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 $\text{Se}(\text{CH}_2\text{CH}_2\text{COOH})_2(\text{CH}_2\text{CH}_2\text{COO})$

Khalid Doudin, Karl W. Törnroos

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Selenium Carboxylic Acids Betaine; 3,3',3''-Selenotris(Propanoic Acid) Betaine, Se(CH₂CH₂COOH)₂(CH₂CH₂COO)

Khalid Doudin ^{a, *}, Karl W. Törnroos ^b

^a Chemical Engineering and Applied Chemistry, Aston University, Birmingham, B4 7ET, United Kingdom

^b Department of Chemistry, University of Bergen, N-5007 Bergen, Norway

Abstract

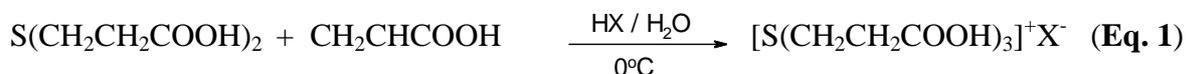
Attempts to prepare [Se(CH₂CH₂COOH)₃]⁺Cl⁻ from Se(CH₂CH₂COOH)₂ and H₂C=CHCOOH in concentrated hydrochloric acid, for the corresponding sulfonium salt, led exclusively to the Se-betaine, Se(CH₂CH₂COOH)₂(CH₂CH₂COO). The Se-betaine crystallises in the space group P2₁/c with the cell dimensions at 223 K, a = 5.5717(1), b = 24.6358(4), c = 8.4361(1) Å, β = 104.762(1)°, V = 1119.74(3) Å³, Z = 4, D_{calc} = 1.763 Mgm⁻³, μ = 3.364 Mm⁻¹. The structure refined to R₁ = 0.0223 for 2801 reflections with F_o > 4σ(F_o). In the crystalline state the molecule is intermolecularly linked to neighbouring molecules by a number of hydrogen bonds; a very strong carboxylic-carboxylate bond with an O⋯O distance of 2.4435(16) Å, a medium strong carboxylic-carboxylate bond with an O⋯O distance of 2.6431(16) Å and several weak O⋯H(CH₂) with O⋯C distances between 3.2 and 3.3 Å. In the carboxylic group involved in the very strong hydrogen bond the O⋯H bond is *antiperiplanar* to the C=O bond while the O-H bond is *periplanar* to the C=O bond in the second carboxylic group. Based upon the C-O bond lengths and the elongation of the O-H bond involved in the strong hydrogen bond one may describe the compound as strongly linked units of Se(CH₂CH₂COOH)(CH₂CH₂COO)₂ rather than Se(CH₂CH₂COOH)₂(CH₂CH₂COO). The selenium atom forms two strong intramolecular 1,5-Se⋯O contacts, with a carboxylate oxygen atom, 2.9385(12) Å, and with a carboxylic oxygen atom, 2.8979(11) Å. To allow for these contacts the two organic fragments have been forced into the *periplanar* conformation. The molecule is only slightly asymmetric with regard to the C-Se-C bond angles but is very asymmetric with regard to the torsion angles.

* Corresponding author: K Doudin, k.doudin@aston.ac.uk

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1. Introduction

Some 60 years ago Schöberl and Lange [1] showed that chlorides and bromides of $[S(CH_2CH_2COOH)_3]^+$ could be prepared in high yield by addition of 3,3'-thiobis(propionic acid) to propionic acid (acrylic acid) in strongly acidic aqueous solution, Eq. 1.



The isolated salts were stable and non-hygroscopic solids and were purified by crystallisation from ethanol. When aqueous solutions of the salts were heated, however, the weakly soluble betaines, the corresponding bases of the sulfonium salts, crystallised from the solution upon cooling, Eq. 2.



Apparently, these sulfonium cations are so acidic that an equilibrium exists with Cl^- and Br^- in aqueous solutions. The corresponding salts derived from $HOOCCH_2SCH_2CH_2COOH$ were also prepared, Eq. 1, and were found to behave rather similarly [1]. However, all attempts to prepare sulfonium salts with two or three acetic acid groups failed, only the corresponding bases, the weakly soluble betaines, previously named *thetins* [2], were formed. This suggests that the acidity of this class of cations follows the following sequence: $[(PrA)_3S]^+ \sim [(PrA)_2(AcA)S]^+ \ll [(PrA)(AcA)_2S]^+ \sim [(AcA)_3S]^+$; PrA and AcA being abbreviations for propionic acid and acetic acid, respectively.

Since salts of $[S(CH_2COOH)_3]^+$, and also $[Se(CH_2COOH)_3]^+$ [3], are presently unknown, a structural study of their corresponding betaines was recently performed [4]. In this work it was shown that the cause for the very weakly basic nature of these compounds was due to two strong intramolecular I,4-X...O contacts that seem to prevail in aqueous solutions as viewed by the low solubility of these compounds in water. The fairly equal S...O and Se...O intramolecular distances in the two betaines suggested the latter interactions to be the stronger ones [4]. The possibility of only one such contact in $[(PrA)_2(AcA)S]^+$ and none in $[(PrA)_3S]^+$ might therefore be the reason for the acidity sequence as mentioned above.

To further examine the effect of this type of interactions a study on the readily available $[S(CH_2CH_2COOH)_3]^+$ halides [1] and the corresponding, but unknown, selenonium salts was started. However, when attempting to prepare the selenonium salts from $Se(CH_2CH_2COOH)_2$, as described for the sulfonium salts [1] Eq.1, only the Se-betaine, **1**, could be isolated from the reaction mixture.



Apparently, some factor(s) make this betaine far less basic than the corresponding S-betaine. Since suitable crystals of this betaine were readily obtained a structural study was performed. Various spectroscopic data and accurate crystal structures of several relevant reference compounds like $X(CH_2COOH)_2$ [5], $X(CH_2CH_2COOH)_2$ [6-8] and $X(CH_2COOH)_2(CH_2COO)$ X being S and Se, have been published [4].

2. Results and discussion

2.1. Synthesis and analysis

The Se-betaine, $\text{Se}(\text{CH}_2\text{CH}_2\text{COOH})_2(\text{CH}_2\text{CH}_2\text{COO})$, was readily obtained in pure state by only one crystallisation from water of the precipitate formed in the strongly acidic solution. The yield of purified product was quite high, 58%, although no attempts were made to maximise the yield. The mother liquor from the first precipitation, prior to the purification; see the instability of $[\text{S}(\text{CH}_2\text{CH}_2\text{COOH})_3]^+\text{X}^-$ in warm water [1], was not found to contain other products than the isolated betaine. Apparently, the following equilibrium, Eq. 3, (X being S and Se), is strongly shifted to the left for X = S and to the right for X = Se at room temperature.



There is no evidence suggesting the Se-betaine to be significantly less soluble than the corresponding S-betaine. No attempts were made to force the latter equilibrium to the left by using an acid with an anion of lower proton basicity [9] and a solvent of lower donicity [10].

The ^1H NMR spectra did only show two types of CH_2 groups, at 3.0 ppm (2- CH_2) and 3.6 ppm (3- CH_2) in D_2O and at 2.95 ppm (2- CH_2) and 3.46 ppm (3- CH_2) in DMSO-d_6 . Apparently, the NMR technique does not distinguish between the two carboxylic groups and the one carboxylate group in the betaine. It is notable that the signal due to the 3- CH_2 protons is some 0.5 ppm downfield from that of the 2- CH_2 protons. For several alkyl-substituted seleno-propanoic acids, $\text{RSeCH}_2\text{CH}_2\text{COOH}$ [11, 12], and $\text{Se}(\text{CH}_2\text{CH}_2\text{COOH})_2$ [8] the ^1H NMR signals due to these CH_2 groups are most difficult to separate. The distinct separation, ~ 0.5 ppm, is probably due to a significant selenonium character of the Se-betaine. This suggestion is substantiated by the downfield shift of the ^{77}Se NMR signal from 2,2"-selenobis(propanoic acid), 198 ppm. The downfield shift from $\text{Se}(\text{CH}_2\text{COOH})_2(\text{CH}_2\text{COO})$, 54 ppm, may be more difficult to judge since ^{77}Se NMR shifts are known to be most dependent upon the size of the alkyl group [13].

The IR spectra of this compound are indeed most complicated reflecting not only the two different groups being linked to the central atom but also a significant amount of asymmetry. This was also observed for the betaines derived from $[\text{X}(\text{CH}_2\text{COOH})_3]^+$ [4]. One may particularly mention the cluster of peaks due to the carbonyl groups ranging from a shoulder at 1778 cm^{-1} , presumably due to a free carboxylic group, and to a strong peak at 1556 cm^{-1} . The latter peak may be assigned to $\nu_{\text{as}}(\text{COO}^-)$, observed at 1654 cm^{-1} and at 1643 cm^{-1} in $\text{S}(\text{CH}_2\text{COOH})_2(\text{CH}_2\text{COO})$, and $\text{Se}(\text{CH}_2\text{COOH})_2(\text{CH}_2\text{COO})$, respectively [4]. The most intense carbonyl peaks, however, were observed in the $1710\text{-}1740\text{ cm}^{-1}$ region. Since the C-O vibrations also appeared as a complex array of peaks in the $1150\text{-}1300\text{ cm}^{-1}$ region no attempts were made to assign the various peaks.

2.2. Comment on the molecular structure

The molecular structure of $\text{Se}(\text{CH}_2\text{CH}_2\text{COOH})_2(\text{CH}_2\text{CH}_2\text{COO})$ together with the atomic number scheme is shown in **Figure 1**. Bond lengths and bond angles together with torsion angles are listed in **Table 1**. As seen from the bond lengths, the bond and the torsion angles, as well as from the intra- and intermolecular bonding and non-bonding interactions,

summarised in **Table 2**, the groups linked to the central selenium atom, A, B and C, are distinctly different. The compound is also slightly asymmetric with regard to the C-Se-C bond angles, C(1A)-Se-C(1B) and C(1A)-Se-C(1C) being $99.31(6)^\circ$ and $99.37(7)^\circ$, significantly larger than the C(1B)-Se-C(1C) bond angle, $97.54(7)^\circ$. All bond angles are larger than in $\text{Se}(\text{CH}_2\text{CH}_2\text{COOH})_2$, $96.48(8)^\circ$ [8], reflecting the space demands of the three fairly bulky ligands linked to the selenium atom in a pyramidal configuration.

The compounds are intermolecularly linked through several hydrogen bonds, the strongest undoubtedly being the one listing O(2B), the hydroxyl oxygen atom, with O(2A)', as shown in **Figure 2**. The distance between these two oxygen atoms is only $2.4335(16)$ Å which, according to current definition [14], is to be characterised as a very strong hydrogen bond. This type of strong intermolecular hydrogen bond between betaines has previously been encountered in 1:1 and 2:1 complexes of pyridine betaine with strong acids [15], in the present hydrogen bonded system the compound itself serves as the strong acid. This type of very strong hydrogen bond has also been observed in the intramolecularly hydrogen bonded betainic form of certain derivatives of EDTA [16]. By forming this strong hydrogen bond the O(2B)-H(2B) bond length is lengthened to $0.98(2)$ Å while the H(2B)---O(2A)^a distance is consequently reduced to only $1.47(2)$ Å; the intermolecular O(2B)-H(2B)---O(2A)^a bond angle being $169(2)^\circ$. As shown in **Figure 1** the carboxylic unit in the B group attains an *antiperiplanar* conformation, the torsion angle being $174(1)^\circ$. Actually, the *periplanar* conformation, usually observed in dimeric units of carboxylic acids [5], is also much obstructed in the present case due to the close presence of a CH₂ group in a neighbouring molecule.

As indicated in **Figure 2** there is also one additional short intermolecular O(H)⋯O distance, $2.6431(16)$ Å. In this hydrogen bond the O-H and H⋯O bond distances are $0.85(2)$ and $1.82(2)$ Å, respectively, with an O-H⋯O bond angle of $161(2)^\circ$. Contrary to the carboxylic unit in the B group this unit in the C group is perfectly in a *periplanar* conformation. It is apparent that the C-C(O)OH fragment in carboxylic acids is most flexible and that the conformation of this fragment may be determined by the location and the donor-acceptor properties of the neighbouring atoms. In the present structure several oxygen atoms are located quite close to neighbouring methylene carbon atoms that may indicate some O⋯H interactions. Selected non-bonding distances together with non-bonding angles are summarised in **Table 2**. Of particular interest are the two very short intramolecular 1,5-Se⋯O distances, Se⋯O(1B) and Se⋯O(2A), only $2.8979(11)$ and $2.9385(12)$ Å. The C(1A)-Se⋯O(1B) and C(1B)-Se⋯O(2A) angles, $159.70(5)$ and $162.24(5)^\circ$, are fairly close to the ideal one for secondary bonding [17]. The Se⋯O(1C) distance, O(1C) being a carboxylic oxygen atom, is far longer, $3.3943(12)$ Å, and does not indicate any interaction with the central selenium atom. Since no other atoms were found to be sufficiently close to the central atom to suggest further intermolecular interactions the present compound may in principle be considered as a penta-coordinated compound with three Se-C bonds and two very strong Se⋯O interactions.

The torsion angles, listed in **Table 1**, reveal a complex picture. The co-ordinating O(2A) and O(1B) oxygen atoms are close to being *periplanar* to C(1A) and C(1B), the C(1A)-C(2A)-C(3A)-O(2A) and C(1B)-C(2B)-C(3B)-O(1B) torsion angles being $24.3(2)$ and $-11.7(2)^\circ$, respectively. The O(2C) atom, presumably the best candidate of the two oxygen atoms in this carboxylic acid fragment to co-ordinate to the selenium atom [5], is antiperiplanar to C(1C), the C(1C)-C(2C)-C(3C)-O(2C) torsion angle being $-173.99(13)^\circ$.

The bond lengths and bond angles in the Se-C1-C2-C3 fragments are all in the expected range and are in principle as observed in $\text{Se}(\text{CH}_2\text{CH}_2\text{COOH})_2$ [8]. The Se-C(1C) bond, a

bond that is not involved in secondary bonding, is slightly shorter than Se-C(1A) and Se-C(1B). The Se-C(1A)-C(2A) and Se-C(1B)-C(2B) bond angles are slightly but significantly smaller than Se-C(1C)-C(2C), presumably due to the strong 1,5-Se \cdots O(2A) and 1,5-Se \cdots O(1B) interactions. The C1-C2-C3 bond angles in the three fragments are fairly similar, $\sim 114^\circ$.

The strongly hydrogen bonded groups, the carboxylate group in A and the *antiperiplanar* carboxylic group in B, and also the medium hydrogen bonded but *periplanar* carboxylic group in C, are all planar within experimental error; see **Table 1** for the C-C-O and O-C-O bond angles. While the O-C-O bond angles are rather similar, from 122.3° in B to 124.7° in A and C, the C-C-O bond angles are quite different but do not reflect that O(2A) and O(1B) make strong contacts with the central selenium atom. Of particular interest are the C=O and C-O bond lengths. In group C these bond lengths are as anticipated for a carboxylic group. 1.206(2) and 1.325(2) Å [18]; in A and B, however, the C-O bond lengths to the oxygen atoms being involved in the very strong hydrogen bond, O(2A) and O(2B), are significantly changed, from ~ 1.25 Å, as expected for a carboxylate group [19], to 1.291(2) Å for the C(3A)-O(2A) bond length and from ~ 1.32 to 1.286(2) Å for the C(3B)-O(2B) bond length. Actually, the C-O bond lengths listed in **Table 1** may allow one to consider the title compound in its crystalline state to consist of strongly hydrogen bonded units of Se(carboxylic acid)(carboxylate)₂ rather than Se(carboxylic acid)₂(carboxylate). With the structural data available the complexity in the IR spectrum of this compound can readily be understood.

2.3. Concluding Remarks

The Se-betaine, Se(CH₂CH₂COOH)₂(CH₂CH₂COO), appears to owe its extremely low basicity to the presence of two exceptionally strong 1,5-Se \cdots O interactions. The fairly low solubility of this compound in water, as was also experienced for the betaines derived from [S(CH₂COOH)₃]⁺ and [Se(CH₂COOH)₃]⁺ [5], suggests that these interactions are retained in aqueous solutions. The weaker and more flexible stature of the selenium-carbon bonds may be the cause for the formation of the 1,5-Se \cdots O interactions preventing salts of [Se(CH₂CH₂COOH)₃]⁺ to be formed in strongly acidic solutions.

3. Experimental

3.1. Materials and instrumental

3-Bromopropanoic acid, Fluka, 98% puriss, and propenoic (acrylic) acid, Aldrich 99%, were used as received. Selenium, Merck, was of 99.5% purity. The FTIR spectra, KBr and Nujol, were recorded with an OMNIC 410 FT-IR system. ¹H, ¹³C and ⁷⁷Se NMR spectra were recorded at a ¹H frequency of 600 MHz on a Bruker DRX-600 spectrometer. Internal TMS and internal Me₂Se were used as chemical shift references. Additionally, 2,2'-selenobis(propanoic acid), Se(CH₂CH₂COOH)₂ [8], and Se(CH₂COOH)₂(CH₂COO) [4] were used as chemical shift references.

3.2. Preparation of 3,3',3''-selenotris(propanoic acid) betaine, **1**, C₉H₁₄O₆Se Se(CH₂CH₂COOH)₂(CH₂CH₂COO).

To a heterogeneous mixture of 1.0 g, 4.4 mmol, $\text{Se}(\text{CH}_2\text{CH}_2\text{COOH})_2$, in 10 ml concentrated HCl was slowly added 0.60 g, 8.3 mmol, $\text{CH}_2=\text{CHCOOH}$. The selenium compound dissolved as the reaction proceeded due to the reaction heat. The reaction mixture was stirred for two days at room temperature. Upon cooling to 0°C the Se-betaine precipitated rapidly. After one crystallisation from water the product was analytically pure and the crystals proved satisfactory for an X-ray study. Yield 0.17 g, 58%, mp 160°C .

^1H NMR (D_2O): 3.0 ppm (6H, t), 2- CH_2 , 3.6 ppm (6H, t), 3- CH_2 . ^1H NMR (DMSO-d_6): 2.95 ppm (6H, t), 2- CH_2 , 3.46 ppm (6H, t), 3- CH_2 , 12.9 ppm (2H, s) (0.01 M). See **Figure 3 A** for the ^1H NMR in D_2O

^{13}C NMR (D_2O): 176.5 ppm, 1-C, 31.5 ppm 2-C and 37.6 ppm, 3-C; $^1J_{\text{Se}} = 53$ Hz. ^{13}C NMR (DMSO-d_6): 172.9 ppm, 1-C, 29.7 ppm, 2-C and 34.9 ppm, 3-C; $^1J_{\text{Se}} = 54$ Hz. See **Figure 3 B** for the ^{13}C NMR in D_2O

^{77}Se NMR (D_2O): 381.6 ppm relative to 60% Me_2Se in CDCl_3 , 54 ppm and 198 ppm downfield from $\text{Se}(\text{CH}_2\text{COOH})_2(\text{CH}_2\text{COO})$ and $\text{Se}(\text{CH}_2\text{CH}_2\text{COOH})_2$, respectively.

IR (KBr), cm^{-1} : C=O: 1778 (sh), 1743 (s), 1725 (s), 1656 (s); C-O: 1290 (s), and 1212-1135 (several peaks); C-Se: 633, 599. IR (Nujol), cm^{-1} : C=O: 1743 (s), 1726 (s), 1714(s) and 1644 (sh); C-O: 1307 (s), and 1214-1150 (several peaks); C-Se: 636, 600. See **Figure 3 C** for the FTIR/Nujol.

3.3. Crystal structure determination.

The X-ray data for $\text{Se}(\text{CH}_2\text{CH}_2\text{COOH})_2(\text{CH}_2\text{CH}_2\text{COO})$ were collected on a Bruker-AXS SMART2K CCD diffractometer equipped with an Oxford Cryostream crystal cooling system. In excess of one full sphere of data was collected and reduced using SMART and SAINT [20]. Gaussian face indexing absorption correction, incident beam correction, structure solution, refinement and graphical illustrations were made with SHELXTL [21]. Final fractional coordinates are given in **Table 3**, and further crystallographic details are listed in **Table 4**. Complete data on the structural work of $\text{Se}(\text{CH}_2\text{CH}_2\text{COOH})_2(\text{CH}_2\text{CH}_2\text{COO})$ is deposited with the Cambridge Crystallographic Data Centre, Cambridge, CCDC no. **153717**. The positions of the two carboxylic H-atoms were refined, whereas all other H-atoms were positioned geometrically. All H-atoms were assigned an equivalent isotropic displacement factor of 1.2 that of the parent atom.

Crystallographic data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-153717. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@ccdc.cam.ac.uk].

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References

- [1] A. Schöberl, G. Lange, Über die Addition von Mercaptocarbonsäuren an ungesättigte Säuren und eine neue Darstellungsweise von Sulfoniumsalzen, *Justus Liebigs Annalen der Chemie* 599(2) (1956) 140-160.
- [2] A. Delisle, Ueber Thetincarbonensäuren, *Berichte der deutschen chemischen Gesellschaft* 25(2) (1892) 2450-2453.
- [3] A. Fredga, *Arsskrift (Year Book)*, Uppsala University, 1935.
- [4] K. Doudin, K.W. Törnroos, 2,2',2''-Thiotris(acetic acid) betaine, $S(CH_2COOH)_2(CH_2COO)$, and 2,2',2''-selenotris(acetic acid) betaine, $Se(CH_2COOH)_2(CH_2COO)$, *Journal of Molecular Structure* 1134 (2017) 611-616.
- [5] K.I. Doudin, R.K. Berge, K.J. Børve, J. Songstad, K.W. Törnroos, 2,2'-Selenobis(acetic acid), $Se(CH_2C(O)OH)_2$: an old compound with a novel structure, *Journal of Molecular Structure* 554(2-3) (2000) 149-161.
- [6] K. Prout, S. Hernandezcassou, 3,3'-Thiodipropionic and 3,3'-Dithiodipropionic Acids, *Acta Crystallogr B* 38(Jan) (1982) 338-340.
- [7] H. Ramsis, A. Ennaciri, J.L. Delarbre, L. Maury, Analysis of the vibration spectra of 3,3'-thiodipropionic acid and its alkaline salts, *J Raman Spectrosc* 29(4) (1998) 331-341.
- [8] K.I. Doudin, J. Songstad, K.W. Tornroos, 3,3'-Selenobis(propionic acid), *Acta Crystallogr C* 57 (2001) 439-440.
- [9] S.H. Strauss, The Search for Larger and More Weakly Coordinating Anions, *Chem Rev* 93(3) (1993) 927-942.
- [10] V. Gutmann, *The donor-acceptor approach to molecular interactions* Plenum Press, New York and London, 1978.
- [11] K.I. Doudin, R.K. Berge, N.Å. Frøystein, J. Songstad, Preparation and NMR studies of 3-selenaheptadecanoic and 4-selenaoctadecanoic acid, $RSe(CH_2)_nC(O)OH$ ($R = C_{14}H_{29}$, $n = 1$ and 2), and their methyl esters, *Journal of the Chemical Society, Perkin Transactions 1* (5) (2000) 723-729.
- [12] K. Doudin, *Spectroscopic and Structural Studies of Seleno-Substituted Carboxylic Acids*, Department of Chemistry, University of Bergen, Bergen-Norway, 2000.
- [13] N.P. Luthra, A.M. Boccanfuso, R.B. Dunlap, J.D. Odom, Studies in Se-77 and Te-125 Nuclear Magnetic-Resonance - Substituent Effects and Polarizability, *Journal of Organometallic Chemistry* 354(1) (1988) 51-62.
- [14] A. Novak, *Hydrogen bonding in solids correlation of spectroscopic and crystallographic data*, Structure and Bonding, Berlin, 1974, pp. 177-216.
- [15] Z. Degaszafra, M. Gdaniec, M. Grundwaldwyspianska, I. Kowalczyk, M. Szafran, Strong Hydrogen-Bonds in 1/1 and 2/1 Complexes of Pyridine Betaine with Strong Acids, *Journal of Molecular Structure* 322 (1994) 297-308.
- [16] V. Kettmann, J. Lokaj, C. Ducampsanguesa, M. Figlarz, M. Touboul, Structure of N-(2-Hydroxyethyl)Ethylendiaminetriacetic Acid, *Acta Crystallogr C* 49 (1993) 1182-1184.
- [17] N.W. Alcock, Secondary Bonding to Nonmetallic Elements, *Advances in Inorganic Chemistry and Radiochemistry* 15 (1972) 1-58.
- [18] L. Leiserowitz, Molecular Packing Modes - Carboxylic-Acids, *Acta Crystallogr B* 32(Mar15) (1976) 775-802.

[19] M. Viertorinne, J. Valkonen, I. Pitkänen, M. Mathlouthi, J. Nurmi, Crystal and molecular structure of anhydrous betaine, $(\text{CH}_3)_3\text{NCH}_2\text{CO}_2$, Journal of Molecular Structure 477(1-3) (1999) 23-29.

[20] Bruker-AXS. SMART and SAINT. Area Detector Control and Integration Software. Broker Analytical X-ray Systems Inc., Madison, Wisconsin, USA, 1998.

[21] Broker AXS. SHELXTL version 5.10. Broker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 1998

Table 1

Bond lengths (Å) and bond angles (°) in the A, B and C groups of $\text{Se}(\text{CH}_2\text{CH}_2\text{COOH})_2(\text{CH}_2\text{CH}_2\text{COO})$, with estimated standard uncertainties

	A	B	C
Bond length			
Se-C(1)	1.9666(15)	1.9699(14)	1.9611(14)
C(1)-C(2)	1.524(2)	1.521(2)	1.521(2)
C(2)-C(3)	1.513(2)	1.519(2)	1.512(2)
C(3)-O(1)	1.226(2)	1.238(2)	1.206(2)
C(3)-O(2)	1.291(2)	1.286(2)	1.325(2)
Bond angle			
Se-C(1)-C(2)	111.60(11)	111.39(10)	113.12(10)
C(1)-C(2)-C(3)	114.77(13)	113.43(12)	114.00(12)
C(2)-C(3)-O(1)	120.89(15)	119.87(13)	124.09(14)
C(2)-C(3)-O(2)	114.40(13)	117.77(13)	111.25(12)
O(1)-C(3)-O(2)	124.70(16)	122.35(14)	124.63(14)
C(1A)-Se-C(1B)	99.31(6)		
C(1B)-Se-C(1C)	97.54(7)		
C(1A)-Se-C(1C)	99.37(7)		
Σ C-Se-C	296.2(2)		
Torsion angle			
C(1C)-Se-C(1)-C(2)	120.31(11)	-140.62(10)	
C(1B)-Se-C(1)-C(2)	-140.38(11)		70.15(11)
C(1A)-Se-C(1)-C(2)		118.54(11)	170.94(10)
Se-C(1)-C(2)-C(3)	-67.92(16)	58.97(14)	68.88(14)
C(1)-C(2)-C(3)-O(1)	-156.58(16)	-11.7(2)	7.8(2)
C(1)-C(2)-C(3)-O(2)	24.3(2)	169.24(13)	-173.99(13)

Table 2

Selected non-bonding distances (Å) and non-bonding angles (°).

Se····O(1B)	2.8979(11)	< C(1A)-Se····O(1B)	159.70(5)
Se····O(2A)	2.9385(12)	< C(1B)-Se····O(2A)	162.24(5)
Se····O(1C)	3.3943(12)	< C(1A)-Se····O(1C)	132.43(5)
		< C(1B)-Se····O(2C)	122.28(5)
O(2B)····O(2A) ^a	2.4435(16)		
O(2C)····O(2B) ^b	2.6431(16)		

^a Symmetry operation used to generate equivalent atom: 1 + x, y, 1 + z^b Symmetry operation used to generate equivalent atom: 2 - x, 1 - y, 1 - z

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^2$) for $\text{Se}(\text{CH}_2\text{CH}_2\text{COOH})_2(\text{CH}_2\text{CH}_2\text{COO})$

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	Z	U(eq)
Se	2723(1)	6360(1)	2473(1)	19(1)
C(1A)	3264(3)	6928(1)	961(2)	26(1)
C(2A)	1119(3)	7330(1)	554(2)	31(1)
C(3A)	-1306(3)	7100(1)	-459(2)	26(1)
O(1A)	-2902(3)	7396(1)	-1295(2)	45(1)
O(2A)	-1519(2)	6581(1)	-334(1)	30(1)
C(1B)	6129(3)	6298(1)	3875(2)	22(1)
C(213)	6243(3)	6441(1)	5647(2)	21(1)
C(3B)	4599(3)	6084(1)	6399(2)	21(1)
O(1B)	3046(2)	5782(1)	5512(1)	28(1)
O(28)	4864(2)	6116(1)	7956(1)	29(1)
H(2B)	6270(40)	6339(7)	8550(20)	34
C(1C)	2788(3)	5719(1)	1107(2)	23(1)
C(2C)	2819(3)	5187(1)	2029(2)	22(1)
C(3C)	427(3)	5066(1)	2495(2)	22(1)
O(1C)	-1448(2)	5329(1)	2038(2)	34(1)
O(2C)	643(2)	4627(1)	3426(2)	34(1)
H(2C)	-720(40)	4556(8)	3660(20)	40

Table 4Crystal data and structure refinement parameters for $\text{Se}(\text{CH}_2\text{CH}_2\text{COOH})_2(\text{CH}_2\text{CH}_2\text{COO})$

Empirical Formula	$\text{C}_9\text{H}_{14}\text{O}_6\text{Se}$
Formula Weight ($\text{g}\cdot\text{mol}^{-1}$)	297.16
Crystal System	Monoclinic
Space Group	$\text{P2}_1/\text{c}$
a (Å)	5.5717(1)
b (Å)	24.6358(4)
c (Å)	8.4361(1)
β (°)	104.762(1)
Temperature (K)	223(2)
V (Å ³)	1119.74(3)
Z	4
Wave Length (Å)	0.71073
D_{calc} ($\text{Mg}\cdot\text{m}^{-3}$)	1.763
μ (mm^{-1})	3.364
F(000)	600
Crystal Size (mm)	0.350x0.076x0.026
Crystal Colour / habit	Colourless / Needle
θ range (°)	1.65 - 30.46
Completeness to θ (%)	100
<i>hkl</i> ranges	-7/7; -35/34, - 12/12
Reflections Collected	19036
Transmission Coeff. min. / max.	0.37668/ 0.91668
Independent Reflections	3396
$R_{\text{int}} / R_{\sigma}$	0.0270 / 0.0236
Data / parameters	3396/151
Goodness of fit (S) on F^2	1.023
$R_1(I > 2\sigma(I)) / \text{all data}$	0.0223/0.0322
$wR_2(2\sigma(I)) \text{ all data}$	0.0516/0.0534
Largest difference peak and hole ($\text{e}/\text{Å}^3$)	0.396/-0.409

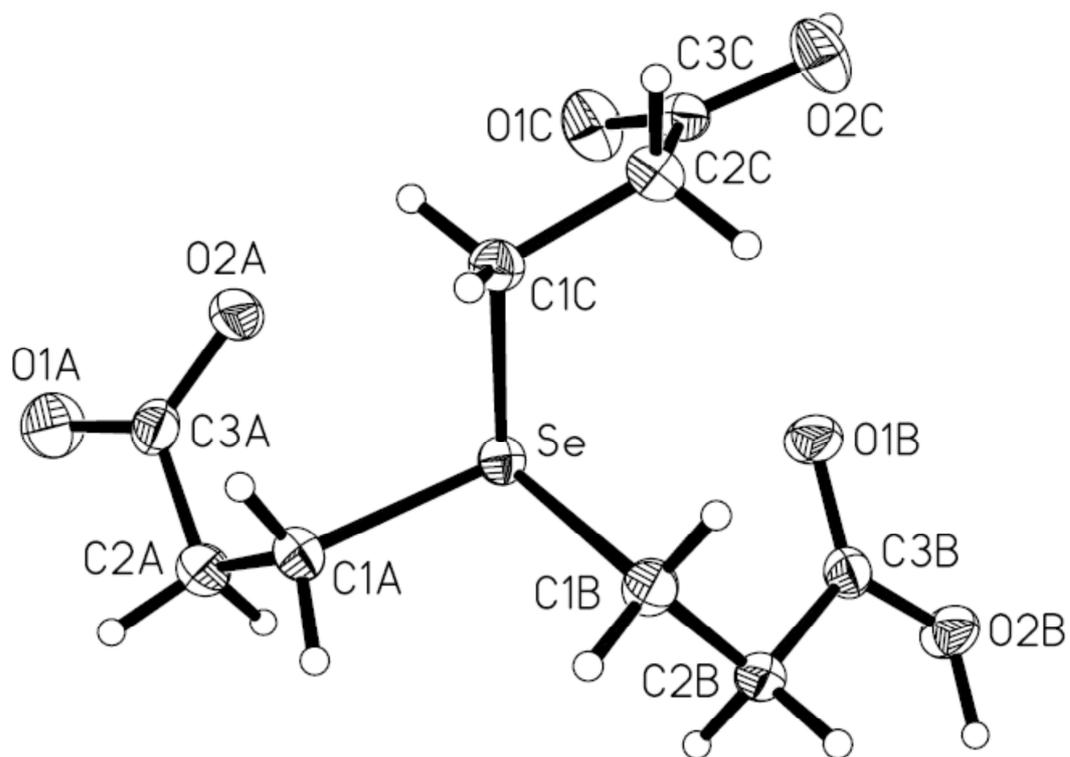


Figure 1 The molecular structure of Se(CH₂CH₂COOH)₂(CH₂CH₂COO). Atomic displacement ellipsoids are given at a probability of 50%.

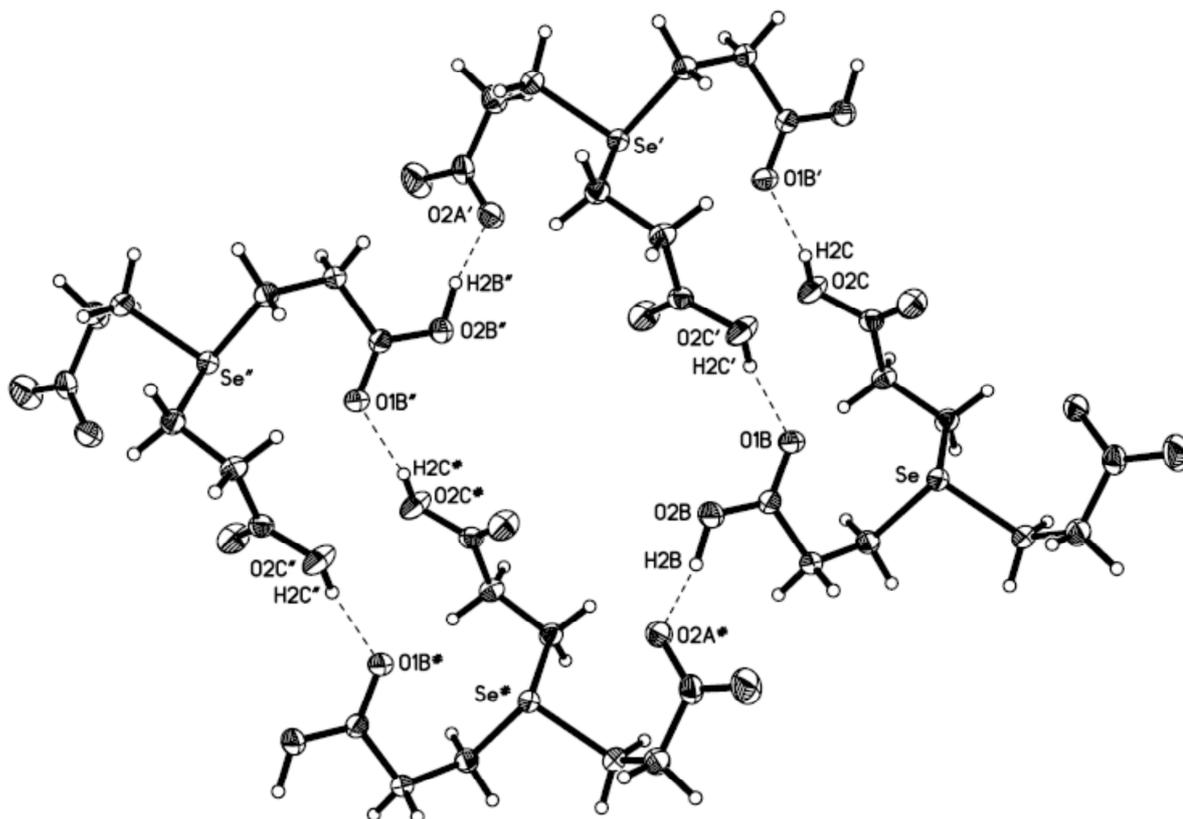


Figure 2 Representation of the hydrogen-bonding pattern in $\text{Se}(\text{CH}_2\text{CH}_2\text{COOH})_2(\text{CH}_2\text{CH}_2\text{COO})$ involving four molecules.

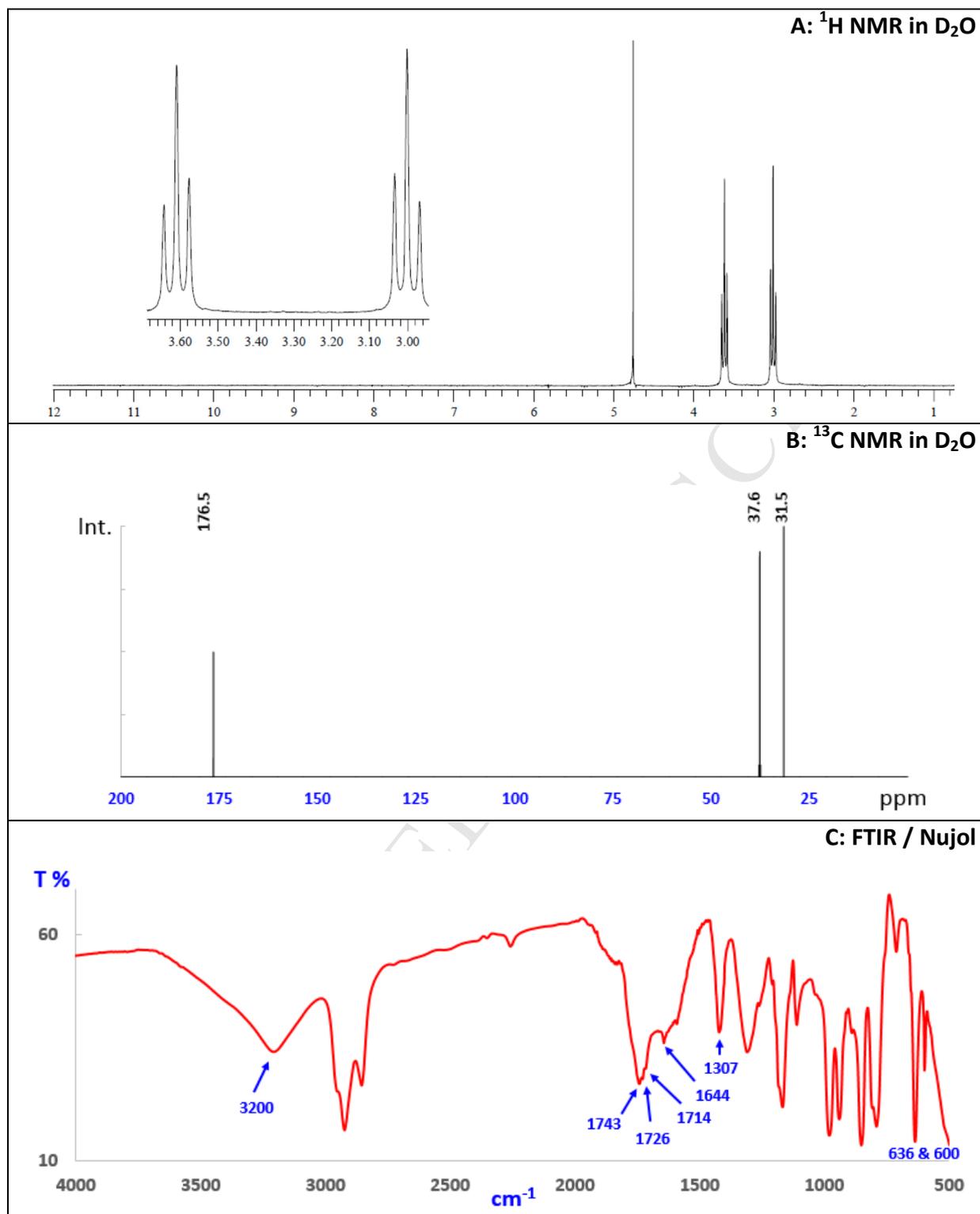


Figure 3 A: ^1H NMR, B: ^{13}C NMR and C: FTIR spectra of $\text{Se}(\text{CH}_2\text{CH}_2\text{COOH})_2(\text{CH}_2\text{CH}_2\text{COO})$

Highlights

- Se-Betaine was synthesised and characterised by FTIR, NMR and crystallography
- The selenium atom forms two strong intramolecular 1,5-Se····O interactions
- Its low solubility suggests that the interactions retained in aqueous solutions