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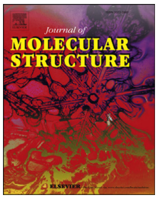

2,2′,2″-Thiotris(acetic acid) betaine, $S(CH_2COOH)_2(CH_2COO)$, and 2,2′,2″-selenotris(acetic acid) betaine, $Se(CH_2COOH)_2(CH_2COO)$

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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.

1. 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.

$$S(CH_2COOH)_2(CH_2COO) \tag{1}$$

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).

$$S(CH_2COOH)_2 + (ClCH_2COOH) \xrightarrow[2)H^+,\ pH\sim1]{1)6h,\ 100^\circ C,\ pH\sim7} \mathbf{1}$$

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 eq. (1).

$$Se(CH_2COOH)_2(CH_2COO) \tag{2}$$

Based upon the similar form of the crystals and their rather comparable but low solubility in water, ~5 g/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],

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particularly with regard to the ligating properties of its di- and trianions [6]. This compound, actually a betaine, $HN(CH_2COOH)_2(CH_2COO)$, 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.

2. Results and discussion

2.1. Synthesis and analysis

Compounds **1** and **2**, were readily obtained in a pure state from only one crystallization 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, $[^+CH_2COO^-]$, 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].

2.2. 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 1721 cm^{-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.

2.3. 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.

2.4. 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 ^1H 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.