 62 (1984) 1003-1007 R C Mehrotra and J Singh.

147) Z. Anorg. Allg. Chem. 512 (1984) 221-230 R C Mehrotra and J V Singh.

148) Inorg. Chim. Acta 19 (1976) 203-208 T Ouhadi, J P Bioul, C Stevens, R Warin, L Hocks, Ph. Teyssie.

149) J. Polym. Sci. Polym. Chem. Ed. 15 (1977), 1035-1041 A Hamitou, R Jerome and Ph. Teyssie.

150) J. Polym. Sci. Polym. Lett. 8 (1970) 319-321 M. Osgan, J J Pasero and Ph. Teyssie.

151) Synth. Inorg. Met.-Org. Chem. 3 (1973) 181-191 R C Mehrotra, M M Agrawal and A Mehrotra.

152) J. Amer. Chem. Soc. 95 (1973) 5556-5563 D. Coucouvanis and D Piltingsrad.

153) Polyhedron 5 (1986) 1017-1021 R Jain, A K RAi and R C Mehrotra.

154) Cryst. Struct. Commun. 10 (1981) 59-64 J Lamotte, O Dideberg, L Dupont and P Durbut.

155) J. Chem. Soc. Dalton (1972) 1203-1204 R C Mehrotra and A Mehrotra.

156) Inorg. Chim. Acta. 15 (1975) 43-46 S Govil, P N Kapoor and R C Mehrotra.

157) Indian J. Chem. 10 (1972) 532-535 A Mehrotra and R C Mehrotra.

158) Chem. Communs. (1968) 469-470 R C Mehrotra and M M Agrawal.

159) Prox. 7th Rare Earth Res. Conf. (1968) 759-770 R C Mehrotra, M M Agrawal, U D Tripathi and S R Bindal.

160) J. Amer. Chem. Soc. 78 (1956) 6027-6029 R J Jones, E Bindschadler, D Blume, G Karmas, G A Martin, J R Thirtle, H Gilman.

161) Synth. React. Inorg. Met.-Org. Chem. 18 (1988) 9-19, M Aggrawal and R C Mehrotra.

162) Justus Liebigs Ann. Chem. 476 (1929) 113-150 H Meerwein and T Bersin.

163) Inorg. Chem. 11 (1972) 2170-2174 A Mehrotra and R C Mehrotra.

164) J. Inorg. Nucl. Chem. 40 (1978) 349-351 R C Mehrotra, A K Rai and N C Jain.

165) Vestn. Slov. Kem. Drus. 32 (1985) 221-229 N Bulc., L Golic and J Siftar.

166) Acta. Cryst. C 40 (1984) 1829-1831 N. Bulc, L Golic and J Siftar.

167) Polyhedron 4 (1985) 845-852 M Aggrawal and R C Mehrotra.

168) Chim. Ind. (Milano) 44 (1962) 529-531 P Pino, G P Lorenzi and F Ciardelli.

169) Polym. J 7 (1975) 50-61N Yamamoto and I Yamashita.

170) J. Organometal. Chem. 90 (1975) C43-C44 K B Starowieyski, S Pasynkiewicz and M Skowronska-Ptasinska.

171) Makromol. Chem. 82 (1965) 32-40, H Fujii, I Tskuma, T Saegusa, J Furukawa.

172) J. Organometal. Chem. 52 (1973) 269-274 S Pasynkiewicz.

173) Bull. Chem. Soc. Japan 40 (1967), 967-972 T Saegusa, K Hirota, E Hirasawa and J Fujii.

174) Organometallics 4 (1985) 238-241 M J Zaworotko, C R Kerr and J L Atwood.

175) J. Org. Chem. 5 (1940) 106-121 A V Grosse and J M Mavity.

176) Aust. J. Chem. 19 (1966) 373-379 T Mole.

177) Angew. Chem. 75 (1963) 1090-1097 H Lehmkuhl.

178) J. Organometal. Chem. 141 (1977) 283-288, A Kunicki, W Koskinska, M Boleslawski and S Pasynkiewicz.

179) Angew. Chem. 75 (1963) 846-851 H Scherer and I G Seydel.

180) J. Organometal. Chem. 74 (1974) 365-371 E A Jeffery, A Meisters and T Mole.

181) Tetrahedron Lett. (1987) 3257-3260 G Iwasaki and M Shibasaki.

182) J. Amer. Chem. Soc. 108 (1986) 6328-6343 L S Liebeskind, M E Welker and R W Fengl.

183) Izv. Akad. Nauk SSSR Ser. Khim. 10 (1961) 364 L I Zakharkin, G S Kolesnikov, S L Davydova, V V Gavrilenko and A A Kanyshova.

184) J. Organometal. Chem. 127 (1977) 403-414 J L Atwood, W E Hunter and K D Crissinger.

185) Zh. Obshch. Khim. 39 (1969) 2043-2045 L P Stepovik, V A Dovonov, and L A Malygina.

186) Zh. Obshch. Khim. 39 (1969) 123-128 G A fazuvaev, L P Stepovik, V A Dodonov and G V Nesterov.

187) Zh. Obshch. Khim. 38 (1968) 249-251 G A Razuvaev and E V Mitrofanova.

188) Zh. Obshch. Khim. 31 (1961) 2340-2343 G A Razuvaev, E V Mitrofanova and G G Petukhov.

189) Z. Anorg. Allg. Chem. 378 (1970) 245-262 J Weidlein.

190) Angew. Chem. 76 (1964) 817 H Lehmkuhl.

191) J. Organometal. Chem. 43 (1972) 75-80 S Pasynkiewicz and K Dowbor.

192) J. Polym. Sci. 38 (1959) 51-61 M Roha, L C Kreider, M R Frederick and W L Beears.

193) J. Organometal. Chem. 19 (1969) 439-443, W R Kroll and W Naegele.

194) J. Organometal. Chem. 229 (1982) 215-222 A G Davies, Z Florjanczyk, E Lusztyk, and J Lusztyk.

195) J. Organometal. Chem. 74 (1974) 373-384 E A Jeffery, A Meisters, and T Mole.

196) Organometallics 1 (1982) 1021-1025 J L Atwood, D C Hrneir, R Shakir, M S Dalton, R D Priester and R D Rogers.

197) J. Inclusion Phenomen. 1 (1983) 61-69 J L Atwood, R D Priester, R D Rogers and L G Canada.

198) J. Inclusion Phenomen. 3 (1985) 65-69 G H Robinson, S G Bott, H Elgamal, W E Hunter J L Atwood.

199) J. Inclusion Phenomen. 5 (1987) 747-758 S G Bott, A W Coleman and J L Atwood.

200) J. Inclusion Phenomen. 5 (1987) 581-590 S G Bott, A W Coleman and J L Atwood.

201) J. Chem. Soc. A (1968) 2535-2538 J R Jennings, K Wader and B K Wyatt.

202) Makromol. Chem. 131 (1970) 185-203 K Harada, J Furukawa and S Yamashita.

203) J. Polym. Sci. Poly. Lett. 4 (1966) 727-732 H Tani, T Araki and H Yasuda.

204) J. Chem. Soc. A (1968) 2004-2008 J R Horder and M F Lappert.

205) J. Organometal. Chem. 25 (1970) 33-41 T Hirabayashi, K Itoh, S Sakai and Y Ishii.

206) J. Polym. Sci. Polym. Lett. 5 (1967) 681-686 H Higashi and K Watabe.

207) Inorg. Chem. 6 (1967) 1310-1315 T J Hurley, M A Robinson, J A Scraggs and S I Trotz.

208) Organometallics 4 (1985) 1701-1707 M R P van Vliet, P Buysingh, B Kojic-Prodic, G van Koten, K Vrieze and A L Spek.

209) J. Polym. Sci. (A1) 7 (1969) 2269-2280 T Konomi and H Tani.

210) J. Organometal. Chem. 13 (1968) 53-60 J L Atwood and G D Stucky.

211) J. Inorg. Nucl. Chem. 31 (1969) 2329-2341 E E Flagg and D L Schmidt.

212) Z. Anorg. Allg. Chem. 311 (1961) 198-202 R K Mehrotra and R C Mehrotra.

213) Z. Anorg. Allg. Chem. 252 (1944) 323-328 V H Funk and E Rogler.

214) J. Indian Chem. Soc. 39 (1962) 23-27 R C Mehrotra and R K Mehrotra.

215) J. Prakt. Chem. 16 (1962) 251-257 R C Mehrotra and R K Mehrotra.

216) Ark. Kemi 25 (1966) 515-522 S Friberg and M Hansson.

217) Acta Chim. Acad. Sci. Hung. 7 (1955) 421-429 G Gal, G Tokar and I Simonyi.

218) Acta Chim. Acad. Sci. Hung. 10 (1956) 217-226 I Simonyi, G Tokar and G Gal.

219) Acta Chim. Acad. Sci. Hung. 15 (1958) 291-295 G Tokar and I Simonyi.

220) Acta Chim. Acad. Sci. Hung. 37 (1963) 329-338 I Foldesi.

221) J. Amer. Chem. Soc. 75 (1953) 1750-1751 K J Mysels and D M Chin.

222) Izv. Akad. Nauk SSSR Ser. Khim. 11 (1962) 78-86 K A Andrianov, M B Flomberg, L I Sorokina and E I Kirilenko.

223) Bull. Chem. Soc. Japan 53 (1980) 421-423 F Wada and T Matsuda.

224) J. Amer. Chem. Soc. 107 (1985) 1796-1797 S G Bott, H Elgamal, G H Robinson, S G Bott, J A Weeks and W E Hunter.

225) J. Inclusion Phomen. 2 (1984) 367-376 J L Atwood, H Elgamal, G H Robinson, S G Bott, J A Weeks and W E Hunter.

226) Z. Anorg. Allg. Chem. 358 (1968) 44-46 von H Noth and H Suchy.

227) Z. Chem. 13 (1973) 436-438 B Casensky, O Kriz, H Kadlecova.

228) Collect. Czech. Chem. Commun. 43 (1978), 3012-3019 O Kriz, J Machacek.

229) Collect. Czech. Chem. Commun. 41 (1976) 187-192 J. Fusek, F Hanousek and F Haruda.

230) J. Amer. Chem. Soc. 80 (1958) 5377-5380 H C Brown and B C Subba Rao.

231) Naturwiss 39 (1952) 20. O Schmitz-Dumont and V Habernickel.

232) Dokl. Acad. Nauk SSSR Ser. Khim. 152 (1963) 114-116 G A Razuvaev, A I Graevskii, K S Minker and M D Belova.

233) Zh. Obshch. Khim. 58 (1988) 1578-1582 V A Dodonov, L P Stepovik, S M Sofronova and T V Mukhina.

234) J. Chem. Soc. (1963) 1192-1197 A G Davies and C D Hall.

235) Indian J. Appl. Chem. 26 (1963) 109-111 R C Mehrotra and B C Pant.

236) J. Chem. Soc. A (1966) 606-608 C Ercolani, A Camilii and G Sartori.

237) Chem. Communs. (1968) 1332-1333 Y Kai, N Yasuoka, N Kasai, M Kakudo, H Yasuda and H Tani.

238) Dokl. Acad. Nauk SSSR Ser. Khim. 112 (1957) 1050-1053 K A Andrianov, A A hdanov, N A Kurasheva and V G Dulova.

239) Z. Phys. Chem. (A) 165 (1933) 294-310 H Ulich and W Nespital.

240) J. Phys. Chem. 39 (1935) 1125-1133 R A Robinson and D A Peak.

241) Nature 182 (1958) 1211-1214 D C Bradley.

242) J. Amer. Chem. Soc. 85 (1963) 2318-2322 V J Shiner Jr., D Whittaker and V P Fernandez.

243) J. Inorg. Nucl. Chem. 31 (1969) 1609-1613 J G Oliver, P K Phillips and I J Worrall.

244) J. Chem. Educ. 46 (1969) 510-511 I J Worrall.

245) Diss. Abs. (B) 28 (1967) 2344-2345 D C Kleinschmidt.

246) Org. Mass. Spectrom. 2 (1969) 1043-1048 L W Daasch and H M Fales.

247) Koord. Khim. 4 (1978) 1517-1525 N Ya Turova, V A Kozunov, A I Yanovski, N G Bokii, Yu T Struchkov, B L Tarnopolskii and A V Novoselova.

248) J. Inorg. Nucl. Chem. 41 (1979) 5-11 N Ya Turova, V A Kozunov, A I Yanovskii, N G Bokii, Yu T Struchkov and B L Tarnopolskii.

249) J. Inorg. Nucl. Chem. 25 (1963) 779-781 E L Amma.

250) J. Magn. Res. 15 (1974) 162-165 J W Akitt and R H Duncan.

251) J. Phys. Chem. 60 (1956) 1018-1019 D L Guertin, S E Wiberley, W H Bauer, J Goldenson.

252) J. Chem. Soc. (1961) 2601-2605 C G Barraclough, D C Bradley, J Lewis and I M Thomas.

253) Anal. Chem. 25 (1953) 1720-1724 J V Bell, J Heisler, H Tannenbaum, J Goldenson.

254) J. Chem. Soc. A (1970) 2347-2348 J G Oliver and I J Worrall.

255) J. Chem. Soc. A (1970) 845-848 J G Oliver and I J Worrall.

256) Chem. Communs. (1968) 918-919 T N Huckerby, J G Oliver and I J Worrall.

257) Inorg. Nucl. Chem. Lett. 5 (1969) 749-751 T N Huckerby, J G Oliver and I J Worrall.

258) J. Phys. Chem. 36 (1932) 2567-2574 J W McBain and W L McClatchie.

259) Spectrochim Acta. 20 (1964) 8470851 J D Donaldson, J F Knifton and S D Ross.

260) Ark. Kemi 25 (1966) 5230531 S Friberg.

261) Ark. Kemi 25 (1966) 485-490 S Friberg.

262) Acta Chem. Scand. 19 (1965) 2267-2273 S Friberg.

263) Acta Chem. Scand. 19 (1965) 8830887 S Friberg.

264) J. Inorg. Nucl. Chem. 40 (1978) 195-197 C A Wilkie and D T Haworth.

265) Inorg. Chem. 7 (1968) 870-874 G M Bancroft, C Reichert and J B Westmore.

266) Aust. J. Chem. 19 (1966) 1545-1566 C G MacDonald and J S Shannon.

267) Koord Khim 5 (1979) 34038 I K Igumenov, Yu V Chumachenko and S V Zemskov.

268) Phil. Mag. 2 (1926) 1153-1165 A N Sarkar.

269) Proc. Roy. Soc. London (A) 112 (1926) 448-467 W T Astbury.

270) J. Chem. Phys. 27 (1957) 1298-1304 H S Jarrett.

271) J. Amer. Chem. Soc. 88 (1966) 2951-2956 E C LingaFelter and R L Braun.

272) Acta Cryst. B 31 (1975) 2496-2498 B W McClelland.

273) Dokl. Acad. Nauk SSSR Ser. Khim. 133 (1960) 386-388 E A Shugam and L M Shkol'nikova.

274) Kristallografiya 4 (1959) 419-420 L M Shkol'nikova.

275) Inorg. Chem. 2 (1963) 411-412 M L Morris, R W Moshier and R E Sievers.

276) J. Amer. Chem. Soc. 98 (1976) 4503-4515 M Pickering, B Jurado, C S Springer Jr.

277) J. Inorg. Nucl. Chem. 42 (1980) 1069-1071 G-Y Lin, C A Wilkie and D T Haworth.

278) Inorg. Chem. 3 (1964) 348-356 R C Fay and T S Piper.

279) Chem. Communs. (1967) 782-783 C Reichert, J B Westmore and H D Gesser.

280) J. Mol. Struct. 53 (1979) 69-80 M L Morris and R L Hilderbrandt.

281) J. Amer. Chem. Soc. 94 (1972) 8046-8055 E L Muetterties and L J Guggenberger.

282) Polyhedron 6 (1987) 525-529 E W Meijer.

283a) Anal. Chem. 34 (1962) 1086-1089 W E Ohnesorge and A L Burlingame.

283b) Anal. Chem. 39 (1967) 1036-1037 G R Horton.

284) J. Chem. Soc. 121 (1922) 2069-2079 I E Knaggs.

285) Aust. J. Chem. 31 (1978)1455-1462 D Taylor.

286) Vestn. Slov. Kem. Drus. 29 (1982) 211-225 N. Bulc, L Golic and J Siftar.

287) J. Chem. Soc. A (1969) 3006-3011 R D Gillard, S H Laurie and P R Mitchell.

288) Zh. Strukt. Khim. 11 (1970) 164-165 T N Polynova, N P Bel'skaya, D T de Gareiya Banus, M A Porai-Koshits and L I Martynenko.

289) Proc. Indian Natl. Sci. Acad. (A) 42 (1976) i-xxiv R C Mehrotra.

290) Polyhedron 4 (1985) 1141-1142 R C Mehrotra and M Aggrawal.

291) J. Chem. Soc. Chem. Commun. (1972) 189-190 A Mehrotra and R C Mehrotra.

292) Inorg. Chem. 13 (1974) 2381-2386 F J Hollander and D Coucouvanis.

293) Proc. Indian Natl. Sci. Acad. (A) 40 (1974) 215-225 R C Mehrotra and A Mehrotra.

294) Proc. 6th Int. Conf. Coord. Chem. (1961) 296-302 J L Hoard, G S Smith and M Lind.

295) "Chelating Agents and Metal Chelates" (Academic Press, New York) (1964) 183-235, 303 F P Dwyer and D P Mellor.

296) Dokl. Acad. Nauk SSSR Ser. Khim. 244 (1979) 119-122 A I Yanovskii, V A Kozunov, N Ya Turova, N G Furmanova and Yu T Struchkov.

297) J. Organometal. Chem. 35 (1972) 19-25 T Hirabayashi, T Sakakibara, U Ishii.

298) J. Organometal. Chem. 179 (1979) 1-6 L Cocco, D P Eyman.

299) Aust. J. Chem. 21 (1968) 2683-2686 E A Jeffery and T Mole.

300) Bull. Chem. Soc. Japan 39 (1966) 725-728 R Tarao.

301) Bull. Chem. Soc. Japan 50 (1977) 673-679 M Vetsuki and Y Fujiwara.

302) J. Amer. Chem. Soc. 95 (1973) 4142-4147 Vetsuki and Y Fujiwara.

303) Z. Anorg. Allg. Chem. 398 (1973) 241-248 D A Drew, A Haaland, and J Weidlein.

304) J. Organometal. Chem. 32 (1971) 165-179) Y Kai, N Yasuoka, N Kasai and M Kakudo.

305) Chem. Communs. (1969) 575-576 Y Kai, N Yasuoka, N Kasai, M Kakudo, H Yasuda, H Tani.

306) Organometallics 1 (1982) 1179-1183 M J Zaworotko, R D Rogers and J L Atwood.

307) "Inclusion Compounds" (Academic Press, London) 1 (1984) 375-405 J L Atwood, J E D Davies and D D MacNicol.

308) Bull. Chem. Soc. Japan 42 (1969) 1588-1595 H Sato, R Tarao and H Higashi.

309) J. Chem. Soc. Dalton (1972) 447-449 B Sen, G L White and J D Wander.

310) J. Chem. Soc. (1963) 3200-3203 P J Wheatley.

311) J. Chem. Soc. A (1968) 291-297 M Bonamico and G Dessy.

312) J. Chem. Soc. A (1967) 1786-1790 M Bonamico and G Dessy.

313) Chem. Communs. (1966) 135-136 M Bonamico.

314) J. Phys. Chem. 61 (1957) 114-116 R C Wilhoit.

315) J. Amer. Chem. Soc. 73 (1951) 1400-1402 S M McElvain and W R Davie.

316) J. Amer. Chem. Soc. 28 (1906) 608-617 A N Cook.

317) Zh. Neorg. Khim. 23 (1978) 3225-3232 V A Kozunov, N Ya Turova and A V Novoselova.

318) Rec. Trav. Chim. 89 (1970) 175-185 W Fieggen and H Gerding.

319) Rec. Trav. Chim. 89 (1970) 236-244 W Fieggen and H Gerding.

320) J. Oil Colour Chem. Ass. 40 (1957) 863-879, 976-989 J. Weiss.

321) J. Chem. Soc. A (1971) 981-9843 J W Wilson.

322) J. Chem. Soc. (1952) 3252-3260 L M Jackman and A K Macbeth.

323) Chem. Ind. (1961) 1032 M S Bains and D C Bradley.

324) J. Amer. Chem. Soc. 91 (1969) 394-398 V J Shiner Jr. and D Whittaker.

325) J. Org. Chem. 30 (1965) 1174-1179 B J Yager and C K Hancock.

326) Justus Liebigs Ann. Chem. 444 (1925) 221-238 H Meerwein and R Schmidt.

327) Angew. Chem. 39 (1926) 138-143 W Ponndorf.

328) Bull. Soc. Chim. France 37 (1925) 537-742 A Verley.

329) Rec. Trav. Chim. 91 (1972) 477-482 R H T Bleyerveld, W Fieggen and H Gerding.

330) Zh. Neorg. Khim. 23 (1978)1233-1237 V A Kozunov and N Ya Turova.

331) Inorg. Chim. Acta 84 (1984) L17-L19 D L Grossman and D T Haworth.

332) Inorg. Chem. 10 (1971) 1004-1017 J R Hutchison, J G Gordon and R H Holm.

333) J. Amer. Chem. Soc. 94 (1972) 6411-6426 SS Eaton, J R Hutchison, R H Holm, E L Muetterties.

334) Polyhedron 2 (1983) 1329-1335 L Ohman and S Sjoberg.

335) J. Chem. Soc. Dalton (1983) 2513-2517 L Ohman and S Sjoberg.

336) J. Chem. Soc. Dalton (1985) 2665-2669 S Sjoberg and L Ohman.

337) Acta Chem. Scand. (A) 37 (1983) 875-880 L Ohman and S Sjoberg.

338) Acta Chem. Scand. (A) 36 (1982) 47-53 L Ohman and S Sjoberg.

339) Acta Chem. Scand. (A) 35 (1981) 201-212 L Ohman and S Sjoberg.

340) Acta Chem. Scand. (A) 37 (1983) 561-568 L Ohman and S Sjoberg.

341) Inorg. Chem. 23 (1984) 18-23 R J Motekaitis and A E Martell.

342) J. Coord. Chem. 14 (1985) 139-149 R J Motekaitis and A E Martell.

343) J. Coord. Chem. 13 (1984) 143-151, B S Nakani and R D Hancock.

344) S. Afr. I. Chem. 35 (1982) 153-156 R D Hancock and B S Nakani.

345) Polyhedron 1 (1982) 313-318 R A Hancock and S T Orszulik.

346) J. Coord. Chem. 12 (1983) 219-230. H Iwasaki, K Okamoto, J Hidaka, and H Einaga.

347) J. Coord. Chem. 12 (1983) 243-258 K Hayashi, T Ohsawa, K Okamoto, J Hidaka, and H Einaga.

348) J. Coord. Chem. 13 (1984) 221-230 I Ohkura, K Fujiwara, K Ojamoto, J Hidaka, H Einaga.

349) J. Chem. Soc. Dalton (1982) 1377-1379 K Hayashi, K Okamoto, J Hidaka and H Einaga.

350) J. Inorg. Nucl. Chem. 41 (1979) 209-214 S Murakami.

351) Zh. Neorg. Khim. 27 (1982) 27672771 N F Kosenko and I A Andriyuk.

352) Bull. Chem. Soc. Japan 43 I (1970) 119-124 K Saito and K Masuda.

353) Bull. Chem. Soc. Japan 41 (1968) 384-389 K Saito and K Masuda.

354) Nature 186 (1960) 966 B Bosnich, F P Dwyer and A M Sargeson.

355) J. Chem. Educ. 38 (1961) 164-173 R G Pearson.

356) Ber. Bunsenges Phys. Chem. 83 (1979) 518-521 H Rauh and W Knoche.

357) J. Inorg. Nucl. Chem. 36 (1974) 2628-2630 P H Tedesco and J G Quintana.

358) J. Inorg. Nucl. Chem. 34 (1972) 1997-2005 P G Manning and S Ramamoorthy.

359) Indian J. Chem. A 14 (1976) 712-713 N K Mohanty and T K Patnaík.

360) Stud. Univ. Babes-Bolyai Ser. Chem. 13 (2) (1968) 85-88 L Oniciu and E Schmidt.

361) J. Inorg. Biochem. 14 (1981) 339-350 K S Rajan, S Mainer, N L Rajan and J M Davis.

362) Aust. J. Chem. 26 (1973) 1889-1892 A D Toy, T D Smith and J R Pilbrow.

363) Inorg. Chim. Acta 116 (1986) L21-L23 F T Greenaway.

364) Can. J. Chem. 55 (1977) 3689-3699 M Jaber, F Bertin and G Thomas David.

365) Collect. Czech. Chem. Commun. 34 (1969) 3722-3731 L Havelkova and M Bartusek.

366) Inorg. Chem. 16 (1977) 2742-2745 B Perlmutter-Hayman and E Tapuhi.

367) Inorg. Chem. 14 (1975) 1978-1981 F Secco and M Venturini.

368) J. Indian Chem. Soc. 38 (1961) 379-384 R K Pattnaik and S Pani.

369) Rev. Roun. Chim. 15 (1970) 1049-1056 T Goina, M Olariu and L Bocaniciu.

370) Zh. Anal. Khim 25 (1970) 1894-1897 I v Pyatnitskii, L M Glushchenko and N V Khomenko.

371) Helv. Chim. Acta 47 (1964) 2262-2278 R Gut.

372) J. Chem. Soc. Dalton (1976) 1940-1942 R J Irving and M A V R da Silva.

373) Inorg. Chem. II (1972) 1995-2002 W R Wolf, R E Sievers and G H Brown.

374) J. Coord. Chem. 5 (1976) 157-161 T F Schaaf, S C Avanzino, W L Jolly and R E Sievers.

375) J. Amer. Chem. Soc. 64 (1942) 316-324, N Davidson and H C Brown.

376) Makromol. Chem. 44-46 (1961) 398-407 J Furukawa, T Saegusa and H Fujii.

377) Zh. Org. Khim. 20 (1984) 121-124 Ya. B. Kozlikovskii and V A Koshchii.

378) Zh. Org. Khim. 22 (1986) 606-610 Ya B. Kozlikovskii, V A Koshchii and S A Butor.

379) Prog. Inorg. Chem. 17 (1972) 391-566 N Serpone and D G Bickley.

380) Coord. Chem Rev. 6 (1971) 331-375 J J Fortman and R E Sievers.

381) J. Amer. Chem. Soc. 95 (1973) 1825-1829 S S Eaton and G R Eaton.

382) Chem. Communs (1971) 85-87 B Jurado and C S Springer.

383) J. Prakt. Chem. 147 (1936) 226-250 H Meerwein, G Hinz, H Majert and H Sonke.

384) J. Prakt. Chem. 147 (1936) 211-225 H Meerwein.

385) J. Amer. Chem. Soc. 75 (1953) 2404-2407 E D Williams, K A Krieger and A R Day.

386) J. Chem. Soc. (1949) 2641-2646 L M Jackman, A K Macbeth and J A Mills.

387) Nature 164 (1949) 789-790 L M Jackman and J A Mills.

388) Chem. Ind. (1951) 380-384 W A Johnson and G E H Skrimshire.

389) Chem. Ind. (1951) 601-602 J C McGowan.

390) J. Amer. Chem. Soc. 85 (1963) 2337-2338 V J Shiner Jr and D Whittaker.

391) Acta Chim. Acad. Sci. Hung. 16 (1958) 279-290 G Gal, I Foldesi, and E Krasznai.

392) Chem. Ber. 99 (1966) 11-22 H Reinheckel, D Jahnke and G Kretzschmar.

393) Chem. Ber. 97 (1964) 2661-2670 H Reinheckel and D Jahnke.

394) J. Polym. Sci. Polym. Lett. 6 (1968) 389-393 H Tani, T Araki and H Yasuda.

395) Adv. Organometal. Chem. 5 (1967) 225-319 M F Lappert and B Prokai.

396) J. Chem. Soc. B (1968) 1074-1078 A G Davies and B P Roberts.

397) J. Org. Chem. 21 (1956) 712-713 A J Kolka, J P Napolitano and G G Ecke.

398) J. Org. Chem. 22 (1957) 642-646 A J Kolka, J P Napolitano, A H Filbey, and G G Ecke.

399) Zh. Org. Khim. 24 (1988) 827-830 Ya B Kozlikovskii, V A Koshchii, S A Butov, and T F Ovsiyuk.

400) Zh. Org. Khim. 25 (1989) 55-61 Ya B Kozlikovskii, V A Koschchii and T F Ovsiyuk.

401) Zh. Org. Khim. 22 (1986) 1014-1020 Ya B Kozlikovskii, B V cheryaev and V A Koshchii.

402) Zh. Org. Khim. 24 (1988) 1508-1512 V A Koshchii, Ya B Kozlikovskii and A A Koshchii.

403) Zh. Org. Khim. 21 (1985) 2403-2407 Ya B Kozlikovskii and B V Chernyaev.

404) Zh. Org. Khim. 24 (1988) 2576 -2580 Ya B Kozlikovskii, V A Koshchii, S A Butov and D I Olifirov.

405) Zh. Org. Khim. 21 (1985) 565-568 Ya B Kozlikovskii and B V Chernyaer.

406) Zh. Org. Khim. 22 (1986) 2389-2394 Ya B Kozlikovskii, B V Chernyear and A L Litvin.

407) Inorg. Chem. 3 (1964) 875-880 R A Palmer, R C Fay and T S Piper.

408) J. Amer. Chem. Soc. 45 (1923) 3013-3023 W C Child and H Adkins.

409) Wiadomosci Chem. 20 (1966) 145-160 R Piekos.

410) Ark. Kemi 25 (1966) 475-483 S Friberg.

411) J. Inorg. Nucl. Chem. 29 (1967) 1931-1936 K J Eisentraut and R E Sievers.

412) Koord. Khim. 3 (1977) 1296-1298 M I Karpovskaya, N. Ya Turova and A V Novoselova.

413) J. Polym. Sci. (C) 4 (1963) 281-287 J Furukawa, T Saegusa and H Fujii.

414) U S Patent 3032537 (1962) H C Walter.

415) British Patent 785053 (1957) E T Borrows and D G Stewart.

416) J. Polym. Sci. Polym. Chem. Ed. 15 (1977) 865-873, A Hamitou, T Ouhadi, R Jerome and P Teyssie.

417) British Patent 885450 (1961) H Friedrich, W Lehnerer and K Sepp.

418) British Patent 870418 (1961) F H Newth and J D Shimmin.

419) British Patent 887573 (1962) D Y Waddan and F H Newth.

420) British Patent 800449 (1960).

421) Internal Memorandum, Hardman and Holdern Ltd (1957) S K Kemp.

422) J. Amer. Chem. Soc. 58 (1936) 100-102 W G Young, W H Hartung and F S Crossley.

423) Dtsch. Chem. Gesel. Ber. 70 (1937) 1520-1525 H Lund.

424) Acta Chim. Acad. Sci. Hung. 8 (1956) 163-169 G Gal, I Simonyi and G Tokar.

425) Acta Chim. Acad. Sci. Hung. 15 (1958) 211-216 G Gal and I Kraznai.

426) Angew. Chem. 53 (1940) 266-271 T Bersin.

427) J. Amer. Chem. Soc. 72 (1950) 4814-4815 L M Jackman, J A Mills and J S Shannon.

428) Angew. Chem. 69 (1957) 699-706 R Storh, R Seydel and W Hahn.

429) British Patent 970223 (1964).

430) Zh. Org. Khim. 21 (1985)1299-1303 Ya B Koslikovskii, V A Koshchii, S A Butov, and N I Vykhrestyuk.

431) Zh. Org. Khim. 24 (1988) 1504-1508 Ya B Kozlikovskii, B V Chernyaev, and Yu V Myshko.

432) Zh. Org. Khim. 23 (1987) 614-621 Ya B Kozlikovskii, B V Chernyaev, and VV Trachevskii.

433) Zh. Org. Khim. 20 (1984) 2162-2166 Ya B Kozlikovskii and B V Chernyaev.

434) Bull. Chem. Soc. Japan 54 (1981) 3033-3041 S Iguchi, H Nakai, M hayashi, H Yamamoto and K Maruoka.

435) Tetrahedra Lett. 32 (1978) 2903-2906 A Itoh, H Nozaki and H Yamamoto.

436) J. Amer. Chem. Soc. 87 (1965) 5614-5620. H C Brown and P M Weissman.

437) J. Chem. Educ. 38 (1961) 173-179 H C Brown.

438) Melv. Chim. Acta 43 (1960) 338-346 C Tamm.

439) J. Amer. Chem. Soc. 80 (1958) 4138-4140 S Sujishi and J N Keith.

440) J. Amer. Chem. Soc. 78 (1956) 252 H C Brown and R F McFarlin.

441) Israel J. Chem. 1 (1963) 430-440 H C Brown and P M Weissman.

442) J. Amer. Chem. Soc. 84 (1962) 2363-2368 H Haubenstock and E L Eliel.

443) J. Amer. Chem. Soc. 87 (1965) 5620-5625 H C Brown and H R Deck.

444) J. Amer. Chem. Soc. 86 (1964) 1085-1089 H C Brown and C P Gary.

445) J. Amer. Chem. Soc. 86 (1964) 1089-1095 H C Brown and A Tsukamoto.

446) J. Amer. Chem. Soc. 81 (1959) 502-503 H C Brown and A Tsukamoto.

447) Collect. Czech. Chem. Commun. 34 (1969) 118-124 M Capka, V Chvalovsky, K Kochloefl, and M Kraus.

448) Collect. Czech. Chem. Commun. 34 (1969) 1025-1032 M Cerny, J Malek, M Capka, V Chvalovsky.

449) Collect. Czech. Chem. Commun. 34 (1969) 1033-1041 M Cerny, J Malek, M Capka and V Chvalovsky.

450) Collect. Czech. Chem. Commun. 34 (1969) 1823-1826 M Kraus and K Kochloefl.

451) Collect. Czech. Chem. Commun. 34 (1969) 3110-3117 M Capka and V Chvalovsky.

452) Tetrahedron Lett. (1968) 3303-3306 V Bazant, M Capka, M Cerny, V Chvalovsky, K Kochloefl, M Kraus and J Malek.

453) Tetrahedron Lett. (1969) 1739-1742 M Cerhy and J Malek.

454) U S Patent 2837546 (1958) J Nichols.

455) Rec. Trav. Chim. 56 (1937) 137-144 R V Oppenauer.

456) J. Amer. Chem. Soc. 74 (1952) 5133-5135 I Lin and A R Day.

457) Helv. Chim. Acta 34 (1951) 2172-2181 M Hausermann.

458) U S Patent 4835331 (1989) H U Hammershaimb and R R Frame.

459) British Patent 824374 (1959).

460) British Patent 799823 (1958).

461) U S Patent 2917365 (1959) G R Gilbert.

462) U S Patent 2805920 (1957) R W Richardson.

463) U S Patent 2917366 (1959) R C Hansford.

464) J. Electrochem. Soc. 114 (1967) 948-952 J A Aboaf.

465) Int. J. Refract. and Hard Met. 5 (1986) 165-170 G Pauer, H Altena and B Lux.

466) Chem. Rev. 89 (1989), 1447-1465 D J Hart and D-C Ha.

467) J. Amer. Chem. Soc. 106 (1984) 441-443 L S Liebeskind, M E Welker and V Goedken.

468) Farbe and Lack 58 (1952) 351-354 F Schlenker.

469) Farbe and Lack 62 (1956) 9-14 F Schlenker.

470) Farbe and Lack 64 (1958) 174-183 F Schlenker.

471) Kunstoffe 47 (1957) 7-14 F Schlenker.

472) Paint Technol. 18 (1954) 607 J Rinse.

473) Chem. Ind. (1976) 315-316 A R Royle.

474) Chem. Ind. (1975) 203-208 J H W turner and P Womersley.

475) British Patent 806113 (1958) J Rinse, H S Land and S G Kemp.

476) British Patent 832622 (1960) E K Lees.

477) U S Patent 2169577 (1939) T F Bradley.

478) J. Oil Colour Chem. Ass. 41 (1958) 769-779 J H W Turner, S G Kemp, S E Harson.

479) British Patent 809309 (1959) J Rinse.

480) J. Phys. Chem. 59 (1955) 222-225 W O Ludke, S E Wiberley, J Goldenson, W H Bauer.

481) British Patent 835874 (1960) S E Harson.

482) Ind. Eng. Chem. 29 (1937) 58-60 C J Boner.

483) British Patent 850726 (1960).

484) British Patent 853765 (1960) R Williamson and H T Fergusson.

485) U S Patent 2801190 (1957) L Orthner and M Reuter.

486) U S Patent 4771105 (1988) H Shirai, F Yamai, S Inada, H Ike and Y Nakahara.

487a) U S 2347152 (1944) E W Gardiner and G H Denison Jr.

487b) Lubr. Eng. 19 (1963) 76-87 A T Polishuk.

488) British Patent 793152 (1958).

489) British Patent 798186 (1958) S G Kemp.

490) U S Patent 2837493 (1958) F Schlenker.

491) British Patent 824339 (1959) J W Ayers.

492) U S Patent 2873263 (1959) J Lal.

493) British Patent 1397407 (1975) J H W Turner.

494) British Patent 854934 (1960) J Rinse.

495) Wiadomosci Chem. 19 (1965) 3-18 R Piekos.

496) J. Phys. Chem. 62 (1958) 440-444 R G Charles and M A Pawlikowski.

497) Inorg. Chem. 5 (1966) 806-813 R G Linck and R E Sievers.

498) Dokl. Acad. Nauk SSSR Ser. Khim. 128 (1959) 309-311, G A Razuvaev and A I Graevskii.

499) J. Amer. Chem. Soc. 108 (1986) 1730-1735 E Lippmaa, A Samoson, M Magi.

500) Phys. Rev. (B) 28 (1983) 6567-6570 A Samoson and E Lippmaa.

501) J. Magn. Reson. 79 (1988) 255-268 A Samoson and E Lippmaa.

502)J. Amer. Chem. Soc. 108 (1986) 6158-6162 L B Alemany and G W Kirker.

APPENDIX 1

Table I

Melting and boiling points of some aluminium alkoxides. (References in parentheses)

Compound	**m.p. (^{o}C)**	**b.p. (^{o}C/mmHg)**
Aluminium methoxide		$240/10^{-5}$[24] S
Aluminium ethoxide	137[23]	162/1.3[5], 189/5 [314]
Aluminium n-propoxide	106-108 [495]	205/1[5],222.7/5 [314]
Aluminium i-propoxide	29.5,118,137 [26]	95/0.5[146],106/1.5 [5,26,124] 108.5-109.5/0.4[31,324], 139.1/5[314]
Aluminium n-butoxide	101-102 [495]	242/0.7[5],259.6/5[314]
Aluminium i-butoxide	212-215 [495]	236.2/5[314]
Aluminium s-butoxide		167.3/5[314]
Aluminium t-butoxide	206.5-207[116,495]	160/1[5,124] S
Aluminium t-pentoxide		130-135/0.02-0.03[34] S
Aluminium phenoxide	decomp.~110^{o}C[39]	80/0.18[39] S

S: sublimes

Table 11

Melting and boiling points of some aluminium carboxylates and ß-diketonates. (References in parentheses).

Compound	m.p ($^{\circ}$C)	b.p ($^{\circ}$C/mmHg)
Aluminium trilaurate	110 [58]	
Aluminium tripalmitate	98 [55]	
Aluminium tristearate	120 [55,58]	
Aluminium trifuroate	decomp. ~ 235°C [59]	
Aluminium trithenoate	decomp. ~ 220°C [59]	
Aluminium isopropoxide dithenoate	271-272 [59]	
Aluminium acetylacetonate	194.6 [77,276,496]	314-315.6/760 [77]
trans- Aluminium 1,1,1-trifluoro-2,4-pentanedionate	121-122 [67,277]	48/0.25 [90] S
Aluminium 1,1,1,5,5,5-hexafluoro-2,4-pentadionate	73-74[81,276]	45/0.05 [81] S
Aluminium 2,6-dimethyl-3,5 -heptanedionate	153.5-154.5[276]	
Aluminium 2,2,6,6-tetramethyl -3,5-heptanedionate	263-264 [372]	
trans-Aluminium 1-phenyl-1,3-butadionate	223.5-225 [68,90,91]	
Aluminium 3-methyl-2,4-pentanedionate	206-209 [497]	
Aluminium 3-bromo-2,4-pentanedionate	210-212 [497]	

S: Sublimes

Table III

Melting and Boiling points of some aluminium aminoalkoxides. (References in parentheses)

Compound	m.p. (^{o}C)	b.p. (^{o}C/mmHg)
Aluminium bis-isopropoxide mono-2-aminoethoxide	130 [107]	
Aluminium isopropoxide bis-2-aminoethoxide	120 [107]	
Aluminium tris-2-aminoethoxide	90[107]	
Aluminium bis-isopropoxide mono-2-(ethylamino) ethoxide		126/0.6[108]
Aluminium isopropoxide bis-2-(ethylamino)ethoxide		146-147/0.6 [108]
Aluminium tris-2-(ethylamino) ethoxide		150/0.5[108]
Aluminium tris-2-(methylamino) ethoxide		190/2[108]
Aluminium tris-1-methyl-2-(diethylamino) ethoxide		137-138/0.5 [108]

Table IV

Melting and boiling points of some metal aluminium isopropoxides. (References in parentheses).

Compound	m.p(^{o}C)	b.p (^{o}C/mmHg)
$\mathrm{K[Al\,(Oi\text{-}Pr)_4]}$		180-185/0.5[125,289] S
$\mathrm{Cs\,[Al\,(Oi\text{-}Pr)_4]}$		300-310/0.25[125,289] S
$\mathrm{Be\,[Al\,(Oi\text{-}Pr)_4]_2}$		128/0.3[147]
$\mathrm{Mg\,[Al\,(Oi\text{-}Pr)_4]_2}$		114/0.2[136,289]
$\mathrm{Ca\,[Al\,(Oi\text{-}Pr)_4]_2}$		220-230/0.1[136] S
$\mathrm{Sr\,[Al\,(Oi\text{-}Pr)_4]_2}$		190-200/0.1[136,289] S
$\mathrm{Ba\,[Al\,(Oi\text{-}Pr)_4]_2}$		145/ 0.05 [136]
$\mathrm{Sc\,[Al\,(Oi\text{-}Pr)_4]_3}$		145/0.5 [151]
$\mathrm{Cr\,(III)\,[Al\,(Oi\text{-}Pr)_4]_3}$		190/0.6 [141-143]
$\mathrm{Mn\,(II)\,[Al\,(Oi\text{-}Pr)_4]_2}$		145/0.6 [141-143]
$\mathrm{Fe\,(III)\,[Al\,(Oi\text{-}Pr)_4]_3}$		130/0.8 [141-143]
$\mathrm{Fe\,(II)\,[Al\,(Oi\text{-}Pr)_4]_2}$		125/0.8 [142,143]
$\mathrm{Co\,(II)\,[Al\,(Oi\text{-}Pr)_4]_2}$		140/0.6 [141-143]
$\mathrm{Ni\,(II)\,[Al\,(Oi\text{-}Pr)_4]_2}$		120/0.6 [141-143]
$\mathrm{Cu\,(II)\,[Al\,(Oi\text{-}Pr)_4]_2}$		135/0.6 [141-143]
$\mathrm{Y\,[Al\,(Oi\text{-}Pr)_4]_2}$		192/0.5 [151]
$\mathrm{Nb\,(V)\,[Al\,(Oi\text{-}Pr)_4]\,(Oi\text{-}Pr)_4}$		105/0.2 [156]
$\mathrm{Ta\,(V)\,[Al\,(Oi\text{-}Pr)_4]\,(Oi\text{-}Pr)_4}$		107/0.2 [156]
$\mathrm{Nb\,(V)\,[Al\,(Oi\text{-}Pr)_4]_2\,(Oi\text{-}Pr)_3}$		115/0.2 [156]
$\mathrm{Ta\,(V)\,[Al\,(Oi\text{-}Pr)_4]_2\,(Oi\text{-}Pr)_3}$		118/0.2 [156]
$\mathrm{La\,(III)\,[Al\,(Oi\text{-}Pr)_4]_3}$		208/0.5 [151]
$\mathrm{Ce\,(III)\,[Al\,(Oi\text{-}Pr)_4]_3}$		200/0.5 [151]
$\mathrm{Pr\,(III)\,[Al\,(Oi\text{-}Pr)_4]_3}$		192/0.3 [151]
$\mathrm{Nd\,(III)\,[Al\,(Oi\text{-}Pr)_4]_3}$		186/0.3 [151]
$\mathrm{Sm\,(III)\,[Al\,(Oi\text{-}Pr)_4]_3}$		203/0.5 [151]
$\mathrm{Gd\,(III)\,[Al\,(Oi\text{-}Pr)_4]_3}$		195/0.3 [151]
$\mathrm{Dy\,(III)\,[Al\,(Oi\text{-}Pr)_4]_3}$		203/0.5 [151]

Table IV contd...

$\mathrm{Ho\ (III)\ [Al\ (Oi\text{-}Pr)_4]_3}$	180/0.2[151]
$\mathrm{Er\ (III)\ [Al\ (Oi\text{-}Pr)_4]_3}$	187/0.2 [151]
$\mathrm{Yb\ (III)\ [Al\ (Oi\text{-}Pr)_4]_3}$	200/0.5 [151]
$\mathrm{Lu\ (III)\ [Al\ (Oi\text{-}Pr)_4]_3}$	190/0.3 [151]
$\mathrm{Zn\ (II)\ [Al\ (Oi\text{-}Pr)_4]_2}$	140/0.3 [137]
$\mathrm{Cd\ (II)\ [Al\ (Oi\text{-}Pr)_4]_2}$	150/0.3 [137]
$\mathrm{In\ (III)\ [Al\ (Oi\text{-}Pr)_4]_3}$	162/0.5 [163]
$\mathrm{Ga\ (III)\ [Al\ (Oi\text{-}Pr)_4]_3}$	100-105/0.5 [163]
$\mathrm{Al\ [Ga\ (Oi\text{-}Pr)_4]_3}$	105-110/0.2 [163]

S: Sublimes

Table V

Melting and boiling points of some other metal aluminium alkoxides. (References in parentheses).

Compounds	m.p. (^{o}C)	b.p (^{o}C/mmHg)
Lithium tetra-t-butoxyaluminate		335/1[126] S
Sodium tetra(methoxyethoxy) aluminate	110-120[101]	
Calcium tetramethoxyaluminate		220/4[125] S
Magnesium tetraethoxyaluminate	129[495]	190-200/0.05[289]S
Magnesium tetra-n-butoxyaluminate		158/0.1[289]
Calcium tetra-n-butoxyaluminate		170-175/0.1[289]S
Chromium (III) tetraethoxyaluminate		235/0.8[142,143] S
Cobalt (II) tetraethoxyaluminate	decomp.~190^{o}C/0.6mm[145]	
Nickel (II) tetraethoxyaluminate		150/0.6 [146]
Copper (II) tetraethoxyaluminate	decomp. ~200oC/0.8mm[147]	
Chromium (III) tetra-2,2,2-trifluoro ethoxyaluminate		120/0.8[142,143] S
Cobalt (II)tetra-2,2,2-trifluoro ethoxyaluminate		105/0.6 [145]
Nickel (II) tetra-2,2,2-trifluoro ethoxyaluminate		115/0.6[146]
Copper (II) tetra-2,2,2-trifluoro ethoxyaluminate		135/0.5 [147]
Zinc (II) tetra-n-butoxyaluminate		168/0.1 [161]
Zinc (II) tetra-i-butoxyaluminate		167/0.1 [161]
Zinc (II) tetra-sec-butoxyaluminate		160/0.1 [161]
Beryllium tetra-n-butoxyaluminate		155/0.1 [138]
Beryllium tetra-i-butoxyaluminate		152/0.1 [138]

S: Sublimes

Table VI

Melting and boiling points of some dialkyl aluminium alkoxides and amionalkoxides. (References in parentheses).

Compounds	**m.p.(^{o}C)**	**b.p.(^{o}C/mmHg)**
Dimethyl aluminium methoxide	35[7]	120-130/760 [7]
		75.6-76.8/4[300]
Dimethyl aluminium isopropoxide		186/760[7]
Dimethyl aluminium t-butoxide	80-82	102-106/14[7]
Diethyl aluminium methoxide		70.5-72/5 [300]
Diethyl aluminium ethoxide		59/1.5[7,300]
		109/10[498]
Diethyl aluminium t-butoxide	70[7]	87-88/10^{-3}-10^{-4}[7]
Di-n-propyl aluminium t-butoxide		87-89/ 10^{-3}-10^{-4}[7]
Di-n-butyl aluminium t-butoxide	69[7]	110/10^{-3}-10^{-4}[7]
Di-t-butyl aluminium t-ethoxide		207-214/760[7] S
Di-t-butyl aluminium t-butoxide	220[7]	
Dimethyl aluminium aminoethoxide	175[7,207]	
Diethyl aluminium aminoethoxide	105[7,207]	
Dimethyl aluminium (dimethylamino) ethoxide	116-118.8[7]	
Diethyl aluminium (dimethylamino) ethoxide	66[7]	
Diethyl aluminium (diethylamino) ethoxide	91-95[7]	
Diethyl aluminium aminopropoxide	75[7]	

S: Sublimes

Table VII

Melting and boiling points of some alkoxyaluminium halides and hydrides. (References in parentheses).

Compound	**m.p (^{O}C)**	**b.p (^{O}C/mmHg)**
F Al $(Oi\text{-}Pr)_2$	57-62 [211]	
F_2 Al $(Oi\text{-}Pr)_2$	decomp.~340^{O}C[211]	
Cl Al $(Oi\text{-}Pr)_2$	64-68 [211]	
ß-ClAl $(Oi\text{-}Pr)_2$	162 + decomp. [296]	
$Cl_{1.67}Al\ (Oi\text{-}Pr)_{1\text{-}33}$	116 [296]	
Cl_2Al (Oi-Pr)	55-60[211]	
H Al $(Oi\text{-}Pr)_2$	48-51 [211]	
H_2Al (Oi-Pr)	decomposes [211]	
Cl Al $(OC_6H_5)_2$	320 [11]	
$Cl_2Al(OC_6H_5)$	320[11]	
Li $[Al(Ot\text{-}Bu)_3H]$		280/2[126] S

S: Sublimes

APPENDIX 2

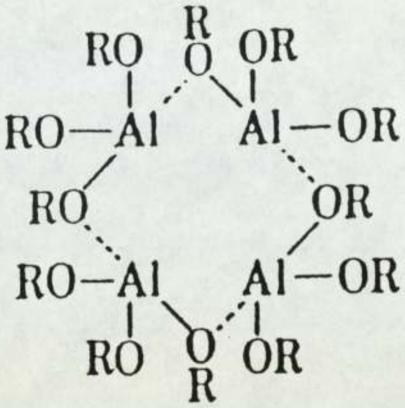


Fig. 1 Aluminium isopropoxide - tetrameric ring structure

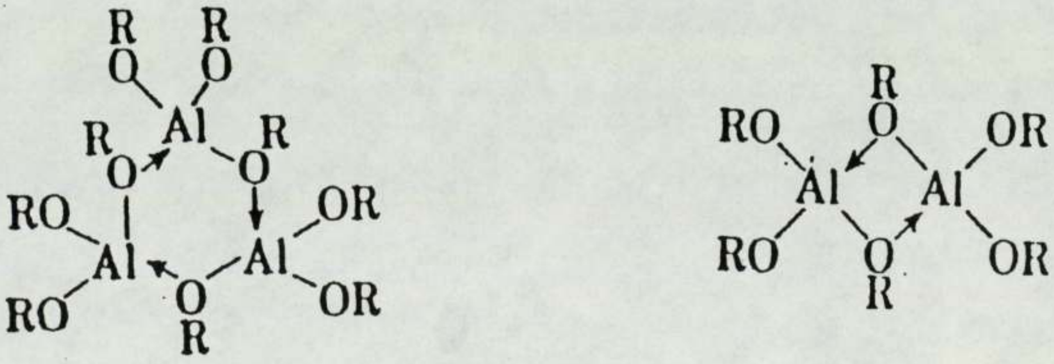


Fig. 2 Aluminium isopropoxide - trimeric and dimeric ring structures

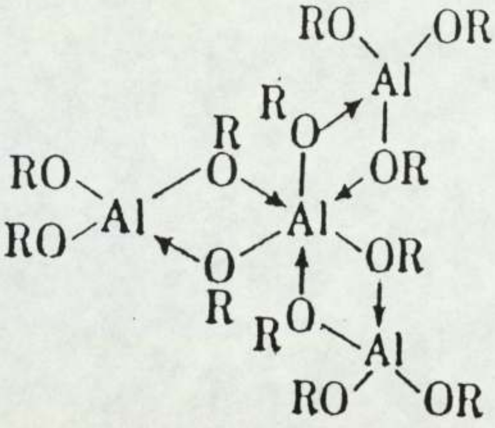


Fig. 3 Aluminium isopropoxide - tetramer, Bradley´s structure

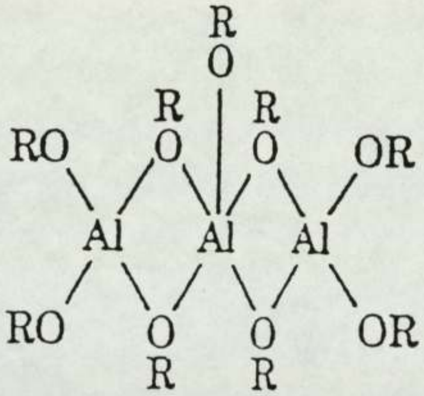


Fig. 4 Aluminium isopropoxide - trimer, Kleinschmidt´s structure

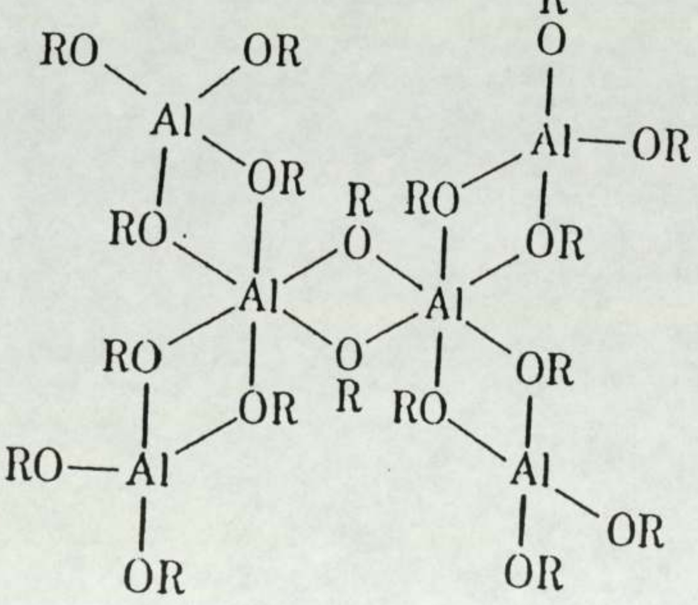


Fig. 5 Aluminium isopropoxide - hexameric structure

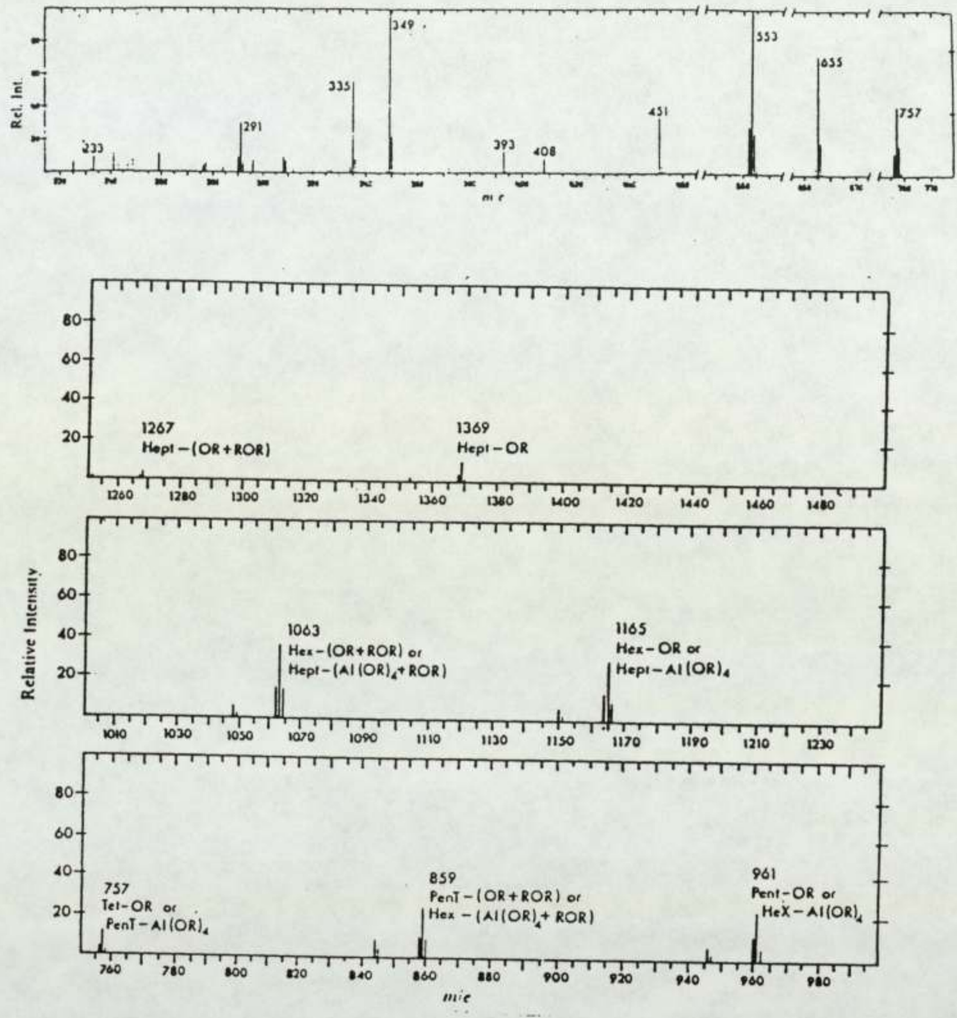


Fig. 6 Aluminium isopropoxide - mass spectrum

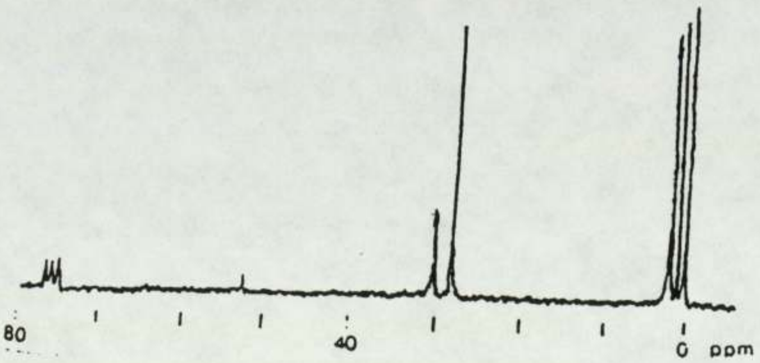


Fig. 7 Aluminium isopropoxide - carbon-13 n.m.r.

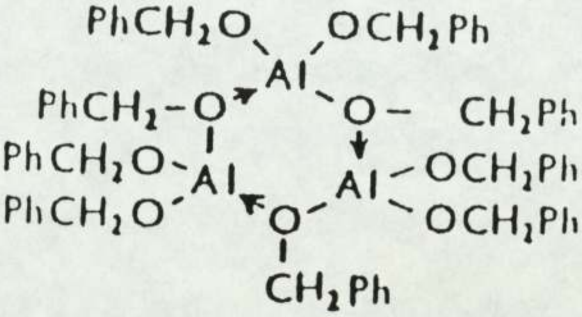


Fig. 8 Tribenzyloxyaluminium(III) - trimeric ring structure

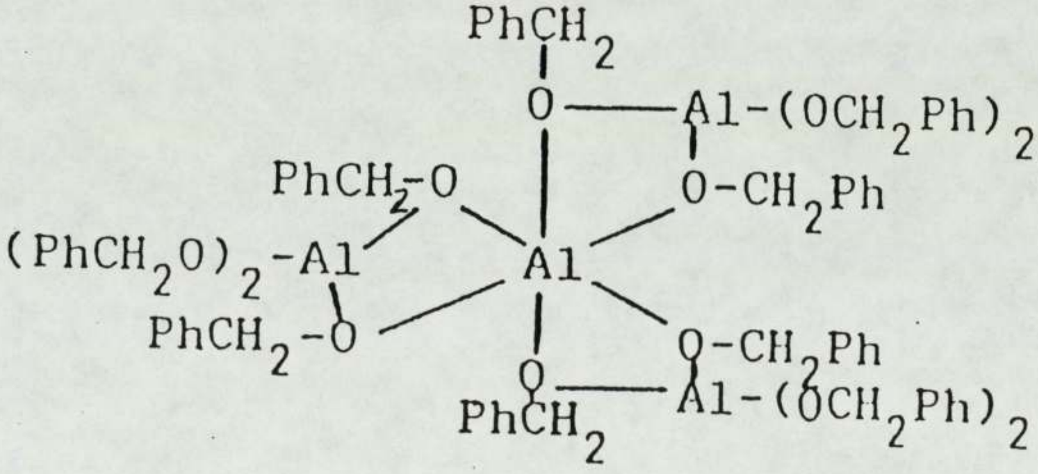


Fig. 9 Tribenzyloxyaluminium(III) - tetrameric structure

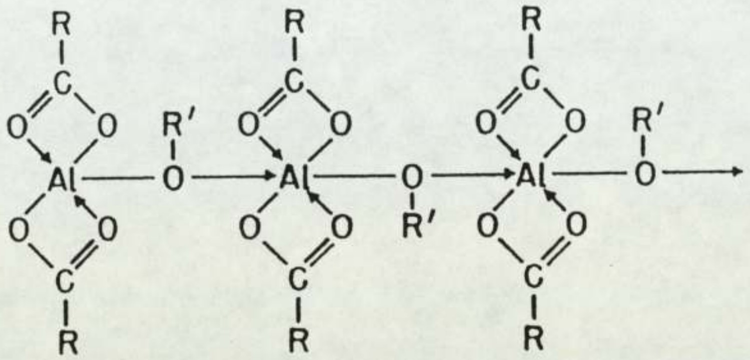


Fig. 10 Aluminium disoap polymer

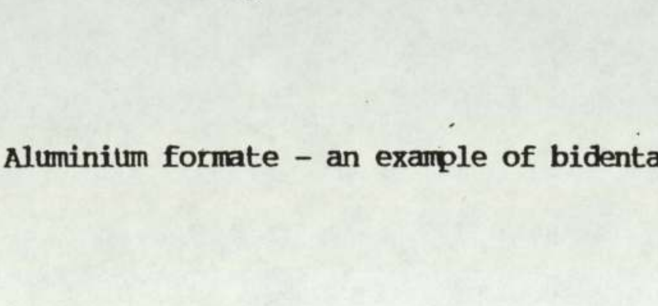


Fig. 11 Aluminium formate - an example of bidentate bonding

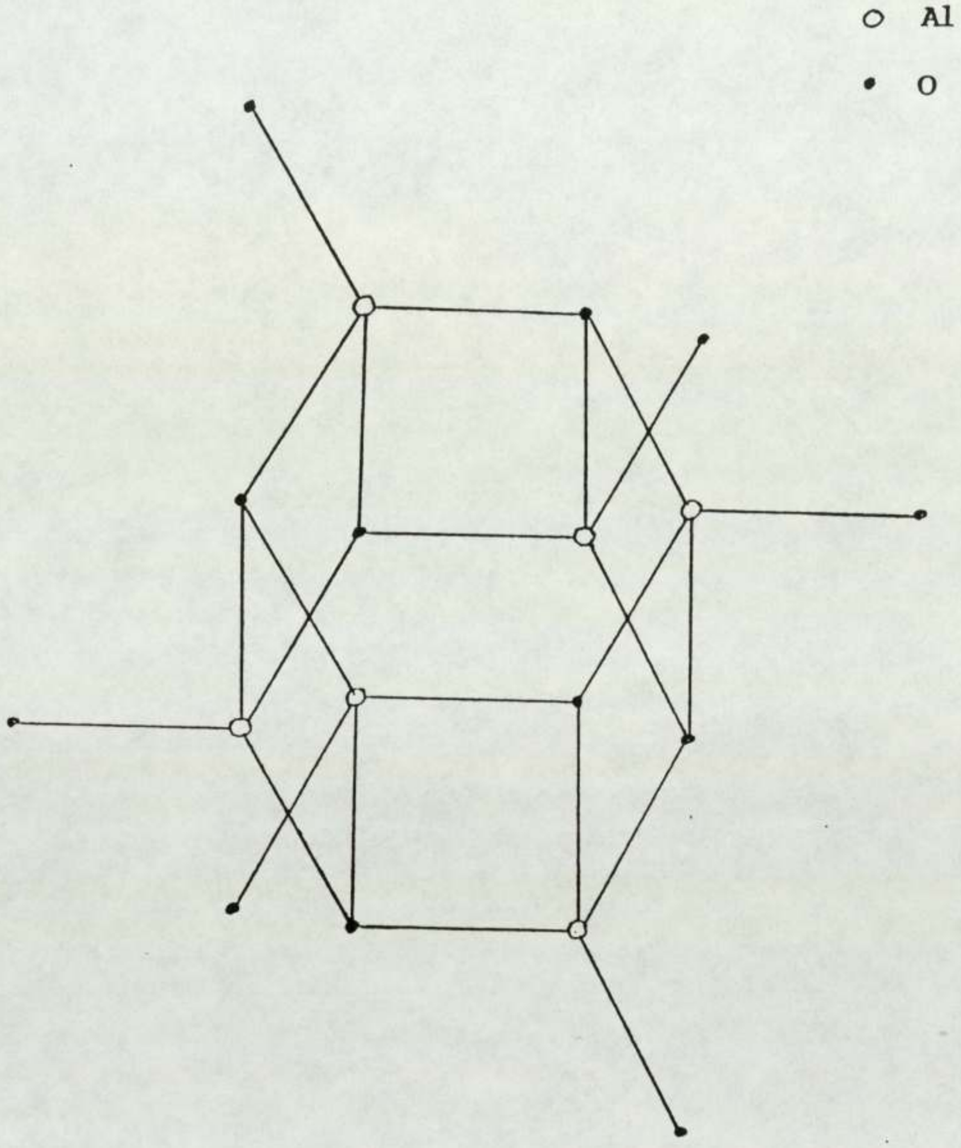


Fig. 12 Oxyaluminium stearate - hexameric structure

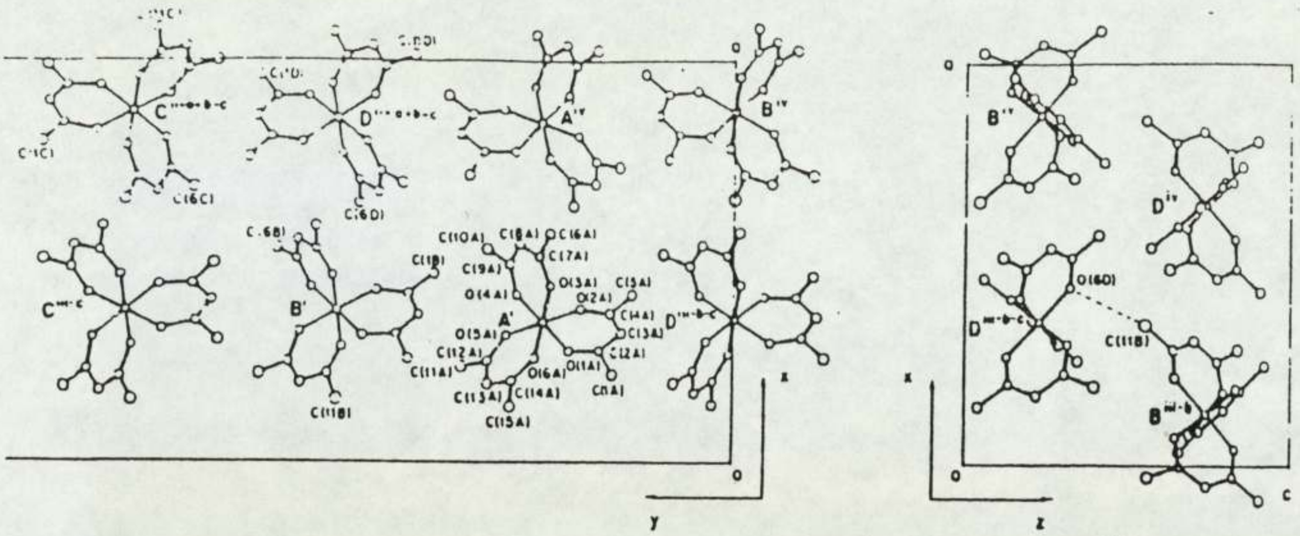


Fig. 13 γ-Aluminium trisacetylacetonate - crystal structure

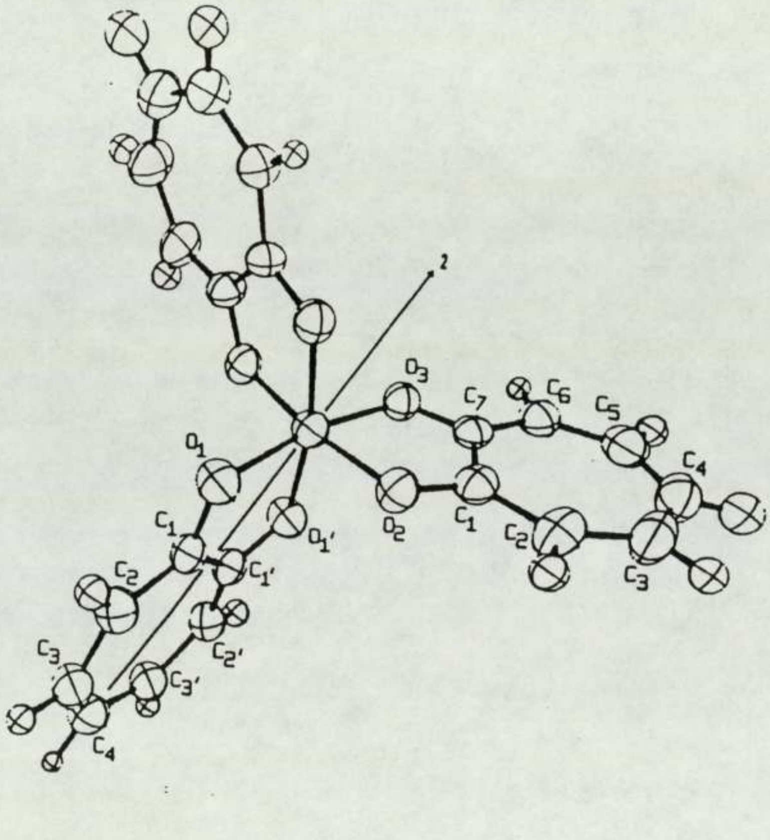


Fig. 14 Tristropolonatoaluminium(III) - crystal structure

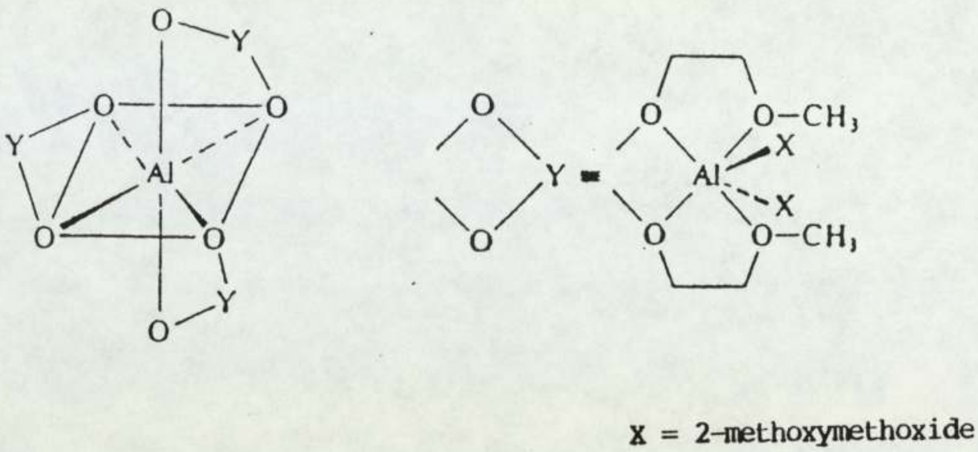


Fig. 15 Tris-(2-methoxyethoxy)aluminium(III)

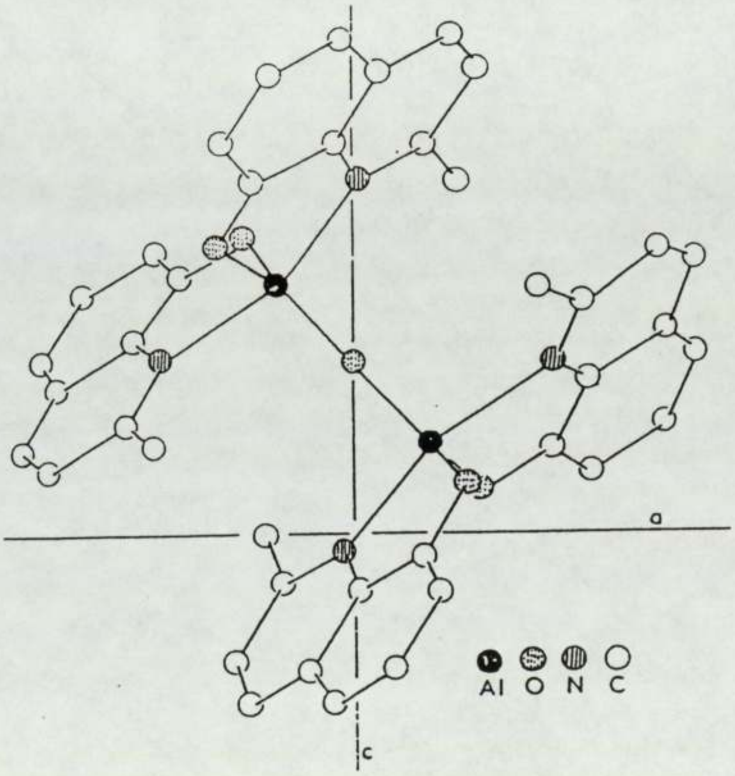


Fig. 16 Aluminium 2-methyl-8-quinolinolate, oxo-bridged complex

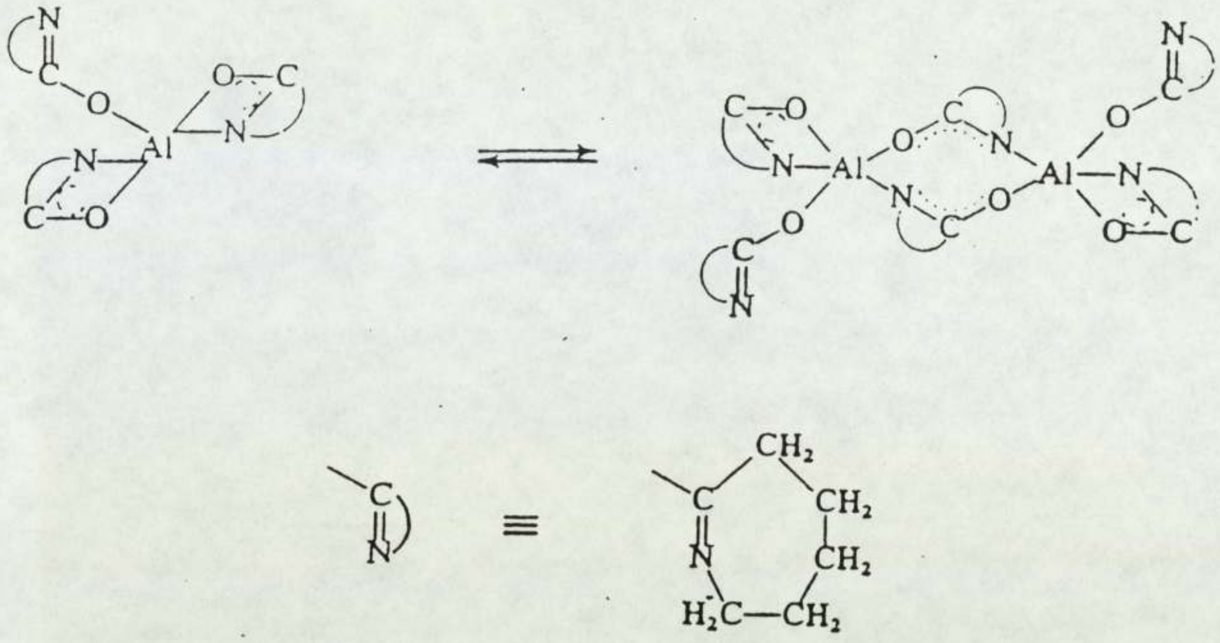


Fig. 17 Aluminium caprolactamate

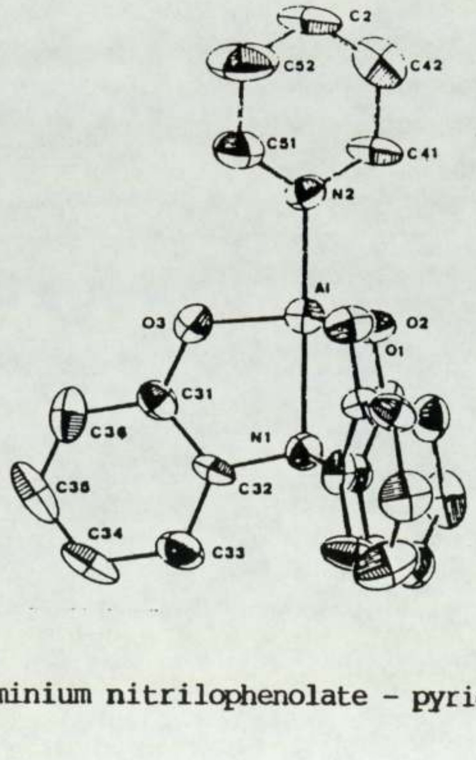


Fig. 18 Aluminium nitrilophenolate - pyridine complex

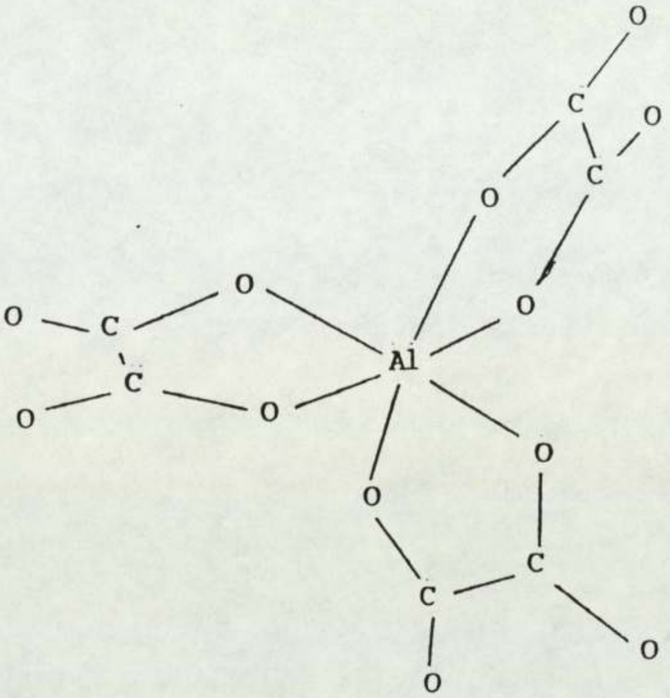


Fig. 19 Sodium aluminium oxalate - aluminium/oxalate co-ordination

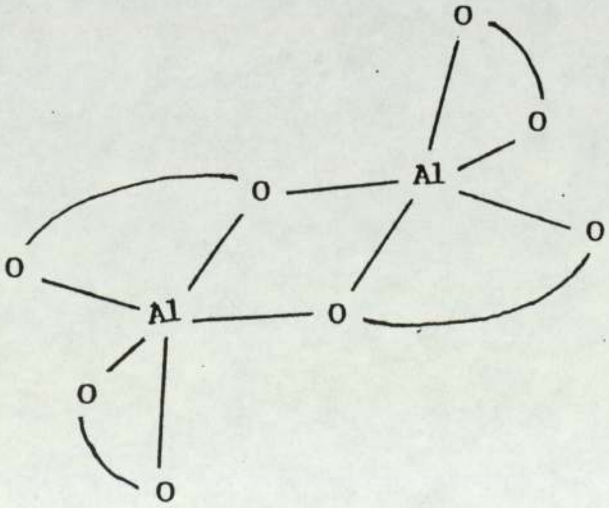
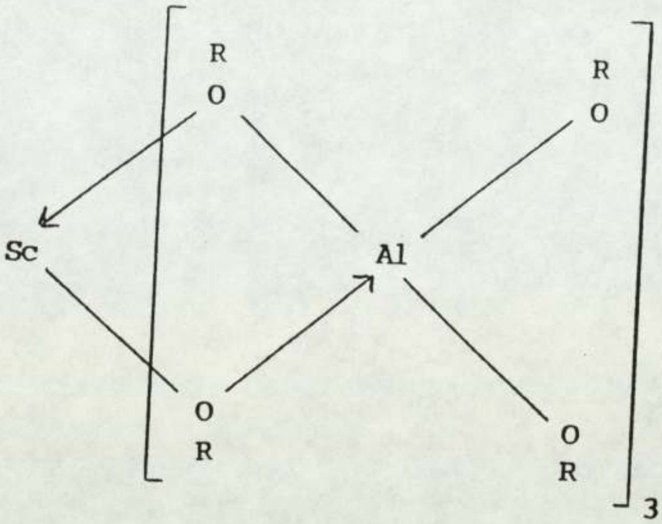
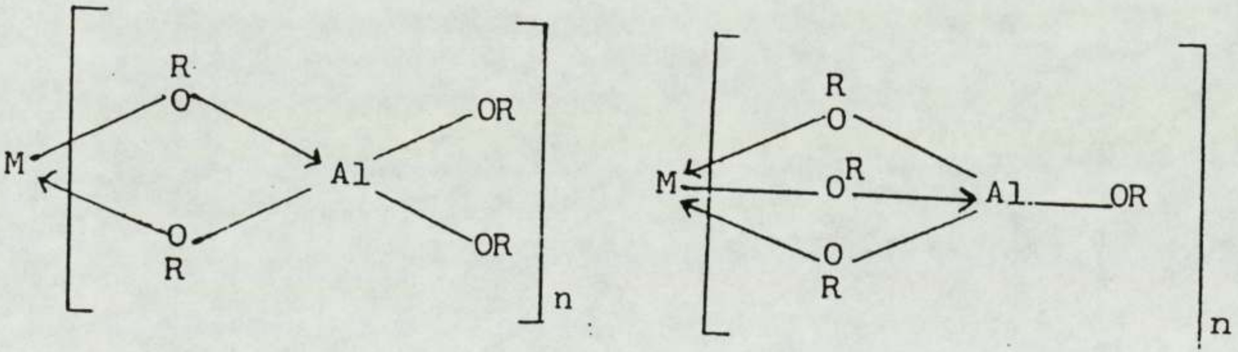


Fig. 20 Barium aluminium ethyleneglycolate - aluminium/oxygen co-ordination



R = isopropoxide

Fig. 21 Scandium aluminium isopropoxide



(I)

(II)

Fig. 22 Transition metal aluminium alkoxides

(I) 4 co-ordinate transition metal

(II) 6 co-ordinate transition metal

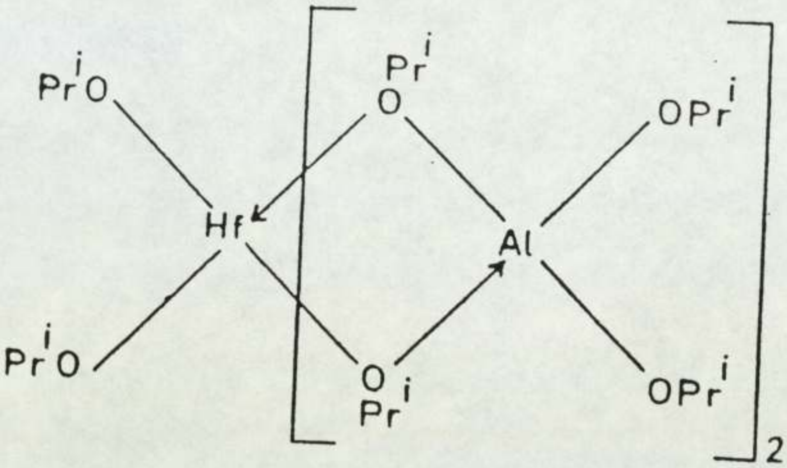


Fig. 23 Hafnium bis-aluminium isopropoxide

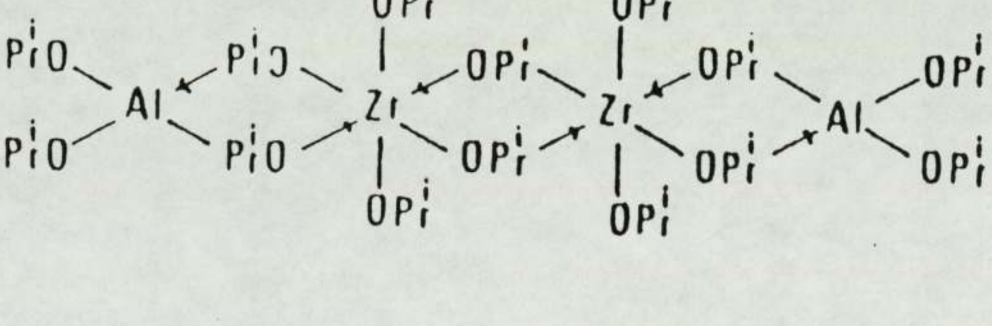


Fig. 24 Zirconium aluminium isopropoxide

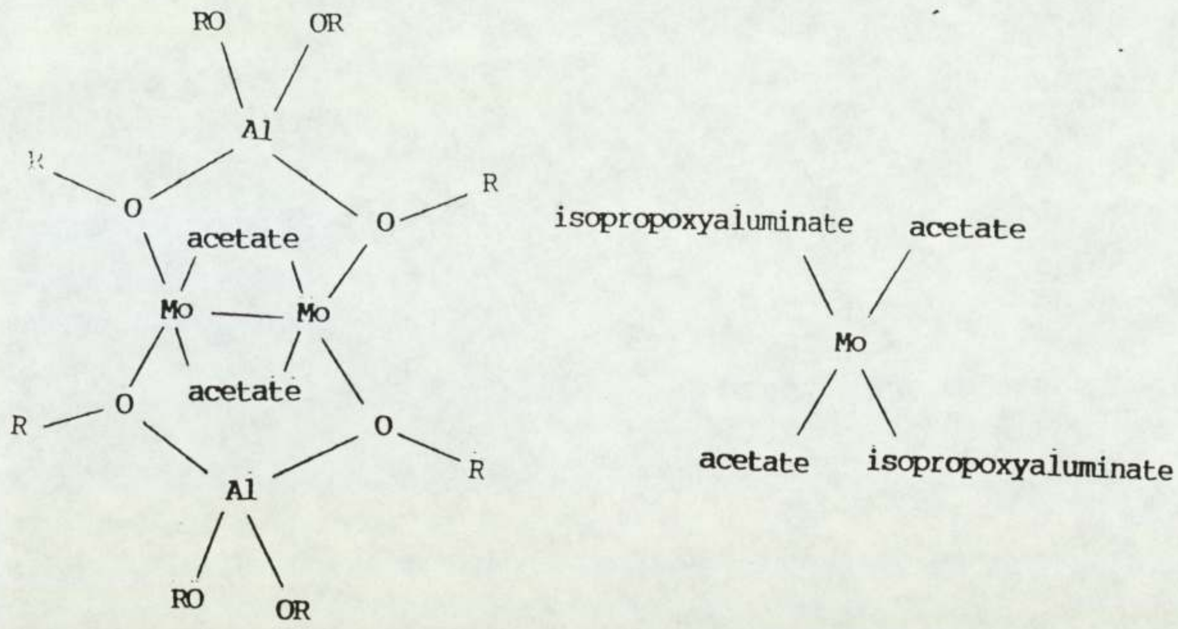


Fig. 25 (Tetraisopropoxyaluminium(III))molybdenum acetate

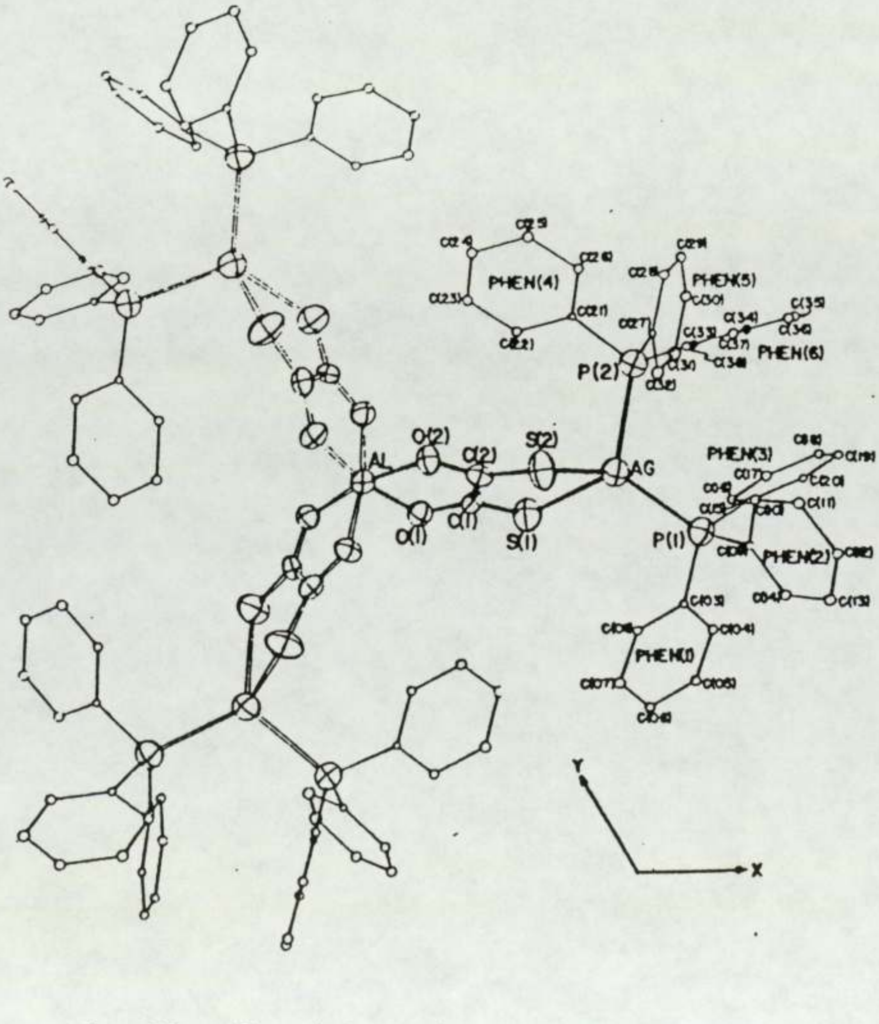
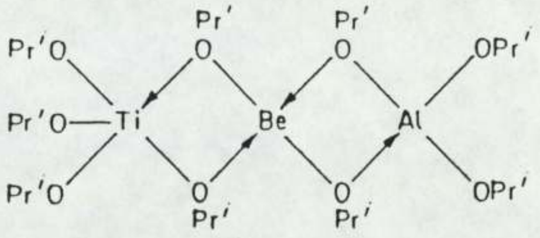
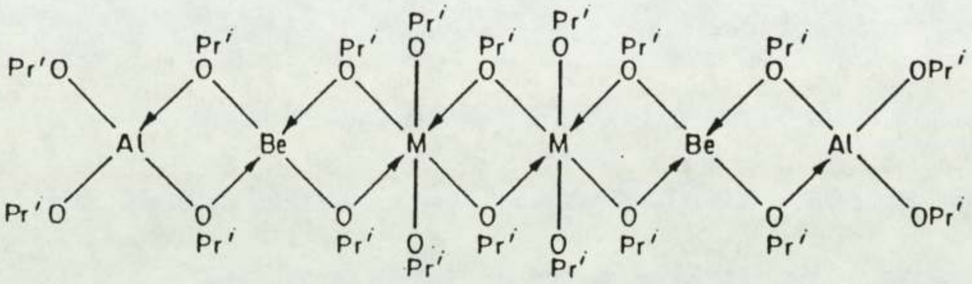


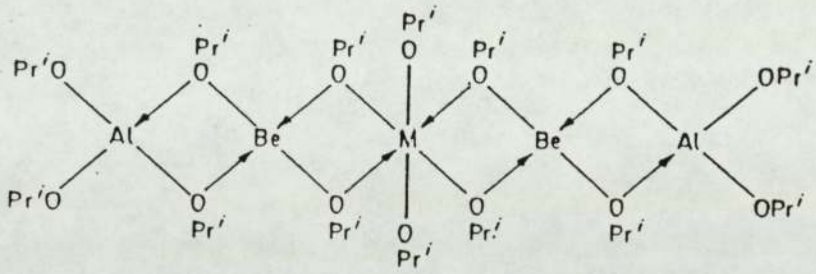
Fig. 26 Silver(I) complex - crystal structure



Monomeric in benzene



Dimeric in benzene M = Zr(IV) or Hf(IV)



Monomeric in benzene M = Zr(IV) or Hf(IV) or Ti(IV)

Fig. 27 Group IVA metal beryllium aluminium isopropoxides

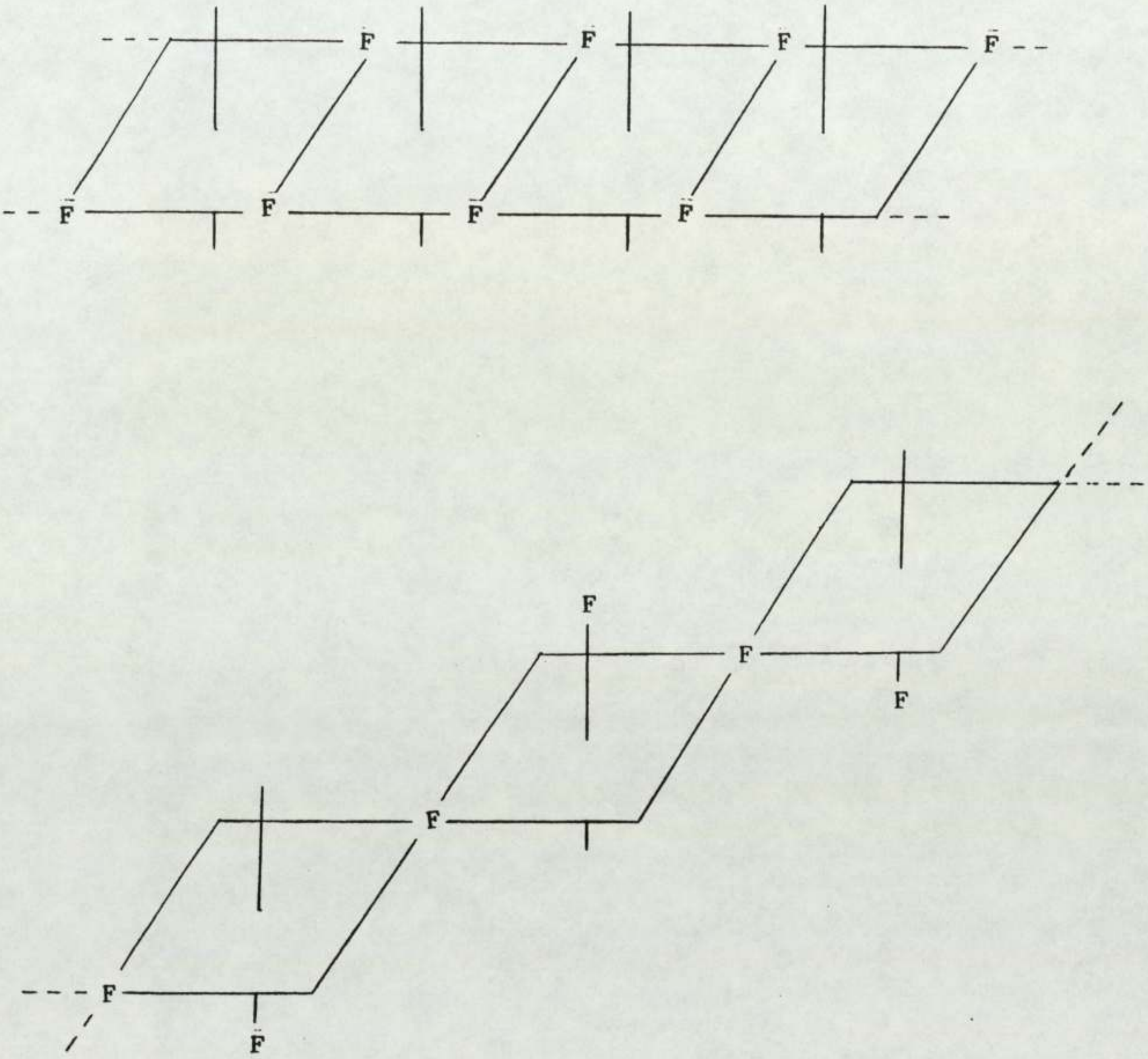


Fig. 28 Fluoroaluminium isopropoxides - proposed structures

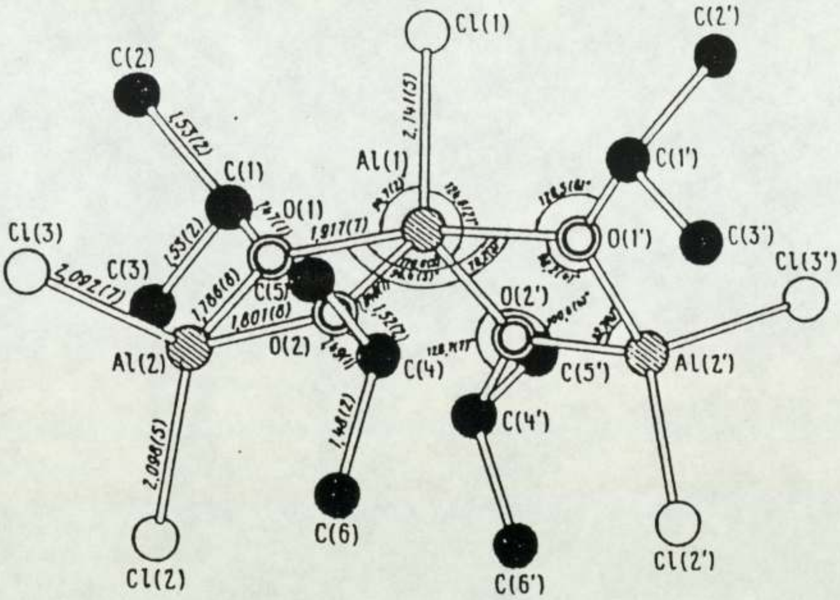


Fig. 29 Structure of the $Al_3Cl_5(OPr\text{-}iso)_4$ molecule.

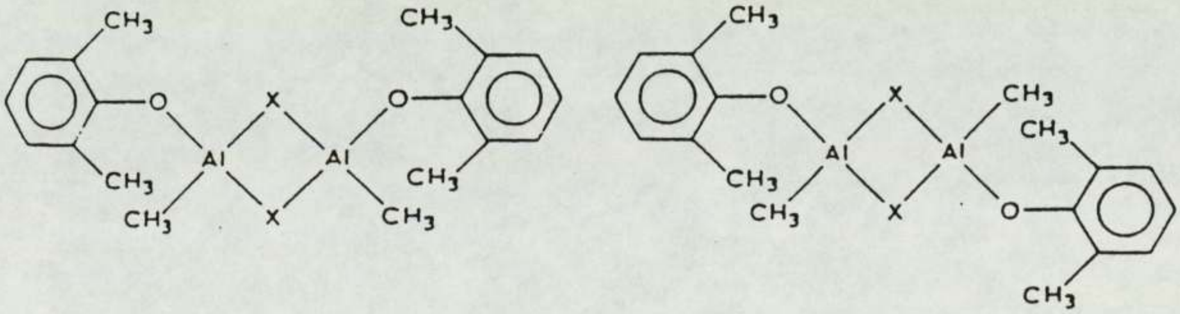


Fig. 30 2,6-dimethylphenoxy,methylaluminium halide

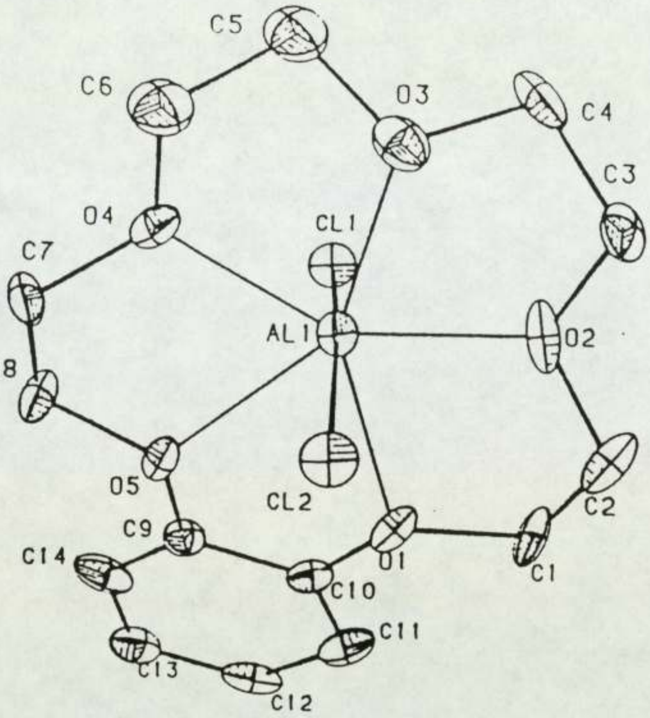


Fig. 31 Benzo-15-crown-5 complex with aluminium chloride

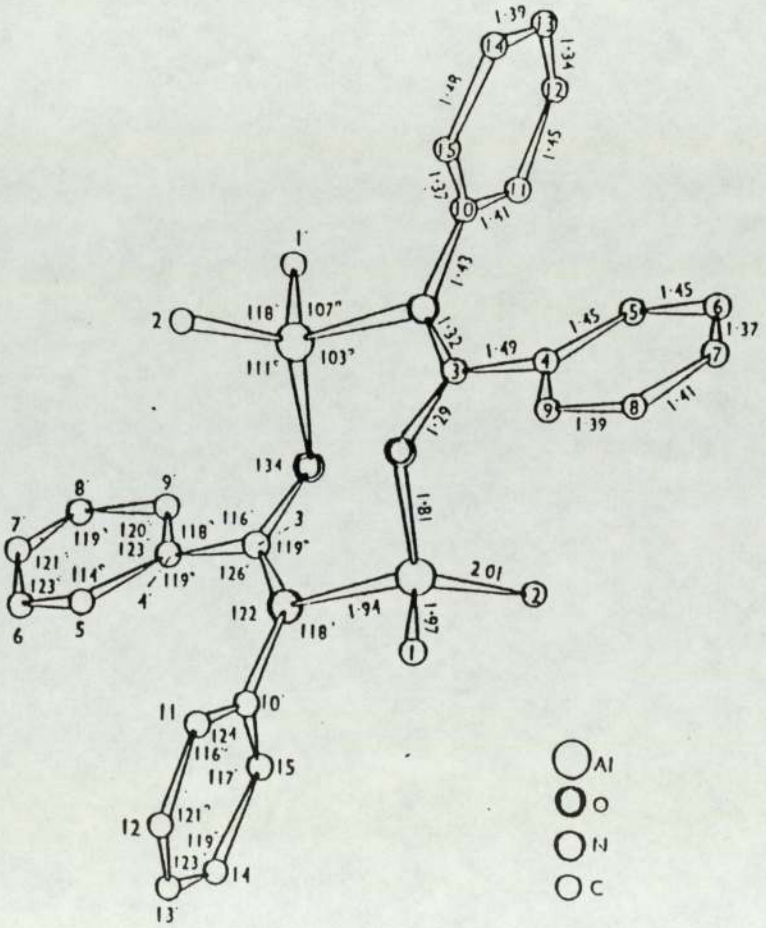


Fig. 32 Dimethylaluminium isocyanate - crystal structure

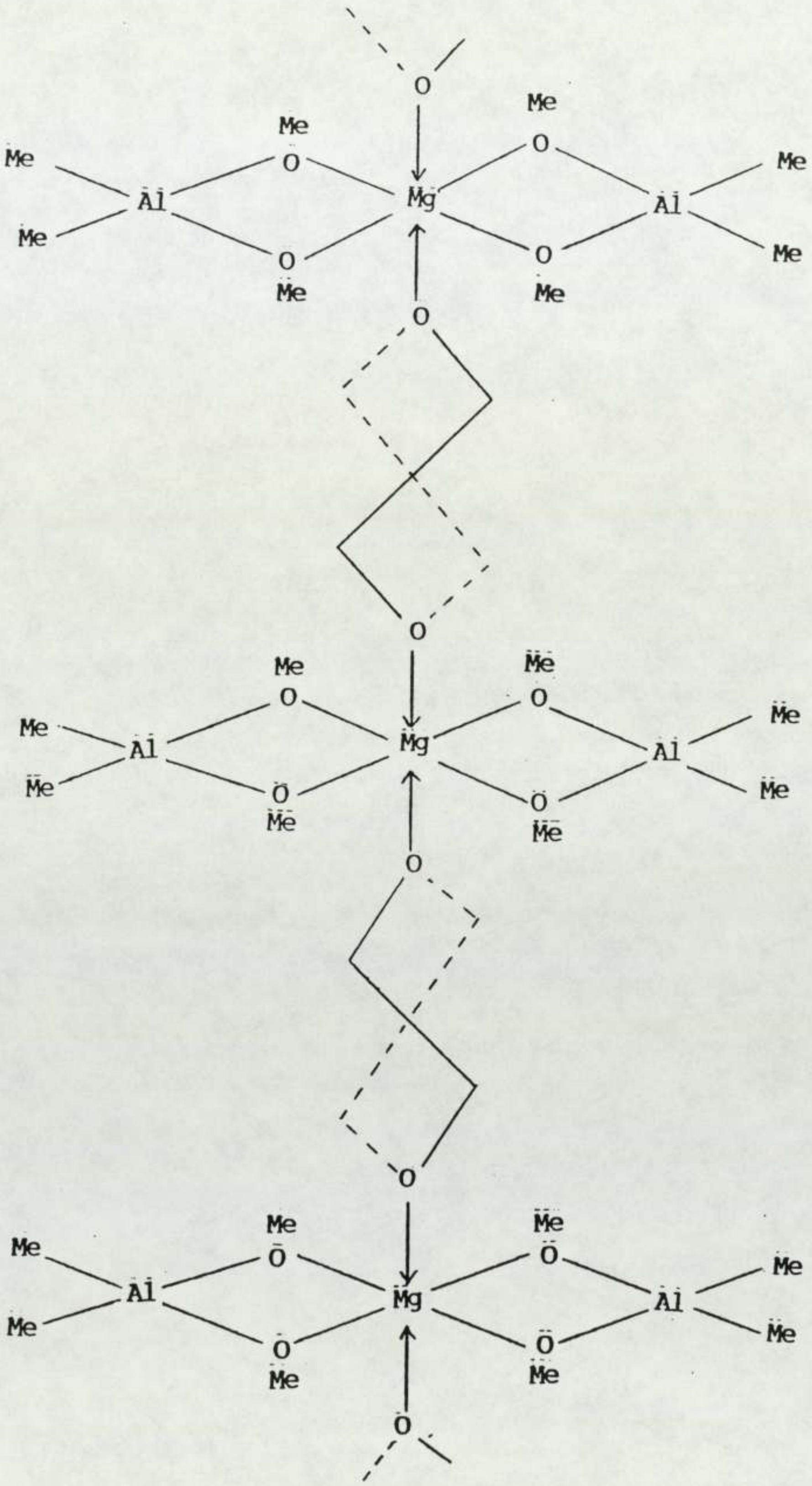


Fig. 33 Magnesium dimethyldimethoxyaluminate - dioxan bridged

crystal structure

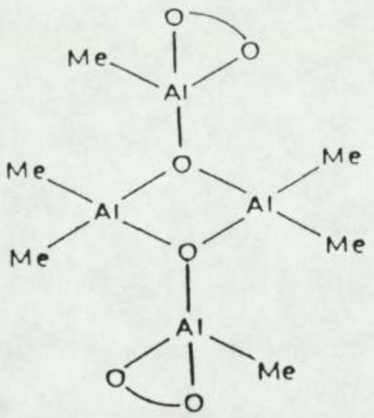


Fig. 34 Methylaluminium acetylacetonate - oxo-bridged structure

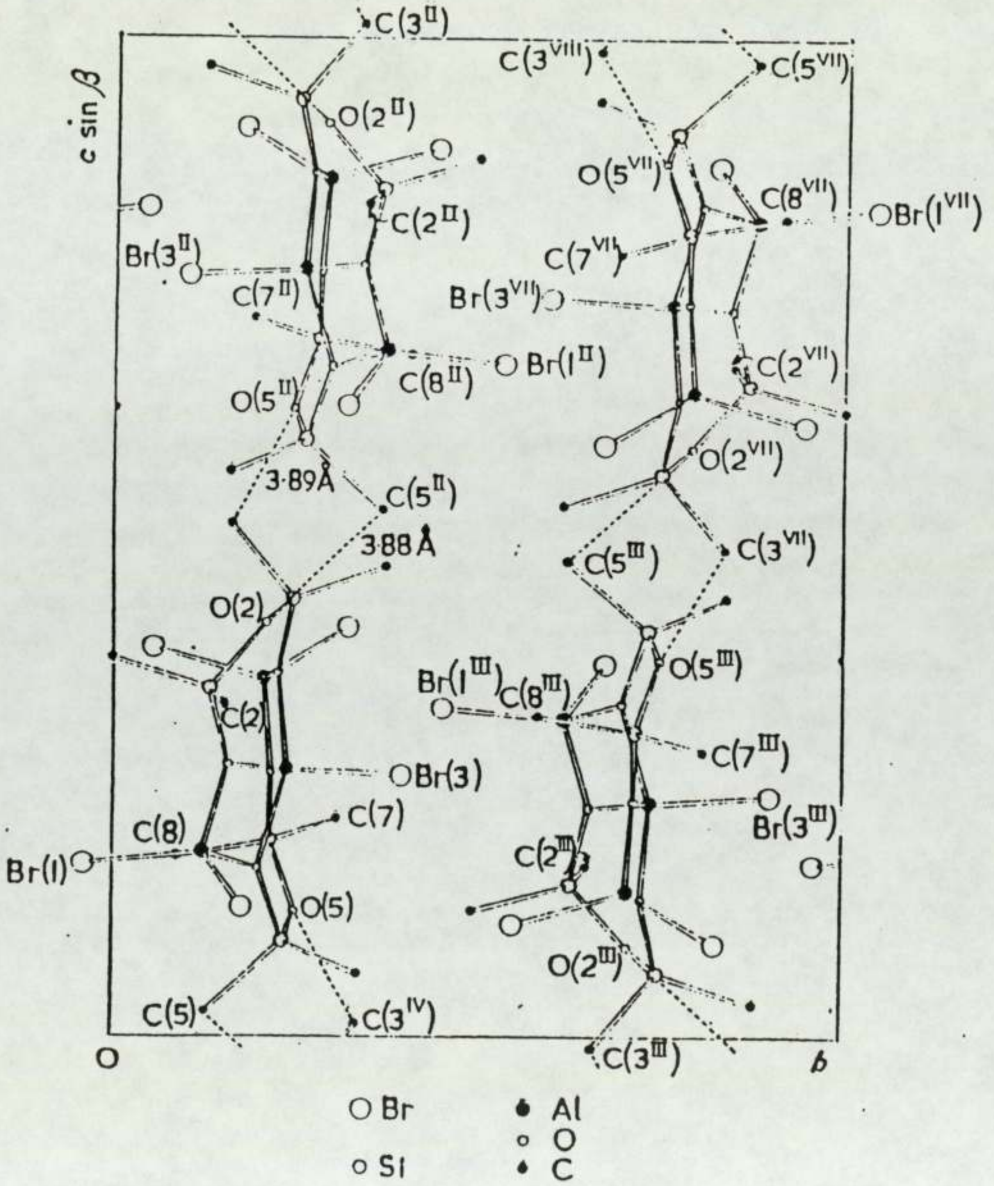
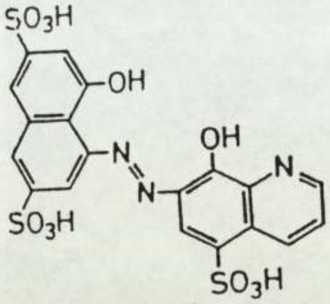
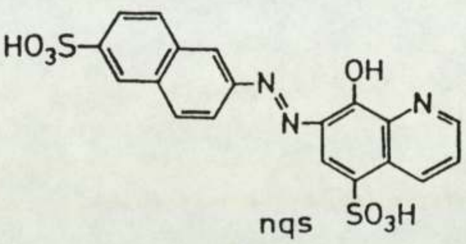


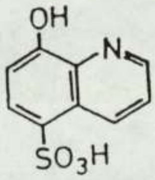
Fig. 35 Aluminosiloxane polymers



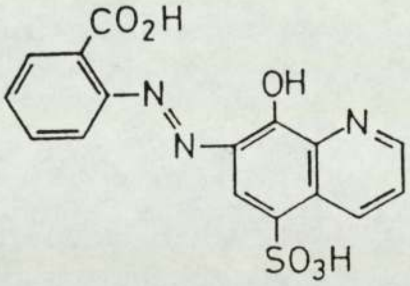
hns



nqs



hqs



pqs

Fig. 36 Some quinolinol derivatives used to complex aluminium ions for kinetic studies

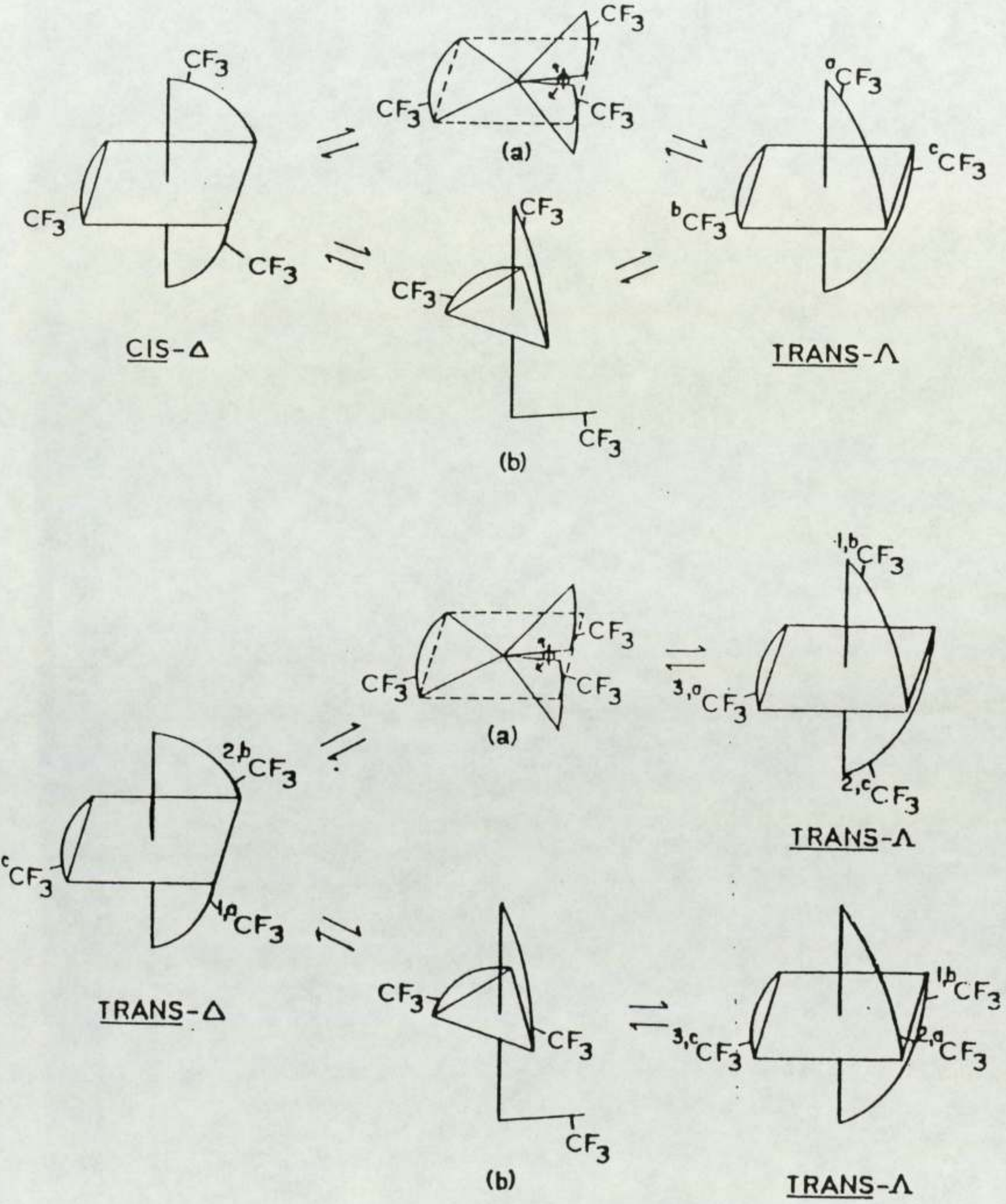


Fig. 37 (a) Rhombic twist mechanism

(b) Bond rupture mechanism

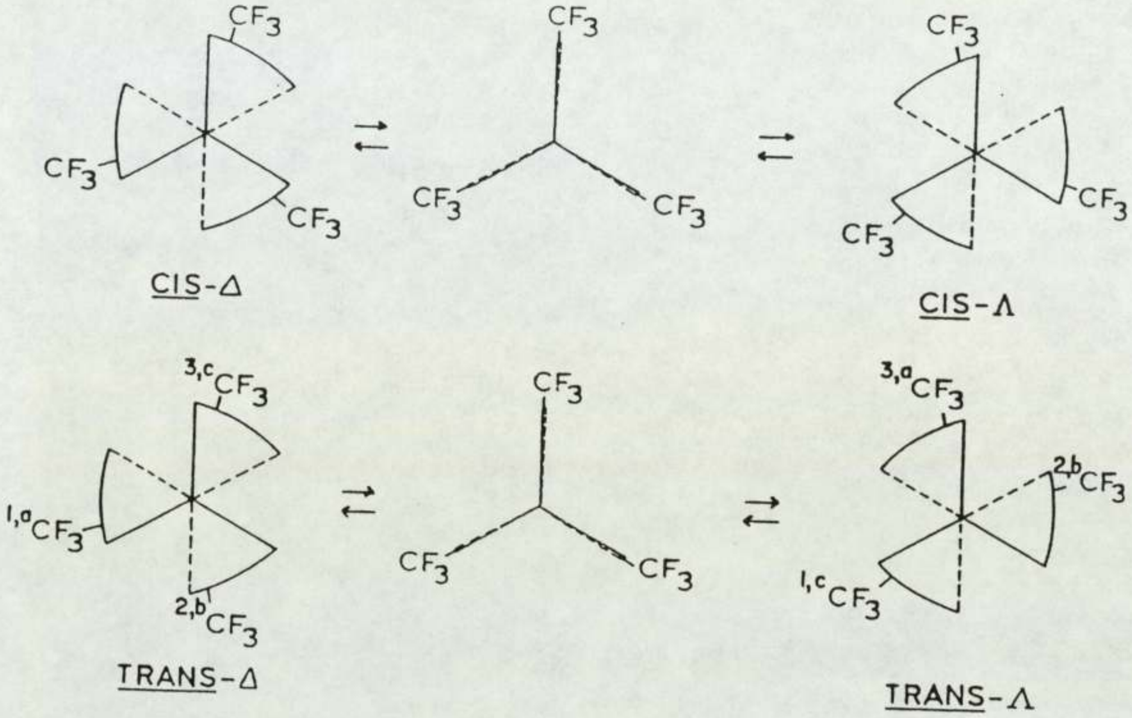
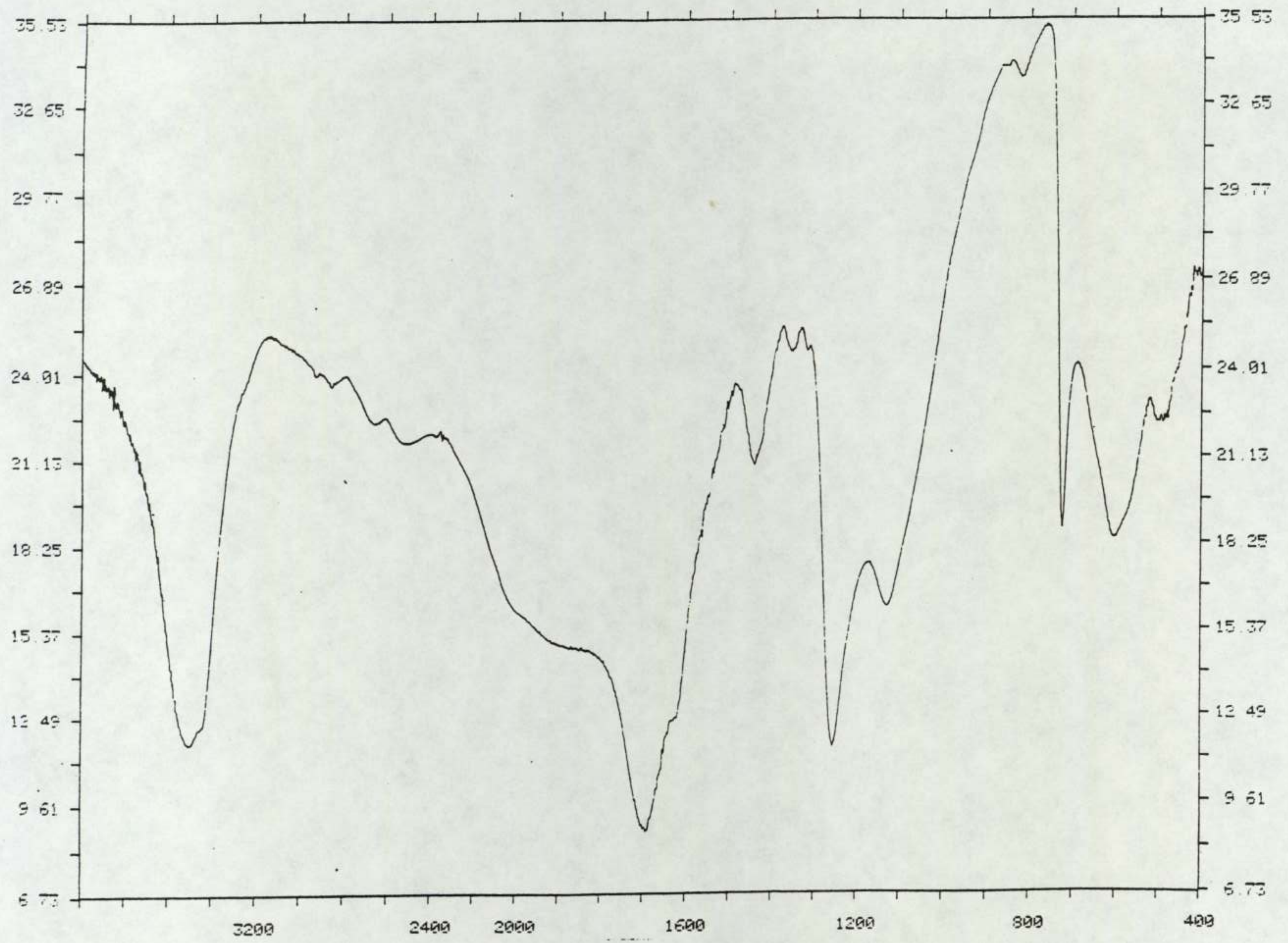


Fig. 38 Trigonal twist mechanism

APPENDIX 3



MODEL 1710 FTIR

DATE: 2.5-90

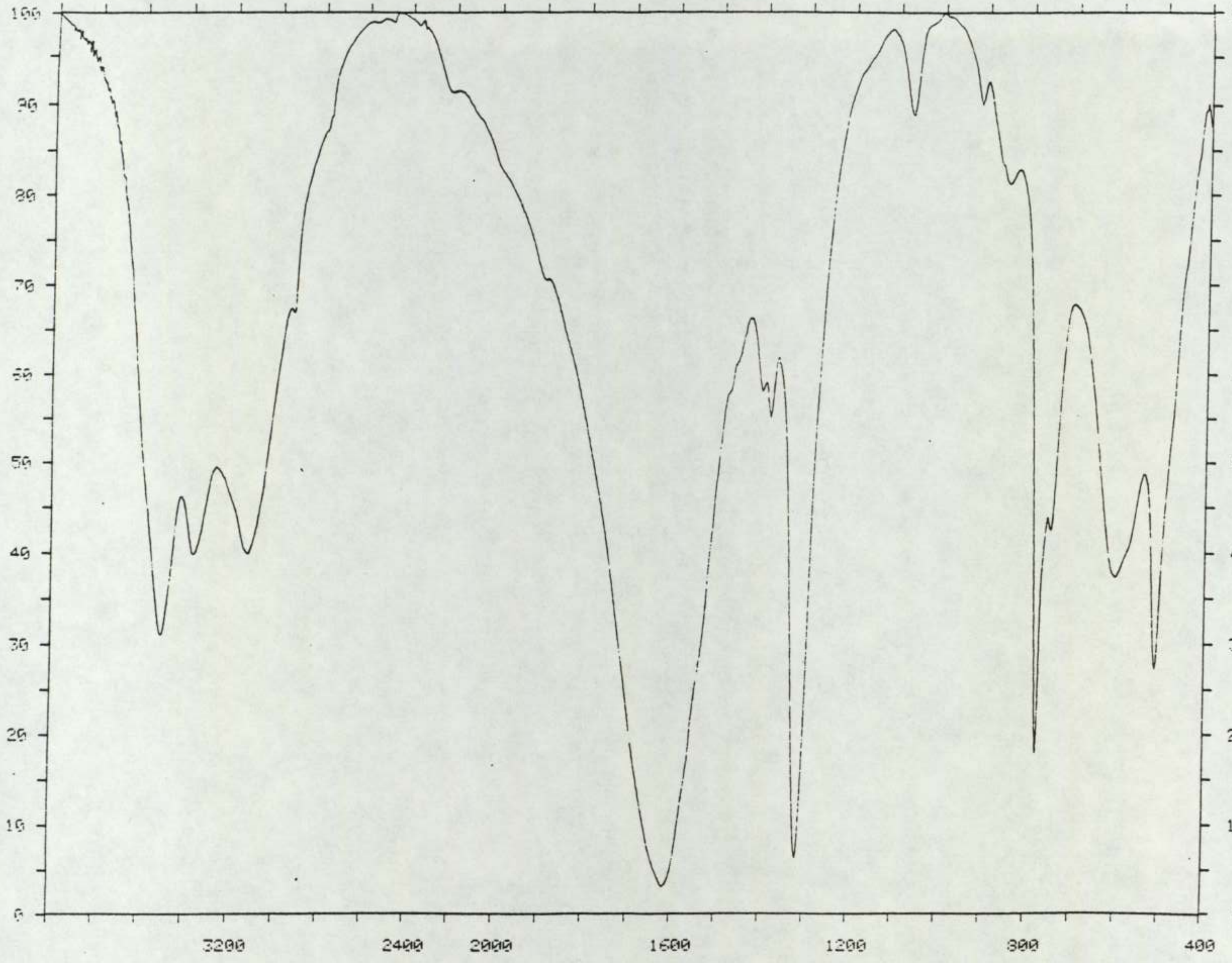
SAMPLE: Alox(05)

OPERATOR:

ABSCISSA RANGE 4000.0 - 400.0
ORDINATE RANGE 6.73 - 35.53
CHART EXPANSION 0.50

RESOLUTION 4 CM-1
NO. OF SCANS 50

Aluminium Oxalate



Strontium Aluminium Oxalate

MODEL 1710 FTIR

DATE: 2-5-90

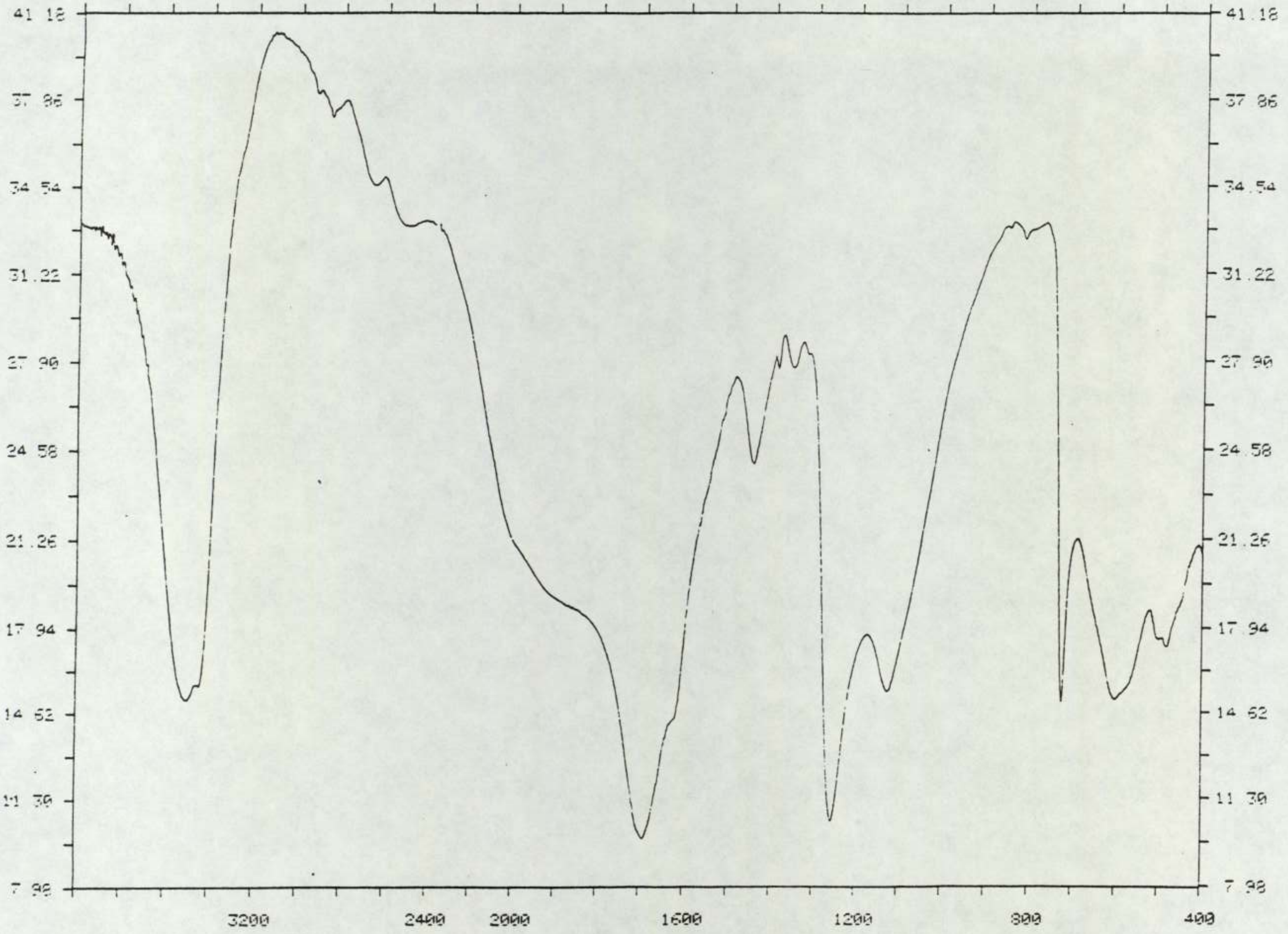
SAMPLE: SrAlox (02)

OPERATOR:

ABSCISSA RANGE 4000 0 - 400
ORDINATE RANGE 0 00 - 100
CHART EXPANSION 0 50

RESOLUTION 4 CM-1
NO. OF SCANS 50

0.738 ABEX : 2 FLAT : 2 SMO



MODEL 1710 FTIR

DATE: 2.5.90

SAMPLE: Ba Alox (ou)

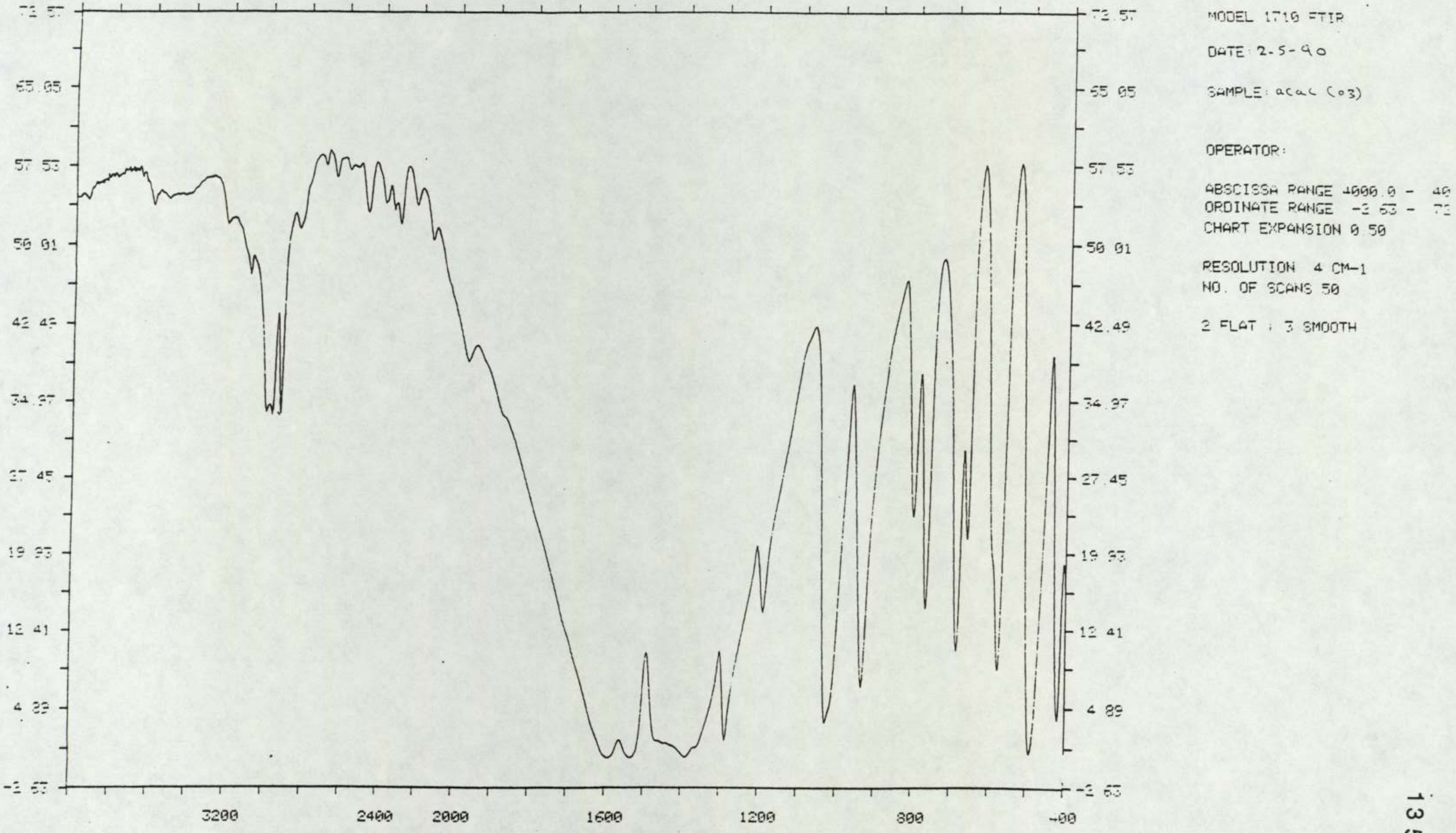
OPERATOR:

ABSCISSA RANGE 4000.0 - 400
ORDINATE RANGE 7.98 - 41
CHART EXPANSION 0.50

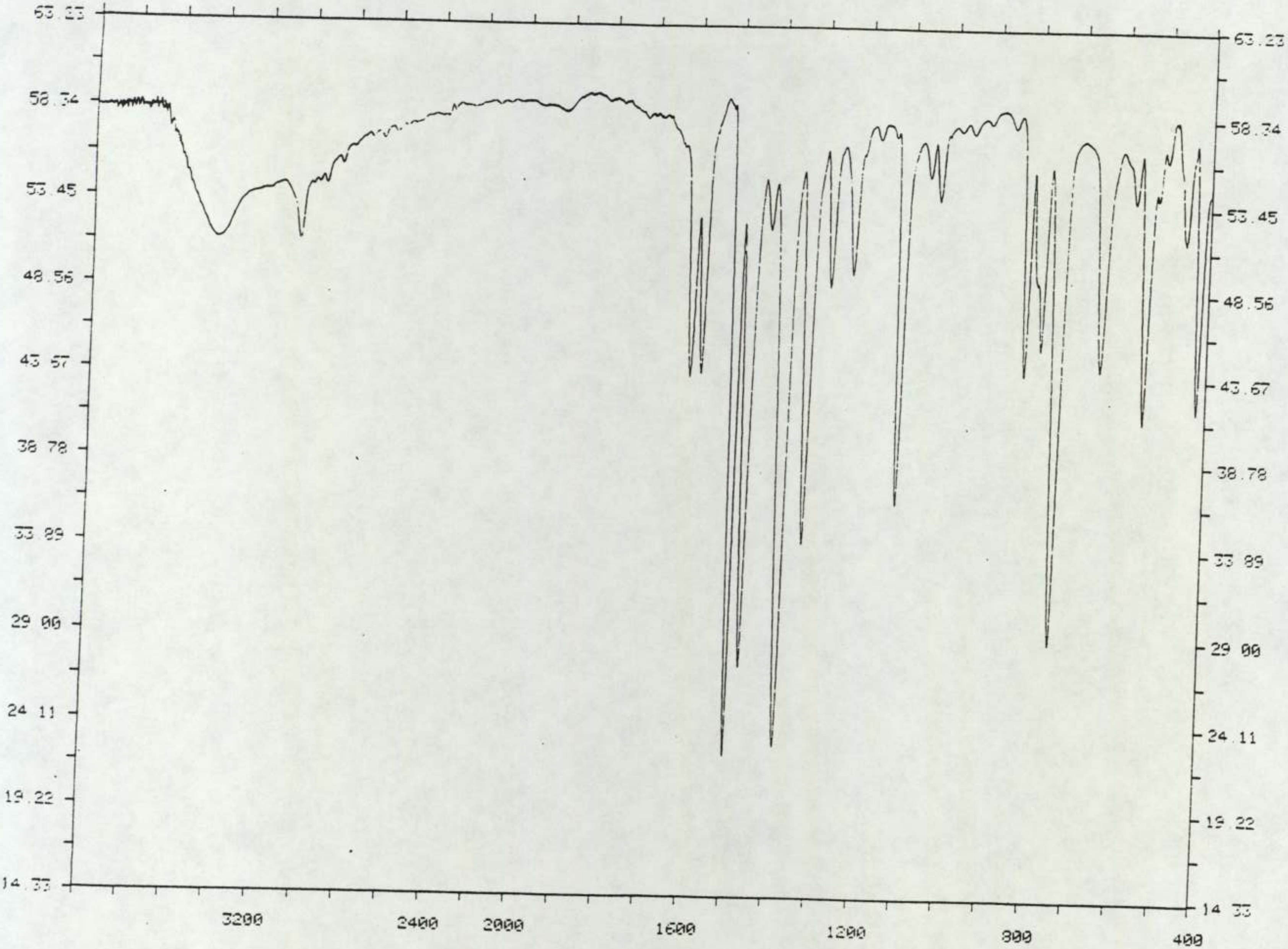
RESOLUTION 4 CM-1
NO. OF SCANS 50

2 FLAT : 2 SMOOTH

Barium Aluminium Oxalate



Aluminium Acetylacetonate



MODEL 1710 FTIR

DATE: 2. 5. 96

SAMPLE: 8-hyd (01)

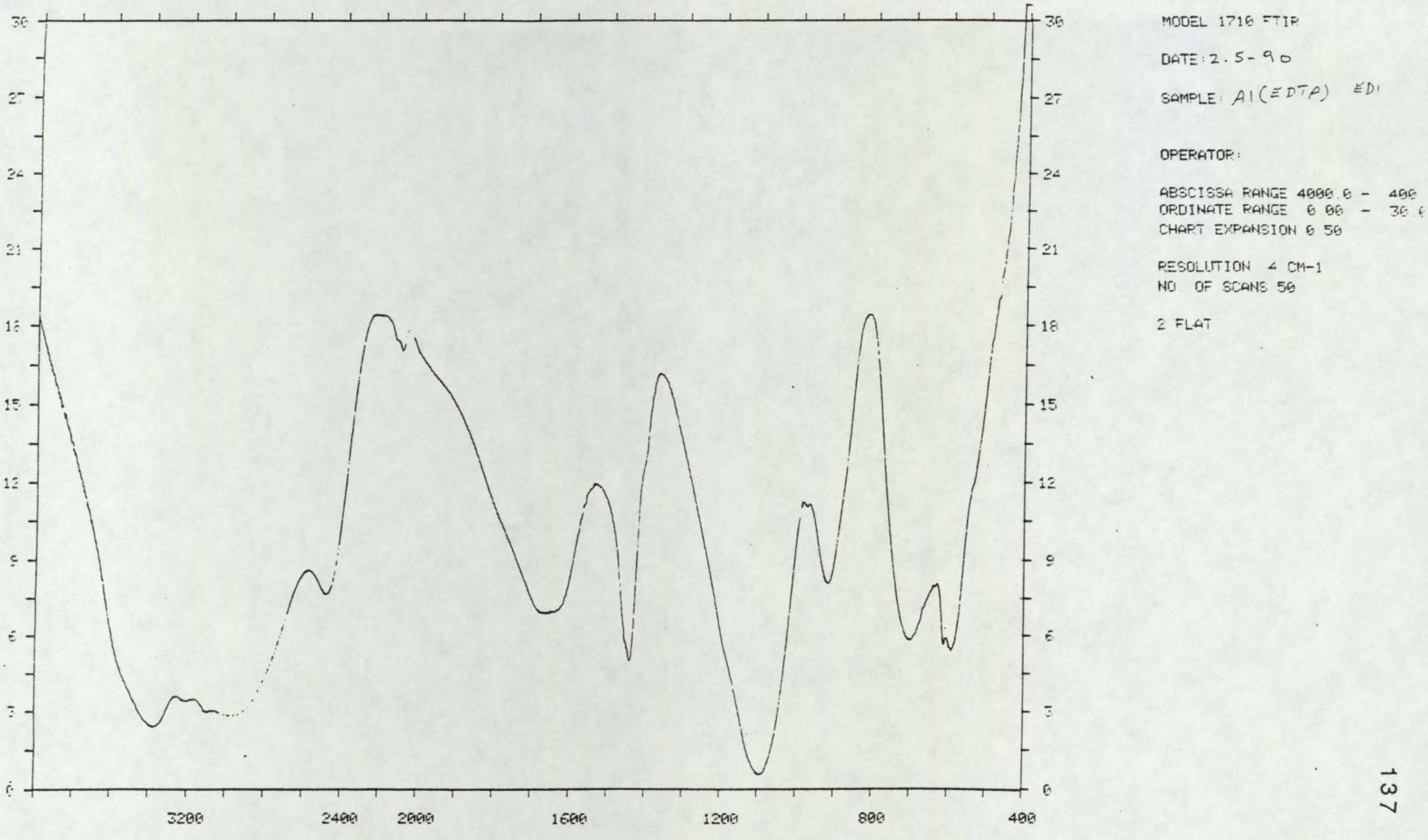
OPERATOR:

ABSCISSA RANGE 4000.0 - 400.0
ORDINATE RANGE 14.33 - 63.23
CHART EXPANSION 0.50

RESOLUTION 4 CM-1
NO. OF SCANS 50

2 FLAT ; 3 SMOOTH

Aluminium 8-hydroxyquinolinolate



MODEL 1710 FTIR

DATE: 2.5-90

SAMPLE: Al(EDTA) ED

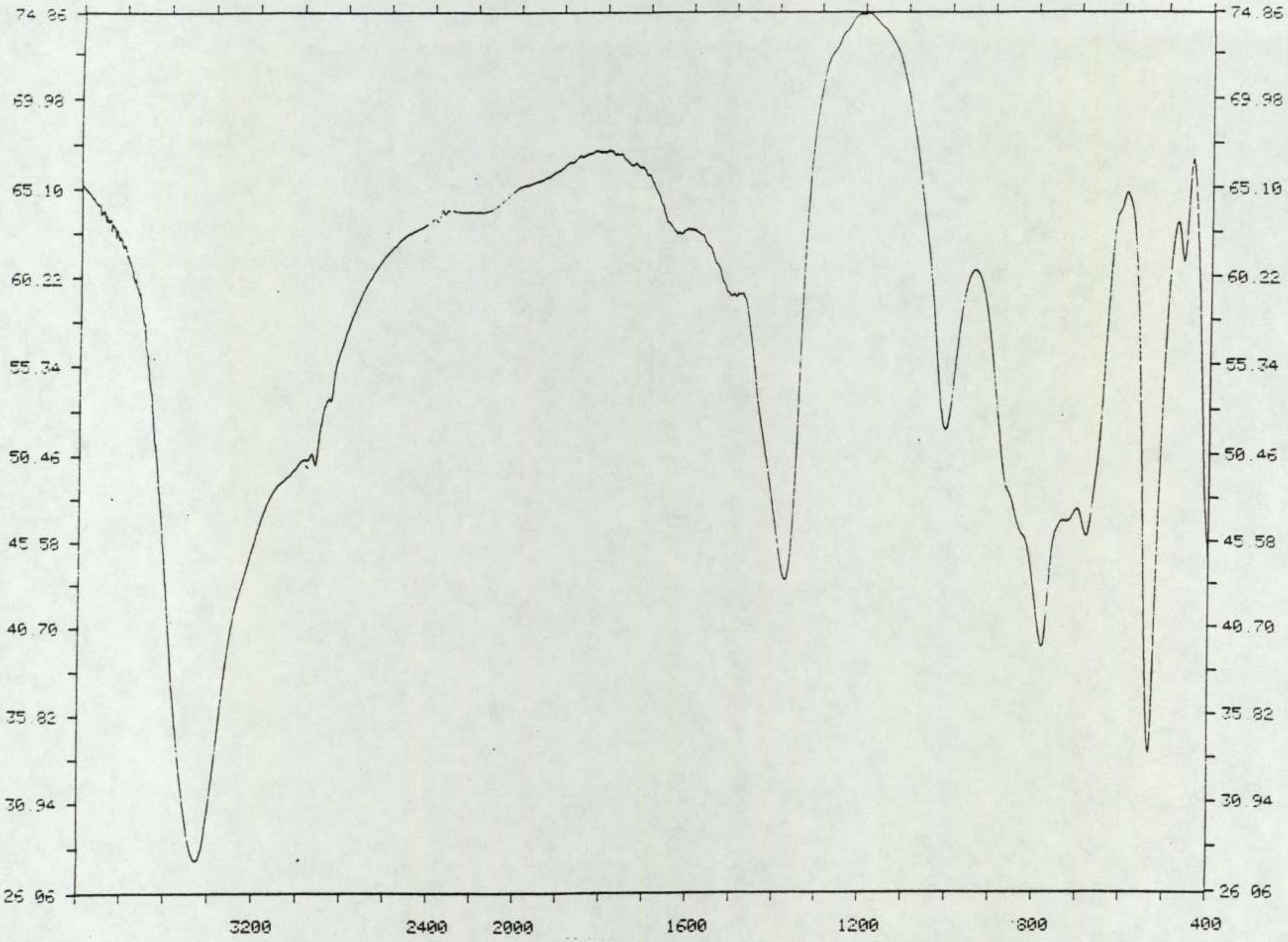
OPERATOR:

ABSCISSA RANGE 4000.0 - 400
ORDINATE RANGE 0.00 - 30.0
CHART EXPANSION 0.50

RESOLUTION 4 CM-1
NO. OF SCANS 50

2 FLAT

Aluminium - EDTA complex



MODEL 1710 FTIR

DATE: 2-5-90

SAMPLE: $(LiAl(O^iPr)_4$

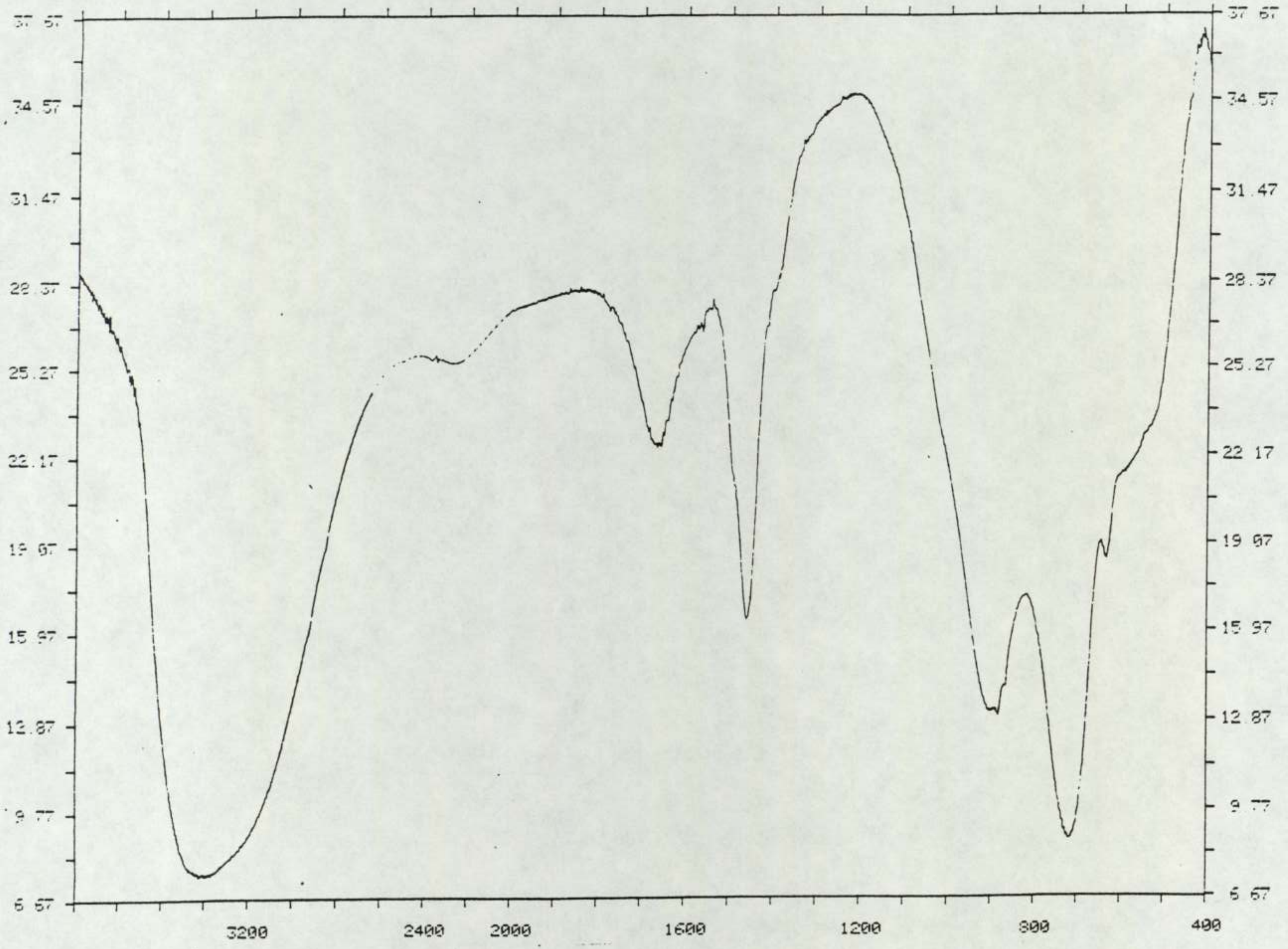
OPERATOR:

ABSCISSA RANGE 4000.0 - 4
ORDINATE RANGE 26.06 - 7
CHART EXPANSION 0.50

RESOLUTION 4 CM-1
NO. OF SCANS 30

2 FLAT ; 3 SMOOTH

Lithium Aluminium Isopropoxide



MODEL 1710 FTIR

DATE: 2.5.90.

SAMPLE: Na Al(OⁱPr)4

OPERATOR:

ABSCISSA RANGE 4000.0 - 40
ORDINATE RANGE 6.57 - 37
CHART EXPANSION 0.50

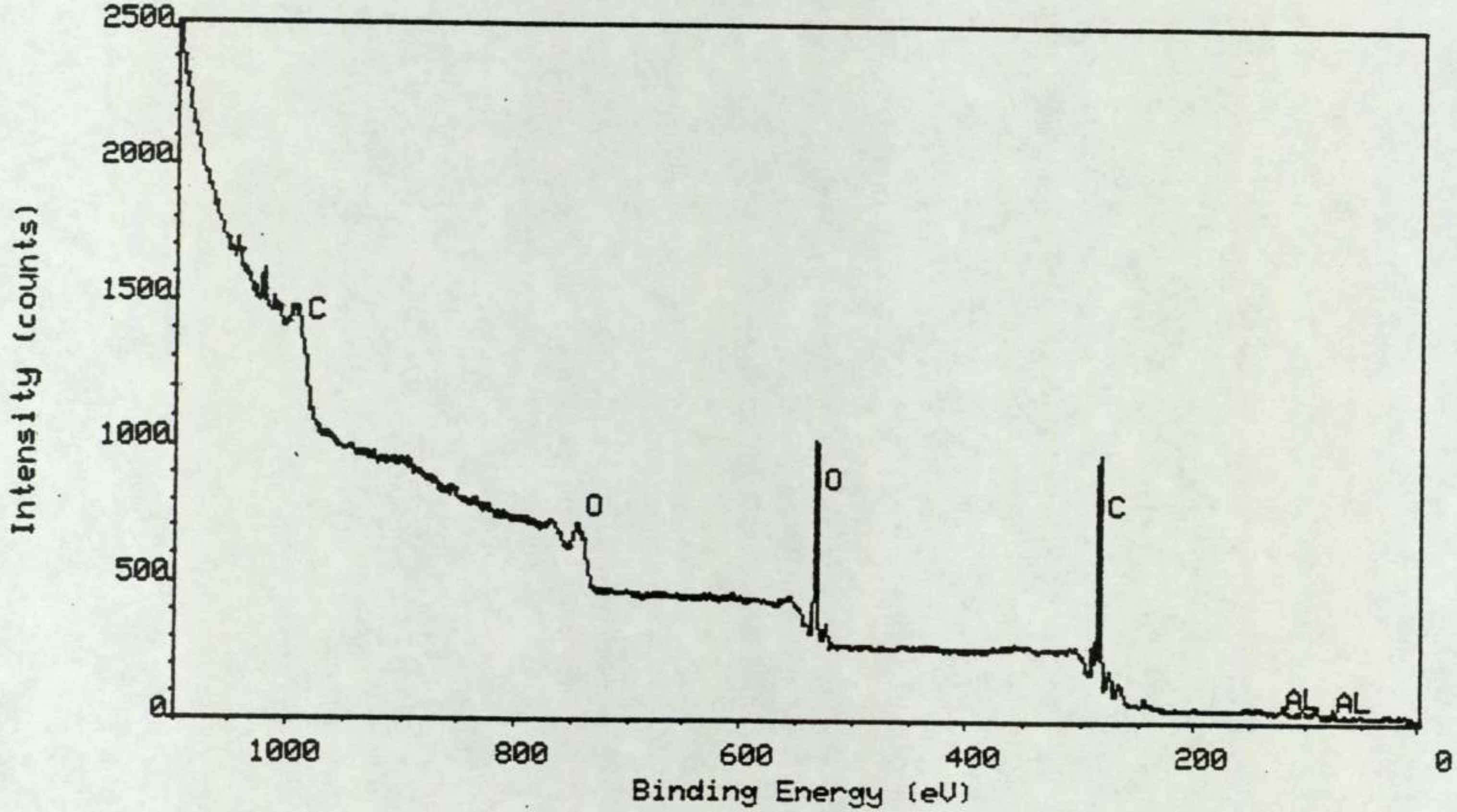
RESOLUTION 4 CM-1
NO. OF SCANS 30

2 FLAT

Sodium Aluminium Isopropoxide

*

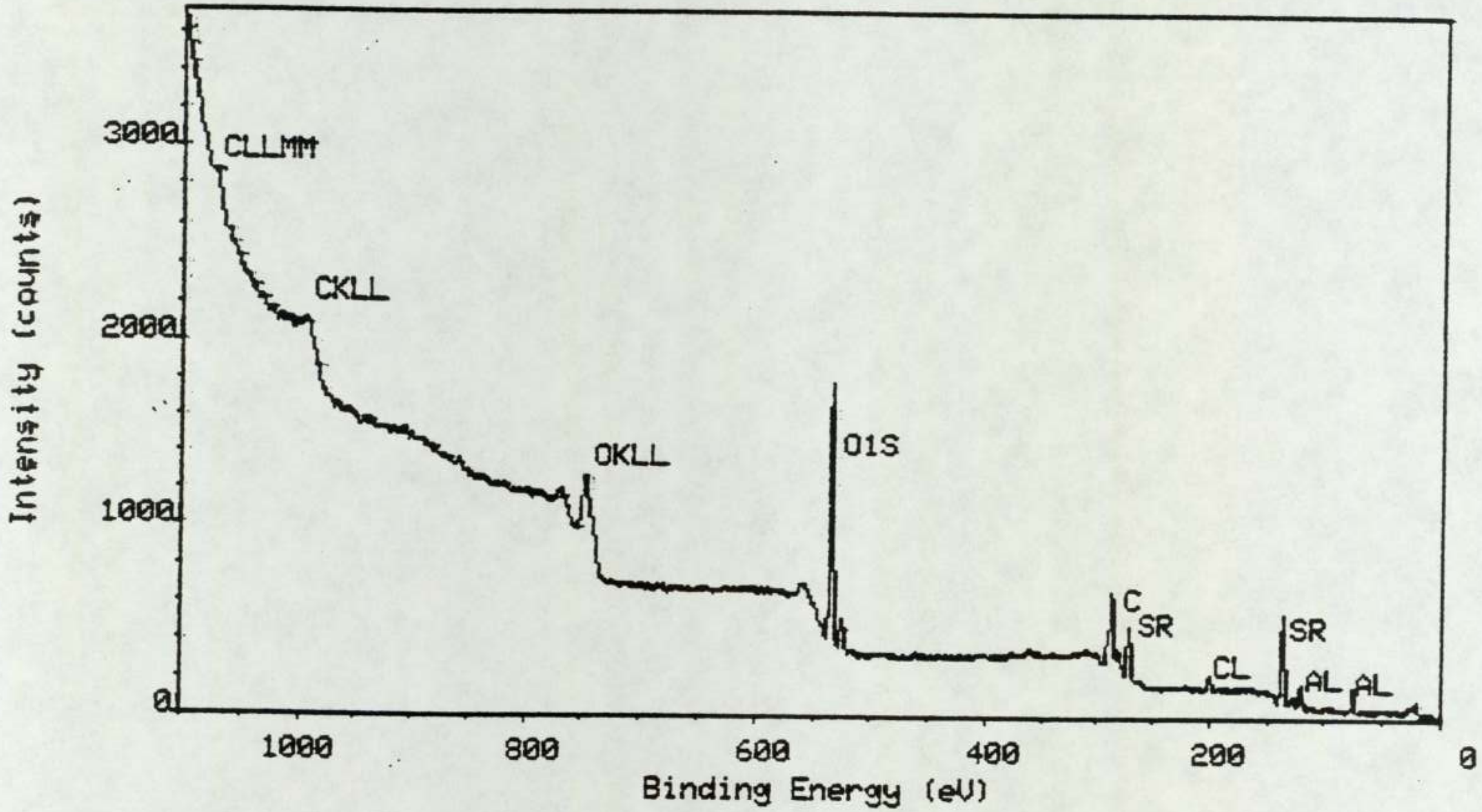
Title: OCTAHEDRAL O5,AlOx
Run:PHO5   Reg: 1 (WIDE) Scan: 1 Base: 91 Max Cts/s: 9582



Aluminium Oxalate

*

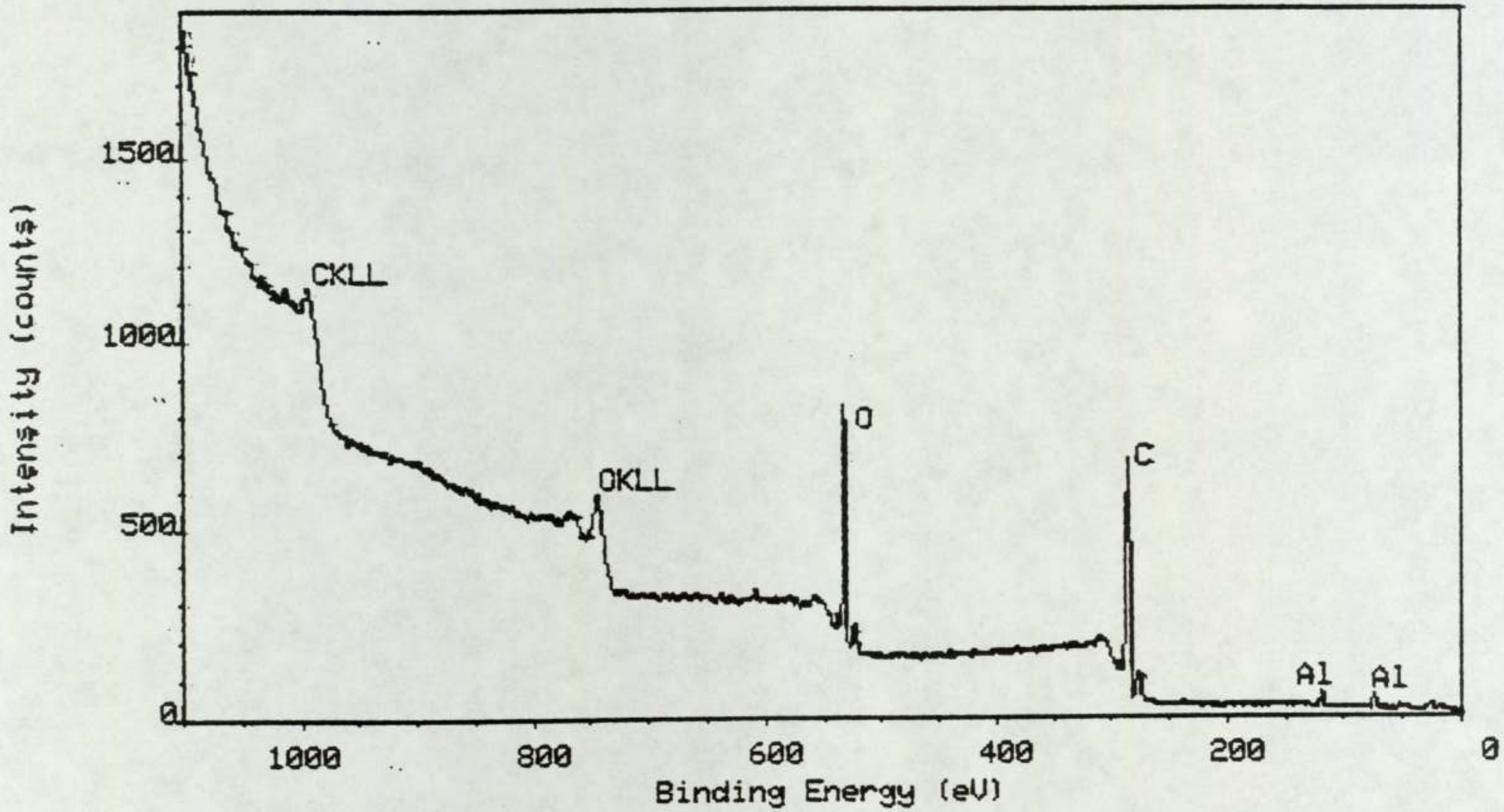
Title: OCTAHEDRAL - 02,SRALOX
Run:PHO2   Reg: 1 (WIDE) Scan: 1 Base: 174 Max Cts/s: 14270



Strontium Aluminium Oxalate

*

Title: OCTAHEDRAL - 03,ALacac
Run:PH03 Reg: 1 (WIDE) Scan: 1 Base: 84 Max Cts/s: 7249



Aluminium Acetylacetonate