A Novel Five-co-ordinate Pentagonal-planar Complex: *X*-Ray Structure of the Tris-(O-ethyl xanthato)tellurate(II) Anion

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Summary The tris-(*O*-ethyl xanthato)tellurate(II) anion, as its tetraethylammonium salt, has been shown by *X*-ray methods to have a planar-pentagonal structure.

Five-co-ordination polyhedra are invariably assigned trigonal-bipyramidal and square (tetragonal) pyramidal configurations or geometries intermediate between these two limiting types. In relation to these, structures based on the pentagonal-planar geometry, where the five ligand atoms are coplanar with the central atom and directed towards the corners of a pentagon, have not been considered likely because of the overcrowding of the ligands in the pentagonal plane.[1]

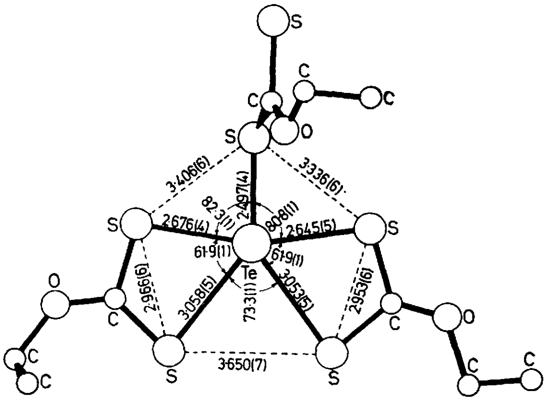

FIGURE Structure of the $[Te(Et\ xan)_3]^-$ anion showing pentagonal-planar co-ordination about the tellurium atom and relevant molecular dimensions. The estimated standard deviations are given in parentheses. The TeS_5 plane and the plane passing through the S_2CO- atoms of the monodentate ligand form a dihedral angle of 80°. The distance between the tellurium atom and the non-bonded oxygen and sulphur atoms of the monodentate xanthate are 3·26(1) and 5·067(5) Å respectively.

We report here the structure of the $[Te(Et\ xan)_3]^-$ anion (where xan represents the S_2CO-group) which was isolated[2] as its tetraethylammonium salt (Figure). The tellurium atom is bonded to five sulphur atoms, at each corner of a pentagon, and the TeS_5 group is essentially planar with the maximum displacement from the mean plane *ca.* 0·10 Å. The minimum interionic contact distance involving the tellurium atom, 3·76 Å, is to an ethyl carbon atom of an adjacent complex anion, agreeing well with normal van der Waals distances. The environment of the tellurium atom, we believe, provides the first authentic example of five-co-ordinate pentagonal-planar geometry.

The overall geometrical features observed for the $[Te(Et\ xan)_3]^-$ anion are consistent with the valence shell electron pair repulsion of the seven electron pairs in the valence shell of a tellurium atom.[3] These appear to be distributed in a pentagonal-bipyramidal arrangement, with two sterically active lone pairs directed along the axial line; *i.e.* this complex anion provides an example of the hitherto unconsidered AX_5E_2 type of five co-ordination. It is also interesting to note that valency shells containing seven electron pairs are rare for non-transition metal compounds.[4]

The environment of the tellurium atom is asymmetric as two of the Te–S bonds [3·053(5) and 3·058(5) Å] are longer than the other three [2·645(5), 2·676(4), and 2·497(4) Å]. One long bond is contained in each chelate ring and the two occupy adjacent positions in the pentagonal plane. Otherwise the molecular dimensions of the $[Te(Et\ xan)_3]^-$ anion agree well with expected values.

We also note that other compounds of tellurium(II), *e.g.* $[Te(Et\ xan)_2]$,[5] $[Te(Me\ xan)_2]$,[6] and $[Te(S_2(CNEt_2)_2]$,[7] show a slight tendency towards planar five co-ordination. In each there are four Te–S bonds which appear to be close to normal covalent distances, while the fifth sulphur atom, which is derived from a symmetry related molecule, approaches the tellurium atom at a much greater distance (*ca.* 3·55 Å).

Only two of the co-ordinating ethylxanthato- groups of $[Te(Et\ xan)_3]^-$ function as bidentate ligands whereas the third is bonded to the tellurium atom through one of its sulphur atoms. Monodentate behaviour of the xanthate ligand has been well established. Examples occur in square-pyramidal $[Cd(Et\ xan)_3]^-$ [8] and square-planar $[Pt(Et\ xan)_3]^-$ [9] where one and two of the xanthate ligands respectively function only as monodentates. In contrast $[Ni(Et\ xan)_3]^-$ [10] and possibly the corresponding Fe^{II} and Mn^{II} complexes[11] are six co-ordinate with all three xanthates of each compound showing bidentate behaviour.

Crystal data: $C_{17}H_{35}O_3S_6MTe$, yellow prisms, $M = 621·4$, monoclinic, $a = 8·121(1)$, $b = 18·858(2)$, $c = 19·260(2)$ Å, $\beta = 105·22(1)°$, $U = 2846·2$ Å^3, $D_m = 1·43$, $Z = 4$, $D_c = 1·450$ g cm^{-3}, space group $P2_1/c$ (C^5_{2h}, No. 14).

Crystals of the tetraethylammonium salt of tris(*O*-ethyl xanthato)tellurate(II) decompose considerably when exposed to the *X*-ray beam. Consequently, the intensities of 2404 independent reflections, regarded as significant at the 3σ level, were collected in three overlapping sets of data, using three different crystals. These data were measured using a Siemens automatic diffractometer with Cu-K_α radiation (λ 1·5418 Å) to a maximum Bragg angle of 45°, there being very few observable reflections above this limit. Absorption corrections were applied to the individual data sets.

The structure, solved by Patterson and Fourier methods, was refined using a full-matrix least-squares procedure applying anisotropic temperature factors in all except the disordered ethyl carbons of one of the xanthate groups, for which isotropic thermal parameters were maintained. At convergence R was 0·061.

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