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The Crystal Structure of Tetraethylammonium *O*-Ethylxanthate

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In chelates involving transition metal ions with the xanthate anion, $ROCS_2^-$, equivalent M–S bond distances are usually observed. In contrast however, asymmetric coordination of the xanthate anion is often found when the central atom is a main Group V or VI element [1]. The asymmetric coordination of the xanthate ligand is invariably reflected in the associated C–S bond distances with the C–S bond of shorter length being formed with the sulphur atom involved in the weaker M–S interaction. A similar C–S bond asymmetry arises in the anions contained in the sodium salt of the *O*-ethylxanthate anion, exa, for which significant differences are found in the C–S distances [2]. In fact the difference between the short and long C–S distances in this salt is of the order of 0.07 Å, which is comparable to the differences observed in the structures of $As(exa)_3$ [3] and $Sb(exa)_3$ [4]. An inspection of the interionic contacts in the sodium salt reveals that there are near Na···S and Na···O contacts which may be responsible for the distortion of the anion geometry, in particular the C–S and C–O bonds. Similar asymmetric C–S distances have been reported for the potassium salt of exa [5] but here the differences between the relevant interatomic distances fall within the rather large estimated standard deviation values. In order to obtain accurate interatomic distances for the isolated exa anion we have determined the X-ray structure of the tetraethylammonium salt of exa, hereafter $[NEt_4][exa]$, which was chosen in the hope that interactions of the type observed in the alkali metal salts [4, 5] would be avoided.

$[NEt_4][exa]$ was prepared by reacting equimolar proportions of K(exa) and NEt_4Cl in methanolic solution and crystals suitable for X-ray diffraction studies were obtained by the slow evaporation of this solution. Intensity data for 4550 reflections were collected at room temperature on a CAD-4F diffractometer fitted with CuKα radiation (nickel-filtered) $\lambda = 1.5418$ Å. The remeasurement of the intensity values of three reference reflections during the data collection indicated that these values had decreased steadily to about 94% of their initial values at the completion of the intensity measurements; correction was made for this intensity variation. Correction was also made for Lorentz and polarization effects as well as for absorption [6]. After the $I \geqslant 3\sigma(I)$ criterion of observability was applied to the 3219 unique reflections there were 2229 reflections remaining which were used in the subsequent analysis. The density of crystals of $[NEt_4][exa]$ was measured in a benzene/1,2-dibromoethane mixture and indicated presence of solvent of crystallization, which was ascribed to water such that there are two water molecules per unit cell. This feature was also confirmed from the results of microanalyses, hydrogen-1, and carbon-13 NMR of the bulk product.

Crystal Data: $[NEt_4][exa]$, $0.5H_2O$, $C_{11}H_{26}NO_{1.5}S_2$, M = 260.5, monoclinic, $P2_1/m$ (C^2_{2h}, No. 11), $a = 7.343(2)$, $b = 13.456(2)$, $c = 15.674(2)$ Å, and $\beta = 98.92(1)°$, $U = 1496$ Å^3, $D_m = 1.16$, $Z = 4$, $D_c = 1.157$ Mg m^{-3}, F(000) = 552, CuKα (nickel-filtered) radiation, $\lambda = 1.5418$ Å, $\mu = 2.93$ mm^{-1}, absorption corrections applied (max. and min. transmission factors 0.6638 and 0.3814).

The structure was solved using the direct-methods routine EEES in SHELX-76 [6] with a starting set which had been selected from a convergence map based on a set of E-values which had been renormalized to strengthen weak parity groups. The asymmetric unit is comprised of two exa anions each of which lies on a crystallographic mirror plane and one NEt_4 cation situated in a general position, so that the overall stoichiometry is 1:1. Refinement of the positions and individual isotropic thermal parameters for all non-hydrogen atoms yielded *R* 0.28. The structure was refined by full-matrix least-squares methods in which the function $\Sigma w\Delta^2$ was minimized where $\Delta = \|F_o| - |F_c\|$ and *w* was the weight applied to each reflection which was initially set at $w = 1.0$ [6]. All hydrogen atoms were located from subsequent difference maps and were included in the model. Overall isotropic thermal parameters for the methylene and methyl hydrogen atoms were refined with the coordinates of the hydrogen atoms. Anisotropic thermal parameters were introduced for all non-hydrogen atoms and a weighting scheme, $w = 6.4/[\sigma^2(F) + 0.001|F|^2]^{1/2}$, included; at convergence R and R_w were 0.071 and 0.078 respectively. A final difference map revealed an electron density peak of 1.5 e Å^3, located on the mirror plane, which was thought to be due to the presence of a molecule of water or methanol which would be consistent with the measured density but attempts to refine this peak were unsuccessful.

All calculations were performed using the SHELX-76 program system [6]. The fractional atomic coordinates and their estimated standard deviations for all non-hydrogen atoms are listed in Table I and the

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TABLE I. Fractional Atomic Coordinates for Non-hydrogen Atoms for [NEt$_4$] [exa]. (e.s.d.s in Parentheses).

Atom	*x/a*	*y/b*	*z/c*
Exa A			
S(1)	0.7940(3)	0.25	0.0804(1)
S(2)	0.6245(3)	0.25	0.2428(1)
C(1)	0.6125(9)	0.25	0.1344(4)
O(1)	0.4386(6)	0.25	0.0925(2)
C(2)	0.4038(10)	0.25	−0.0018(4)
C(3)	0.1966(10)	0.25	−0.0272(4)
Exa B			
S(1)	0.1062(3)	0.25	0.5963(1)
S(2)	0.3829(3)	0.25	0.7577(1)
C(1)	0.3189(9)	0.25	0.6502(4)
O(1)	0.4710(6)	0.25	0.6066(2)
C(2)	0.4396(10)	0.25	0.5141(4)
C(3)	0.6247(13)	0.25	0.4862(5)
Cation			
N(1)	0.1392(5)	0.0090(3)	0.2515(2)
C(4)	0.2843(7)	−0.0552(4)	0.3068(3)
C(5)	0.4492(8)	0.0026(4)	0.3505(3)
C(6)	0.2158(7)	0.0582(4)	0.1760(3)
C(7)	0.2833(9)	−0.0162(5)	0.1148(4)
C(8)	−0.0181(7)	−0.0631(4)	0.2186(3)
C(9)	−0.1754(8)	−0.0124(4)	0.1609(4)
C(10)	0.0739(7)	0.0967(4)	0.3023(3)
C(11)	−0.0071(9)	0.0661(6)	0.3813(4)

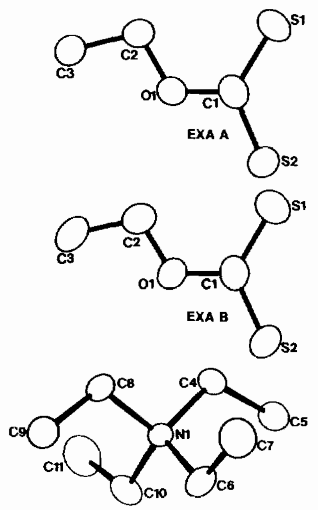

Fig. 1. The numbering scheme used for [NEt$_4$] [exa]. Note that the exa anions lie on a crystallographic mirror plane and therefore only half of each anion is included in the asymmetric unit.

TABLE II. Bond Distances (Å) for Non-hydrogen Atoms for [NEt$_4$] [exa].[a]

Atom	Distance
Exa A	
S(1)–C(1)	1.686(7)
S(2)–C(1)	1.688(6)
C(1)–O(1)	1.342(8)
O(1)–C(2)	1.460(7)
C(2)–C(3)	1.51(1)
Exa B	
S(1)–C(1)	1.657(7)
S(2)–C(1)	1.678(6)
C(1)–O(1)	1.397(8)
O(1)–C(2)	1.432(7)
C(2)–C(3)	1.49(1)
Cation	
N(1)–C(4)	1.521(6)
C(4)–C(5)	1.502(7)
N(1)–C(6)	1.530(6)
C(6)–C(7)	1.507(8)
N(1)–C(8)	1.522(6)
C(8)–C(9)	1.508(8)
N(1)–C(10)	1.521(6)
C(10)–C(11)	1.509(8)

[a] C–H distances in the range 0.50(7) to 1.23(6) Å.

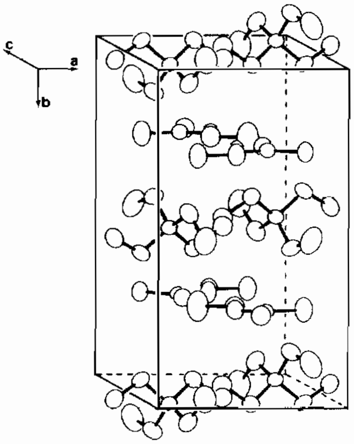

Fig. 2. The unit cell contents for [NEt$_4$] [exa] highlighting the alternate layers of anions and cations.

numbering scheme used is shown in Fig. 1. Bond distances and bond angles are given in Tables II and III respectively. Listings of anisotropic thermal parameters, hydrogen atom parameters, bond distances and bond angles involving hydrogen atoms, interionic contacts, and the observed and calculated structure factor tables have been deposited with the Editors.

Crystals of [NEt$_4$] [exa] are composed of [NEt$_4$]$^+$ cations and [exa]$^-$ anions. A projection of the unit cell contents is shown in Fig. 2 which highlights the alternate layers of anions and cations in the crystal

TABLE III. Bond Angles (°) for Non-hydrogen Atoms for [NEt$_4$] [exa].

Atom	Angle
Exa A	
S(1)–C(1)–S(2)	125.7(4)
S(1)–C(1)–O(1)	121.4(4)
S(2)–C(1)–O(1)	112.9(4)
C(1)–O(1)–C(2)	119.9(5)
O(1)–C(2)–C(3)	106.1(5)
Exa B	
S(1)–C(1)–S(2)	127.4(4)
S(1)–C(1)–O(1)	120.8(4)
S(2)–C(1)–O(1)	111.8(4)
C(1)–O(1)–C(2)	118.7(5)
O(1)–C(2)–C(3)	106.6(6)
Cation	
C(4)–N(1)–C(6)	111.5(4)
C(4)–N(1)–C(8)	106.0(4)
C(4)–N(1)–C(10)	111.9(3)
C(6)–N(1)–C(8)	110.6(3)
C(6)–N(1)–C(10)	105.5(4)
C(8)–N(1)–C(10)	111.5(4)
N(1)–C(4)–C(5)	115.0(4)
N(1)–C(6)–C(7)	114.5(4)
N(1)–C(8)–C(9)	113.5(4)
N(1)–C(10)–C(11)	115.1(5)

lattice. The ions are separated from each other at distances expected from van der Waals radii. The only significant difference between the two exa anions, of the asymmetric unit, is found for the C(1)–O(1) bond distances, *viz.* 1.342(8) Å for exa A and 1.397(8) Å for exa B. Both C–O distances are shorter than 1.437 Å [7], the distance expected for a C–O single bond. In all other aspects the two exa anions are equivalent within experimental error.

Within each exa anion the C–S distances, Table II, are equivalent and lie within the range of 1.81 and 1.61 Å [7], the value expected for C–S single and double bonds respectively. These results are in contrast with those reported for the sodium [2] salt of exa for which both crystallographically unique anions have two distinct C–S distances, *viz.* 1.698(6), 1.650(7) Å and 1.710(6), 1.642(6) Å. It has already been noted that the close interionic Na···S contacts (of approximately 2.9 Å) are likely to be the source of the disparate C–S distances in the sodium salt of exa. As no such close contacts are present (closest S···H contact approximately 2.9 Å) in the structure of [NEt$_4$] [exa] the value of 1.678(3) Å is likely to be a reliable estimate of the C–S distances in the free exa anion. The above observations suggest that in the exa anions of [NEt$_4$] [exa] the π-electrons are evenly delocalized over the $-CS_2$ group.

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