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Abstract

The title compounds, $X(CH_2COOH)_2(CH_2COO)$, X = S, **1**, and X = Se, **2**, have been characterised by FTIR, NMR and MS and by their crystal structures at 123(2) K. The FTIR spectra show two major peaks, at 1396 and 1731 cm^{-1} in **1** and at 1390 and 1721 cm^{-1} in **2**. The ^{77}Se NMR signal of **2** at 325.5 ppm is 83.4 ppm downfield from the signal of $Se(CH_2COOH)_2$ indicating a substantial selenonium character of **2**. The two compounds are isostructural and have a pyramidal configuration. The C—X—C bond angles range from 99.29 to 103.14° in **1** and from 97.56 to 99.87° in **2**. The X — C — C = O torsion angles for the three substituents are most different; one of the carboxylic acid groups attains the *anti*-conformation with rather short S····O(H) and Se····O(H) distances, 2.744 and 2.750 Å, the other acid group is *synclinal* and with longer S····O=C and Se····O=C distances, 3.063 and 3.090 Å, whereas the carboxylate group is in the X — C — C plane with X····O—C distances of 2.869 and 2.908 Å in **1** and **2**. The presence of these strong X····O interactions is suggested to be the cause for the very low Bronsted basicity of this class of betaines preventing salts of the corresponding acids, the presently unknown $[X(CH_2COOH)_3]^+$ - cations, to be isolated. The molecules are linked together with two fairly strong but different hydrogen bonds to the carboxylate oxygen atoms with O····O distances of 2.493 and 2.580 Å in **1** and 2.489 and 2.581 Å in **2** and with one X····O=C contact, 3.244 Å in **1** and 3.209 Å in **2**. The carbonyl oxygen atoms do not participate significantly in intermolecular hydrogen bonding and there are no contacts between the heteroatoms.

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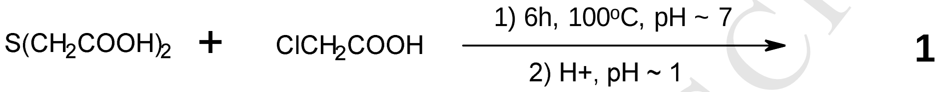
Introduction

More than a century ago Delisle [1] observed that a reaction took place when an aqueous solution of sodium sulfide and an excess of chloroacetic acid was heated. Upon acidification of the reaction mixture the dibasic acid, "dimethyl-thetin-di-karbonsaiire" (2,2’,2’’-Thiotris(acetic acid) betaine),**1**, precipitated and crystallized from a large volume of warm water.

$S(CH_2COOH)_2(CH_2COO)$ **1**

The same compound could also be prepared by prolonged heating of a neutralized aqueous solution of 2,2’-thiobis(acetic acid) and chloroacetic acid, eq. (1).



$$S(CH_2COOH)_2 + ClCH_2COOH \xrightarrow[\text{2) H+, pH} \sim 1]{\text{1) 6h, 100}^{o}\text{C, pH} \sim 7} \mathbf{1}$$

Some 40 years later Fredga [2] made, in similar ways, the corresponding selenium compound, "dimethyl-selenetin-di-karbonsaiirc" (2,2’,2’’-selenotris(acetic acid) betaine), **2**, from K_2Se or from $Se(CH_2COOH)_2$, as described for **1** in equation (1).

$Se(CH_2COOH)_2(CH2COO)$ **2**

Based upon the similar form of the crystals and their rather comparable but low solubility in water, ~5g/L, Fredga [2] concluded that the compounds might be homologous. He particularly commented upon the fact that **2**, a dibasic acid, was a fairly strong acid with a pK_{a1}, of 1.75, i.e. comparable with oxalic acid. According to Behaghel et al. [3] one may then expect the sulphur compound, **1**, to be a slightly stronger acid.

The isoelectronic nitrogen compound, tribasic nitrilotriacetic acid, $N(CH_2COOH)_3$, has been the subject of extensive studies [4, 5], particularly with regard to the ligating properties of its di- and trianions [6]. This compound, actually a betaine, $HN(CH_2COOH)_2(CH2COO)$, in the solid state, has a pK_{a1} comparable to that of **2** [7, 8]. Salts of the corresponding sulfonium and selenonium cations, the triacids, $[S(CH_2COOH)_3]^+$ and $[Se(CH_2COOH)_3]^+$, however, do not seem to have been isolated. Presumably, these cations are so acidic [2] that their salts may only be obtained from solvents of low donicity [9] and with very weakly basic anions [10]. Schoberi and Lange [11] showed that chlorides and bromides of $[S(CH_2CH_2COOH)_3]^+$ and $[S(CH_2CH_2COOH)_2(CH_2COOH)]^+$, could readily be obtained from aqueous solutions. When attempting to prepare the corresponding salts of $[S(CH_2CH_2COOH)(CH_2COOH)_2]^+$, however, only the betaine could be isolated.

This suggests that S- and Se- betaines, formally the conjugate bases of sulfonium and selenonium cations bearing two or three acetic acid groups as substituents, have a unique stability causing their Brønsted basicity to be very weak. Actually, as pointed out by Fredga [2], their most prominent feature is their ability to act as

Brønsted acids. Even the conjugate base of **2**, $[Se(CH_2COOH)_2(CH_2COO)]^-$, acts as an acid, the second dissociation constant being ~1% of the first [2]. The coordinating ability of **1** and **2**, and their anions, have not been subject of detailed studies as have the anions of $N(CH_2COOH)_3$ [6].

In an attempt to get an improved knowledge of the factors determining the stability of S- and Se- betaines like **1** and **2** we here report on their synthesis, some FTIR, MS and NMR studies together with their crystal structures. Various spectroscopic data and accurate crystal structures of several relevant reference compounds like $S(CH_2COOH)_2$ [12-14]. $Se(CH_2COOH)_2$ [13], $N(CH_2COOH)_3$ [5] and $(CH_3)_3N(CH_2COO)$ [15] have recently been published.

Results and Discussion

Synthesis and analysis

Compounds **1** and **2**, were readily obtained in a pure state from only one crystallisation from water, taking advantage of their limited solubility [2] and the high solubility of all reagents in this solvent. The yields, however, were not particularly high, ~ 20 and ~ 40% for **1** and **2**, respectively, presumably due to the law concentrations of the reagents, insufficient reaction times [1] and the large volume of water required for the final crystallisations [2]. No attempts were made to improve the yields.

The reaction as depicted by eq. (1) may suggest that the two betaines are formed by nucleophilic attack by $X(CH_2COOH)_2$ or preferably by their dianions, on the chloroacetate anion. However, dialkyl sulphides, R_2S, and dialkyl selenides, R_2Se, are known to be fairly powerful nucleophiles toward aliphatic carbon [16] while the anions of $S(CH_2COOH)_2$, $Se(CH_2COOH)_2$ appear to be poor thio- and seleno-nucleophiles [17, 18]. In fact, $S(CH_2COOH)_2$ is known to form only traces of S-alkylated products after long reaction times, even when using $BrCH_2COOH$ instead of $ClCH_2COOH$ [11]. The poor nucleophilicity of $S(CH_2COOH)_2$ was further demonstrated by the present attempts to alkylate this compound by CH_3I in CD_2OD. No trace of the iodide of $[(CH_3S(CH_2COOH)_2]^+$ or any other S-alkylated products could be detected, only the deuterated monomethyl and dimethyl esters were slowly formed, presumably by acid catalysed esterification of the diacid.

Apparently, the mechanism for the formation of the betains **1** and **2** is rather a two-step elimination-addition reaction through an intermediate carbenium type carboxylate anion, $[^+CH2COO^-]$, being formed from the haloacetate anion [11]. This mechanism may explain the ease by which $S(CH_2COOH)_2$ reacts with 2-halopropanoic acids and 2-propenoic acid [11].

FTIR spectra

The KBr-FTIR spectra of the two compounds are, with the obvious exception of the C — X bands, in principle quite similar, suggesting similar structures. However, the spectra are indeed quite complicated, reflecting a significant amount of asymmetry which can have its cause in the two different groups being attached to the central chalcogen atoms. Therefore, no attempts were made to assign the various peaks, particularly since solution spectra could not be obtained due to the low solubility of **1** and **2** in the usual organic solvents. One may note that the carbonyl groups, essentially a singlet in $S(CH_2COOH)_2$, [14], and in $Se(CH_2COOH)_2$, [19], give rise to several peaks and shoulders in the 1640 — 1790 cm^{-1} range. The high-frequency shoulder to the main C=O peaks, 1731 cm^{-1} in **1** and 1721cm^{-1} in **2**, at ~1790 cm^{-1} (**1**) and at ~1784 cm^{-1} (**2**), also detectable in Nujol, is probably due to a ‘’free” carboxylic group whereas the weaker peaks, at 1654 cm^{-1} in **1** and 1643 cm^{-1} in **2** can be assigned to ν_{as} (COO^-), observed at 1631 cm^{-1} in $(CH_3)_3N(CH_2COO)$ [15].

No significant peaks could be detected in the 1400 — 1600 cm^{-1} region suggesting that the strong peaks at 1396 cm^{-1} (**1**) and at 1390 cm^{-1} (**2**) are due to ν_s (COO^-) [15]. If this latter assignment is correct it is apparent that the carboxylate group is significantly weakened, presumably due to interaction with the chalcogen atoms, since the corresponding peak in $(CH_3)_3N(CH_2COO)$ is observed at 1483 cm^{-1} [15]. The large number of strong peaks in the 1300-1100 cm^{-1} region, the region for ν(C-O) and $\nu(CH_2)$, and combinations of these [15], reflects the asymmetry of the present compounds.

Mass spectra

The mass spectra of the compounds are in principle similar but different in the sense that a number of peaks in the mass spectrum of **2** are far stronger than in the spectrum of **1**. This is as anticipated when taking into account the higher polarisability of the selenium atom and thus its better ability to form positively charged species. Thus, whereas the molecular peak at m/z 208 for **1** is very weak, ~ 1%, the corresponding peak for **2** is about 20%. Of particularly high intensity in the spectrum of **2** are the peaks at m/z 198 and at 180, probably representing $[Se(CH_2COOH)_2]^+(-CO_2)$ and the cyclic anhydride $[Se(CH_2COO)_2]^+(-CO_2, H_2O)$, respectively.

NMR spectra

The signal in the ^{77}Se NMR spectra of $Se(CH_2COOH)_2(CH_2COO)$, **2**, in water gives rise to a sharp singlet at 325.5 ppm relative to Me_2Se, 83.4 ppm downfield from $Se(CH_2COOH)_2$ [13]. A comparison with the well documented downfield shifts from Re_2Se to Re_3Se^+ is not possible since this downfield shift in known to be strongly dependent upon the size of the alkyl group, i.e. ~256 ppm ($Me_2Se \rightarrow Me_3Se^+$) and ~150 ppm ($Et_2Se \rightarrow Et_3Se^+$) [20]. However, the observed shift difference from $Se(CH_2COOH)_2$ suggests that the selenium atom in **2** has a substantial selenonium character. ESCA studies on $S(CH_2COOH)_2$ and $S(CH_2COOH)_2(CH_2COO)$, **1**, have similarly shown that the latter compound is essentially a sulfonium salt [21].

The ^{1}H NMR spectra in carefully dried DMSO-d_6 the only organic solvent in which the compounds were sufficiently soluble at room temperature, revealed only one type of methylene proton, at 4.30 ppm in **1** and at 4.15 ppm in **2**. Apparently the protons exchange too rapidly to allow the detection of two types of protons. Traces of water in the applied solvent gave rise to complicated and irreproducible spectra, presumably due to an equilibrium between adducts of **1** or **2** with DMSO and water and in favour of the latter.

Crystal structures

Being isostructural, the compounds are most similar with regard to torsion angles, intra- and intermolecular X---O contacts and hydrogen bond pattern. Thus, **Figure 1** only shows the structure of **1**; the bond lengths and bond angles in both compounds are listed in **Table 1**, whereas torsion angles are listed in **Table 2**. A survey of the most important non-bonding distances together with angles is given in **Table 3**. The C3-C4-O3(O4) part of the molecules represents the unique carboxylate group. -C-COO, while the two carboxylic acid groups are linked to the central atom through C1 and C5.

As suggested by the FTIR study the two compounds are, indeed, asymmetric. The C-X-C bond angles are significantly different, ranging from 99.29(6)° to 103.14(5)° in **1** and from 97.56(6)° to 99.87(6)° in **2**, the larger bond angle being C1-X-C3, the angle between bonds to one carboxylic acid group and the carboxylate group. This widening of the C1-X-C3 bond angle appears to be due to one of the carboxylate oxygen atoms, O4, being located only 2.8690(9) and 2.9076(12) Å from the central chalcogen atom in **1** and **2**, respectively, and close to the plane defined by X, C3 and C4; the X-C3-C4-O4 torsion angle being only 4.54(13)° in **1** and 4.12(18)° in **2**. The two remaining C-X-C bond angles are only slightly larger than the bond angle in Me_2S, 98-8(2)° [22], and 96.3(1)° in Me_2Se [23]. The X-C, C-C, C-O(O-H) and C=O bonds and all bond angles in the organic fragments are as expected. However, the X-C5 bond lengths appear to be slightly elongated and the X-C3-C4 bond angle is somewhat larger than the X-C1-C2 and X-C5-C6 bond angles. The C-O bond lengths follow the usual pattern; ~ 1.21 Å for C=O, ~1.31 Å for C-O(O-H) and intermediate, 1.24-1.26 Å, for the carboxylate C-O bonds [15]. The latter two bond lengths, however, are in both compounds slightly but significantly different. The lengthening of the C-O3 bond may be attributed to the stronger hydrogen bond in which O3 is involved; see below.

The shortest X···O distance is to O5, a hydroxyl oxygen atom. 2.7436(9) Å in **1** and 2.7500(11) Å in **2,** see Figure 2. It is notable that the one carboxylic acid group to which O5 belongs is forced into a rare *anti*-conformation [24] to allow for this short X···O5 contact; the C1-X-C5-C6 torsion angle being 176.41(7)° in **1** and 178.58(10)° in **2**. This oxygen atom is not close to the C3-X-C5 plane and is not significantly influencing the C3-X-C5 bond angle. Actually, O5 is located in such a position that the C1-Se···O5 angle is reasonably close to the Ideal of 180° for secondary bonding, 157.58(4)° in **1** and 154.71(5)° in **2**. Likewise, the C5-X···O4 angle is 154.21(4)° and 149.33(5)° in **1** and **2**, respectively.

The third substituent, the carboxylic acid group linked to X by C1, attains a *synclinal* conformation resulting in fairly long X···O2 distances, 3.0629(4) Å in **1** and 3.0903(12) Å in **2**. The O2 oxygen atom, being a carbonyl oxygen atom, also serves as a link between two chalcogen atoms, the intermolecular X···O distance being 3.2441(11) Å in **1** and 3.2094(12) Å in **2**. All other X···O distances in the molecules are distinctly longer than the sum of the van der Waals' radii, 3.25 Å for S and O and 3.40 Å for Se and O. Since the three X···O distances in the two compounds are quite comparable one may conclude that Se···O contacts are stronger than the corresponding S···O contacts. This apparent stabilization of **2** as compared with **1** may actually suggest $[Se(CH_2COOH)_3]^+$ to be a stronger Brønsted acid than $[S(CH_2COOH)_3]^+$. There are no intermolecular contacts between the X atoms. Thus. one may in principle consider the two compounds as hexacoordinated species with three X—C bonds and three X···O contacts.

The molecules are further linked, see **Table 3**, by fairly short but different hydrogen bonds between O1-H1 and O4, with O···O distances of 2.5795(12) Å (**1**) and 2.5811(16) Å (**2**), and between O5-H5 and O3 with O···O distances of 2.49245(11) Å in **1** and 2.4888(16) Å in **2**, see Figure 3. The angles at the H1 and H5 atoms are in the 160-175° range. It is notable that the two chemically different H atoms refine to about the same geometrical values in each of the two structures, supporting the conclusion that the H-bond involving H5 is significantly stronger than that involving H1. Whereas O2, as mentioned above, is in fairly close contact with two chalcogen atoms and these two atoms only, O6 does not seem to be located close to any X or H(-O) atoms. With this arrangement of hydrogen bonds it is evident that the carboxylic acid units do not form the usual dimerised H-bonding pattern characteristic for most carboxylic acids [24].

Concluding Remarks

The present study has revealed that compounds **1** and **2** are structurally most similar but are highly asymmetric species with regard to torsion angles of the substituents, C-X-C bond angles, with slightly different X-C bond lengths and with three different intramolecular 1,4-X···O interactions. As viewed by the X···O distances the strength of these interactions are X···O (hydroxyl) › X···O-C (carboxylate) » X···O=C (carboxylic). The crystal structures have further revealed the presence of two strong intermolecular hydrogen bonds to the carboxylate oxygen atoms whereas the carboxylic acid C=O oxygen atoms do not take part in H-bonding. These latter observations are the probable cause for the complex FTIR spectra in the carbonyl region.

Finally, some comments on the distinct difference in Brønsted acid-base behaviour of chalcogen cations containing three or two acetic groups as substituents, acting as very strong acids [2], and cations containing three or two propanoic acid groups, acting as moderately strong acids [11]. Apparently, the conjugate bases of the former owe their stability to the presence of two strong 1,4-X···O interactions, X···O (hydroxyl) and X···O (carboxylate), as observed in **1** and **2**. These interactions appear to be so strong that they will survive in aqueous media; cf. the limited solubility of the two betaines in water [2]. The conjugate base of $[X(CH_2CH_2COOH)_3]^+$, however, may not experience this type of stabilization; cf. the elongated structure of $S(CH_2CH_2COOH)_2$ [25] and $Se(CH_2CH_2COOH)_2$ [26]. The easiness by which salts of $[S(CH_2CH_2COOH)_2(CH_2COOH)]^+$ can be isolated [11] suggests that the likely presence of only one 1,4-S···O interaction in the corresponding conjugate base which does not afford sufficient stabilization.

Experimental Section

Materials and instrumental. Chloroacetic acid, Fluka puriss, was used as received. Selenium, Merck, was of 99.5% purity. 2,2'-Thiobis(acetic acid), thiodiglycolic acid, Aldrich 98%, was crystallized from diethyl ether/hexane prior to use. All operations were carefully performed under argon and in argon-flushed solvents. The FTIR spectra were recorded with an QMNIC 410 FT-IR system. NMR spectra were recorded at a ^1H frequency of 600 MHz on a Bruker DRX-600 spectrometer. Internal TMS and internal Me_2Se were used as chemical shift references. Mass spectra were obtained using a Fisons Micromass 7070E double focusing instrument using the direct inlet at the minimum temperature for volatilisation; the instrument was operated at 70 eV electron bombardment energy.

2,2',2"-Thiotris(acetic acid) betaine, $S(CH_2COOH)_2$(CH2COO), 1: To a solution of 1.5 g, 0.01 mol, of $S(CH_2COOH)_2$ in 30 ml H_2O, neutralized with $NaHCO_3$, was slowly added a neutralized solution of 0.94 g, 0.01 mol, of $ClCH_2COOH$, also in 30 ml H_2O. The reaction mixture was refluxed for 2 h. After cooling the solution was acidified to pH ~ 1 with sulphuric acid. The solvent was then removed in vacuum and the residue washed with some cold water. A yield of 0.44 g, 21%, of colourless crystals, suitable for the X-ray study, was obtained from one crystallization from water. mp 176°C. ^1H NMR in DMSO-d_6, 600 MHz, 4.30 ppm (s); ^{13}C NMR in H_2O (with D_2O as lock signal); 44.1 (s), 168.2 (s) ppm. FTIR (KBr), cm^{-1}, C = 0: ~ 1790 (sh), 1731 (s), 1654(w), 1396(s); C-S: 757, 687. MS (m/e) for ^{32}S: 208(Mw) < 1%, 164($-CO_2$) 6%, 150($-CH_2COO$) 7%, 132 ($-CH_2COO$, H_2O) 10%.

2,2",2" - Selenotris(acetic acid) betaine, $Se(CH_2COOH)_2(CH_2COO)$, 2. To 1.74 g, 0.022 mol, black selenium powder, suspended in 75 ml water, was added slowly a solution of 1.89 g, 0.050 mol, $NaBH_4$ in 50 ml water. The reaction mixture was stirred until the colour disappeared and then additionally for 0.5 h. To this reaction mixture was added slowly 6.14 g, 0.065 mol, chloroacetic acid in 100 ml water, neutralized with $NaHCO_3$. This mixture was refluxed for 2 h, then cooled and acidified with sulphuric acid to pH ~ 1.5. 25 ml THF was added to complete the precipitation. The residue was dissolved in warm water, filtered and set aside overnight at 0 °C. Yield 2.12 g, 38%, mp 180 °. ^1H NMR in DMSO-d6, 600 MHz, 4.15 ppm (s). ^{13}C NMR in H_2O (D_2O as lock signal); 41.6 (s), $^1J_{Se\text{-}C}$ = 54 Hz, 169.2 (s) ppm. ^{77}Se NMR in H_2O: 83.4 ppm rel $Se(CH_2COOH)_2$, 325.5 ppm rel. 60% Me_2Se in $CDCl_3$. FTIR(KBr), cm^{-1}, C=O: 1784 (sh), 1721 (s), 1643(w), 1390 (s), C-Se: 671, 649. MS (m/e) for ^{80}Se: 256(Mw) 18%, 238 (-H_2O) 13%, 212 (-COO) 2%, 198 (-CH_2COO) 80%, 180 (-CH_2COO, H_2O) 95%, all fragments showed the expected isotopic distribution.

Attempted alkylation of $S(CH_2COOH)_2$ with methyl iodide. A solution of $S(CH_2COOH)_2$ and methyl iodide in CD_3OD was left in a NMR tube for six days at room temperature. No trace of S-methylated product was detected. The diacid was slowly converted into its mono-trideuterated methyl ester and, more slowly, into its bis-trideuterated methyl ester as viewed by ^1H and ^{13}C NMR spectra. No methyl esters derived from CH_3I could be detected.

X-ray crystallography.

Both compounds yielded hard, colourless strongly rhombic prisms. The X-ray data were collected on a Bruker-AXS SMART 2K CCD diffractometer equipped with an Oxford Cryostream crystal cooling system. In excess of a full reflection sphere were collected by means of 0.3° ω-scans. The data were collected and reduced using SMART and SAINT [27]. Gaussian face indexing absorption correction, incident beam correction, structure solution, refinement and graphical illustrations were made with SHELXTE [28]. Hydrogen atoms in idealised positions were given isotropic displacement parameters equal to 1.5 times the equivalent isotropic displacement factor of the parent carbon atom. The two carboxylic H-atoms were isotropically refined in both structures. Further crystal data on the two structures are given in Table 4.

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-149514 & 149515. 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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Table 1

Bond lengths (Å) and bond angles (°) in $X(CH_2COOH)_2(CH_2COO)$, X = S, **1**, left, and X = Se, **2**, right, with estimated standard uncertainties

	X=S	X=Se
X - C(1)	1.8058(11)	1.9439(14)
X - C(3)	1.8107(10)	1.9463(15)
X C(5)	1.8156(11)	1.9540(14)
C(1) - C(2)	1.5257(14)	1.519(2)
C(3) - C(4)	1.5203(14)	1.517(2)
C(5) - C(6)	1.5202(14)	1.517(2)
C(2) - O(1)	1.3138(13)	1.3162(17)
C(2) - O(2)	1.2107(13)	1.2138(18)
C(4) - O(3)	1.2643(13)	1.2642(18)
C(4) - O(4)	1.2449(13)	1.2484(18)
C(6) - O(5)	1.3098(14)	1.3128(19)
C(6) - O(6)	1.2174(13)	1.2158(18)
O(1) - H(1)	0.84(2)	0.81(3)
O(5) - H(5)	0.92(2)	0.95(3)
<C(1) - X - C(3)	103.14(5)	99.87(6)
<C(1) - X - C(5)	99.29(5)	97.88(6)
<C(3) - X - C(5)	100.13(5)	97.56(6)
Σ<C- X-C	302.56(15)	295.31(18)
<X - C(1) - C(2)	110.50(7)	109.08(10)
<X-C(3)-C(4)	112.38(7)	111.15(10)
<X - C(5) - C(6)	111.18(7)	108.97(10)
<C(1) - C(2) - O(1)	111.24(9)	111.89(13)
<C(1) - C(2) - O(2)	122.46(9)	122.31(13)
<O(1) - C(2) - O(2)	126.21(10)	125.72(13)
<C(3) - C(4) - O(3)	113.54(9)	113.89(13)
<C(3) - C(4) - O(4)	118.68(9)	118.54(13)
<O(3) - C(4) - O(4)	127.79(10)	127.56(14)
<C(5) - C(6) - O(5)	113.12(9)	112.65(12)

<C(5) - C(6) - O(6)	120.21(10)	120.98(14)
<O(5) - C(6) - O(6)	126.67(10)	126.37(14)

Table 2

Torsion angles (°)

	X = S	X = Se
C(3) - X - C(1) - C(2)	94.66(8)	96.63(10)
C(1) - X - C(3) - C(4)	-69.69(8)	-68.70(11)
C(1) - X - C(5) - C(6)	176.41(7)	178.58(10)
C(3) - X - C(5) - C(6)	-78.33(8)	-80.30(11)
C(5) - X - CM - C(2)	-162.56(7)	-164.22(10)
C(5) - X - C(3) - C(4)	-171.82(7)	-168.11(10)
O(1) - C(2) - C(1) – X	-137.52(8)	-139.53(11)
O(2) - C(2) - C(1) X	45.84(13)	43.50(17)
O(3) - C(4) - C(3) X	-175.21(8)	-174.99(11)
O(4) - C(4) - C(3) - X	4.54(13)	4.12(18)
O(5) - C(6) - C(5) X	9.05(11)	11.72(15)
O(6) - C(6) - C(5) - X	-171.13(8)	-168.13(12)

Table 3

Selected intra- and intermolecular non-bonding distances (Å) and angles (°)

	X = S	X = Se
X···O(2)	3.0629(9)	3.0903(12)
X···O(2) [a, b]	3.2441(11)	3.2094(12)
X···O(4)	2.8690(9)	2.9076(12)
X···O(5)	2.7436(9)	2.7500(11)
O(1) ···O(4) [c, d]	2.5795(12)	2.5811(16)
O(5)···O(3) [e, f]	2.4926(11)	2.4888(16)
H1···O(4) [c, d]	1.77(2)	1.80(3)
H5···O(3) [e, f]	1.58(2)	1.54(3)
<O(1)-(H1) ···O(4) [c, d]	160(2)	164(3)
<O (5)-(115) ···O(3) [e, f]	174(2)	175(3)

Symmetry transformations: a) 1-x, -0.5+y, 1.5-z , b) 1-x, -0.5+y, 0.5-z, c) 1-x, -y, 1-z , d) 1-x, 1-y, 1-z , e) x, -0.5-y, 0.5+z , f) x, 0.5-y, -0.5+z. (a, c, e apply to **1**, b, d, f to **2**)

Table 4

X-ray crystallographic data of **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_6H_8O_6S$	$C_6H_8O_6Se$
Formula weight	208.18	255.08
Temperature	123(2) K	123(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 9.2875(15) Å	a = 9.4433(17) Å
	b = 6.5263(16) Å	b = 6.5035(8) Å
	c = 13.424(2) Å	c = 13.5573(15) Å
	• = 101.893(10)°	• = 101.544(12)°
Volume	796.2(3) Å^3	A3 815.8(2) Å^3
Z	4	4
Density (calculated)	1.737 Mg/m^3	2.077 Mg/m^3
Absorption coefficient	0.402 mm^{-1}	4.599 mm^{-1}
Absorption correction	Gaussian face indexed	Gaussian face indexed
Transmission min/max	0.8622 / 0.9764	0.1689 / 0.4892
F(000)	432	504
Crystal size	0.50 x 0.20 x 0.06 mm^3	0.35 x 0.20 x 0.18 mm^3
Theta range for data collection	2.24 to 33.23°	2.20 to 33.03°
Index ranges	$-14 \leq h \leq 14$, $-9 \leq k \leq 9$, $-19 \leq l \leq 20$	$-14 \leq h \leq 14$, $-9 \leq k \leq 9$, $-20 \leq l \leq 20$
Reflections collected	14117	14272
Independent reflections	2927 [R(int) = 0.0258]	2971 [R(int) = 0.0214]
Completeness to theta	95.5%	96.5%
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / parameters	2927 / 126	2971 / 127
Goodness-of-fit on F2	1.044	1.252
Final R indices [I>2sigrna(I))	RI = 0.0295. wR2 = 0.0720	RI = 0.0235, wR2 = 0.0509
R indices (all data)	RI = 0.0385, wR2 = 0.0745	RI = 0.0261, wR2 = 0.0514

Extinction coefficient	0	0.0141(7)
Largest diff. peak and hole	0.524 and -0.341 e. Å^{-3}	0.543 and -0.433 e. Å^{-3}

Figure text

Figure 1. Illustration of compound **1**, isostructural with **2**. Atomic displacement is shown at the 50% probability level

Figure 2. The dotted lines indicating the three 1,4-X···O intramolecular interactions

Figure 3. The red dotted lines indicating the O3···H···O5, and the blue dotted lines indicating the O1···H···O4 intermolecular hydrogen bonding in 2,2',2''-selenotris(acetic acid) betaine.

Text for Contents list

Structural analysis demonstrates that the two compounds are isostructural and of pyramidal configuration. It is argued that the presence of three intramolecular 1,4—X···O interactions is the cause of the high Brønsted acidity of $[X(CH_2COOH)_3]^+$

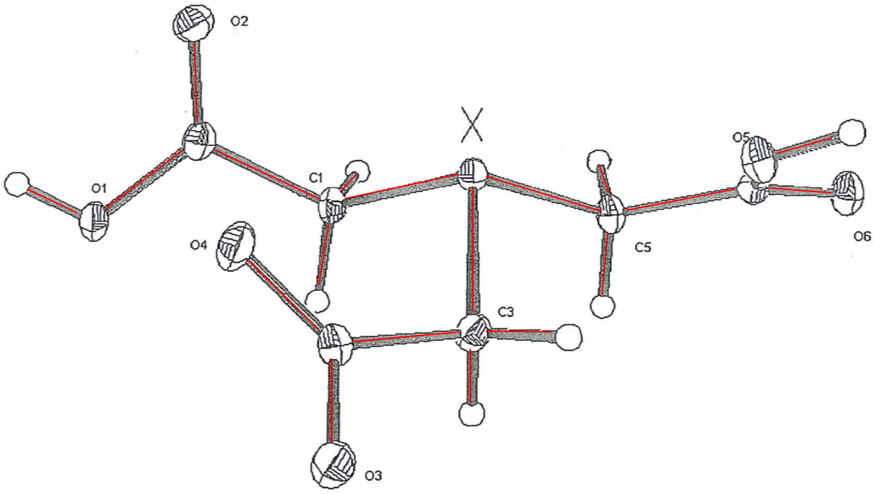

Figure 1: X = S, Se

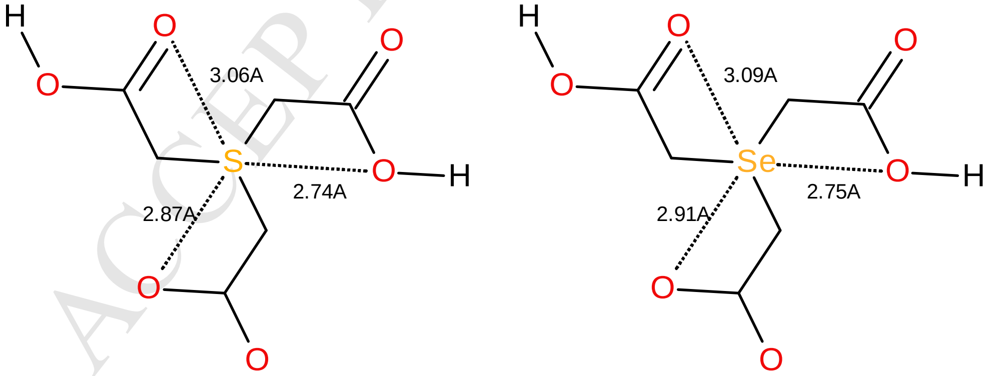

Figure 2:

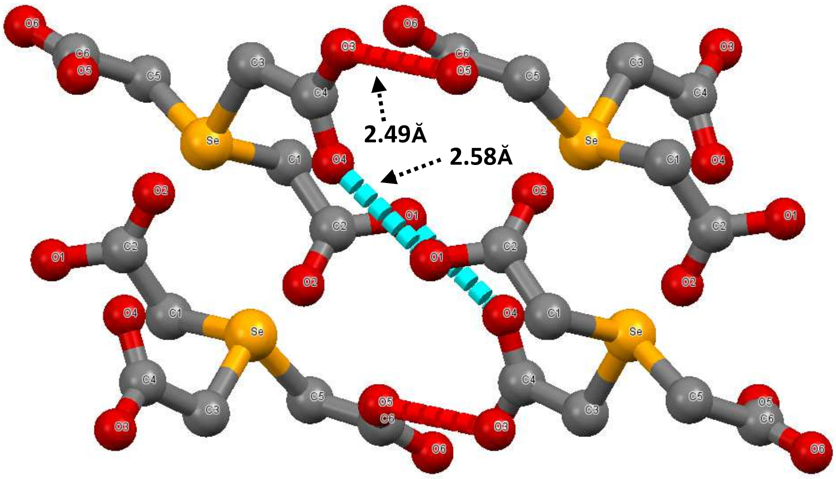

Figure 3:

Highlights

- Betains **1**, **2** were synthesised and characterised by FTIR, NMR, MS and crystallography
- The two compounds are isostructural and have a pyramidal configuration
- The formation mechanism of the Betains is a two-step elimination-addition reaction
- The three 1,4-X···O intramolecular interactions is the cause of high Brønsted acidity