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# The Crystal Structure of Bromo(*o*-ethylxanthato)tellurium(II)

ROBERT W. GABLE, BERNARD F. HOSKINS, ROBYN J. STEEN and GEORGE WINTER

*Department of Inorganic Chemistry, University of Melbourne, Parkville, Vic. 3052 Australia*

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In the course of a general study covering the chemistry of metal haloxanthate complexes [1–3] we have prepared the compound of stoichiometry $Te(S_2COC_2H_5)Br$ by the addition of bromine to $Te(S_2COC_2H_5)_2$ in dichloromethane solution:

$$2Te(S_2COC_2H_5)_2 + Br_2 \rightarrow 2Te(S_2COC_2H_5)Br + (S_2COC_2H_5)_2.$$

It is a dark red, crystalline solid whose molecular weight (336) in chloroform is close to the formula weight (328.7), providing strong evidence that in chloroform solution, $Te(S_2COC_2H_5)Br$ exists as discrete mononuclear molecular units.

There are, however, significant differences between the IR spectra of the solid and its solution (Table I), indicating that $Te(S_2COC_2H_5)Br$ adopts a different molecular form in the solid state. This has been confirmed by a crystal structure analysis which we report here.

Crystal data: $C_3H_5BrOS_2Te$, $M$ = 328.7, monoclinic, $a$ = 10.636(1), $b$ = 6.030(1), $c$ = 13.364(1) Å, $\beta$ = 103.32(1)°, $V$ = 834.0, $D_m$ = 2.66 Mg m$^{-3}$, $Z$ = 4, $D_c$ = 2.617 Mg m$^{-3}$, $F(000)$ = 600, space group $P2_1/c$ (no. 14), Cu K$\alpha$ (nickel filtered) radiation, $\mu$ = 38.01 mm$^{-1}$.

Intensity data were collected on a Siemens single-crystal, automatic three-circle diffractometer. The 1396 independent, observed reflections, where $I \geqslant 3\sigma(I)$, were corrected for Lorentz, polarization and absorption effects.

The structure was determined by Patterson and Fourier methods using a least squares refinement procedure which converged with R 0.077 and Rw 0.072.

TABLE I. IR Absorption Frequencies of $Te(S_2COC_2H_5)Br$ in the 'C–O' and 'C–S' Regions (cm$^{-1}$).

| State | C–O | C–S |
|---|---|---|
| solid | 1285(sh), 1270 | 1018, 990 |
| $CS_2$ solution | 1248, 1235(sh) | 1037, 1001 |

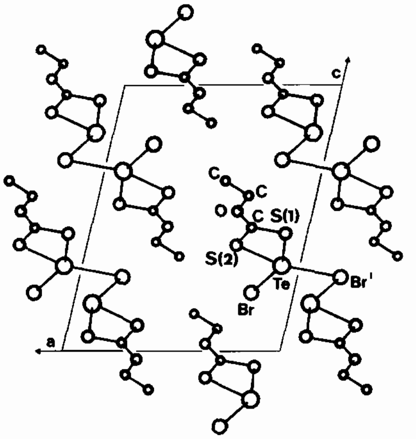

Fig. 1. The unit cell of $[Te(S_2COC_2H_5)Br]_n$ viewed down the [010] direction. The atomic labelling is shown for the asymmetric unit.

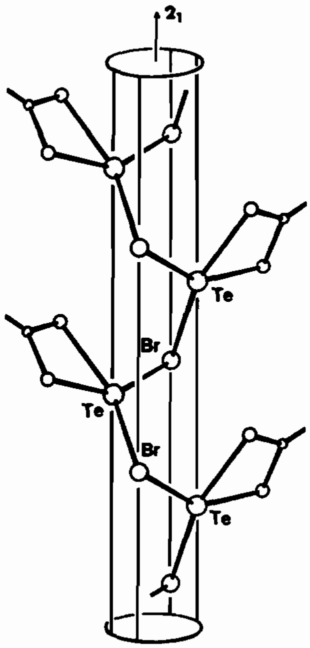

Fig. 2. A portion of the crystal structure of $[Te(SCOC_2H_5)Br]_n$ viewed along the [$\bar{3}01$] direction showing the nature of one of the helices adopted by the Br and Te atoms which extends in the *b*-direction with the periodicity b.

Figure 1 shows the unit cell viewed along the [010] direction. Each tellurium atom is bonded to the two sulphur atoms of the xanthate ligand and two bromine atoms, with each bromine atom bonded to another tellurium atom. The most interesting

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TABLE II. Bond Lengths (Å) and Angles (°) Involving the Tellurium Atom, Standard Deviations in Parentheses.

| Atoms | Separation | Atoms | Angle |
|---|---|---|---|
| Te–Br | 3.052(2) | Br–Te–Br' | 128.40(4) |
| Te–Br' | 2.895(1) | S(1)–Te–Br' | 79.00(6) |
| Te–S(1) | 2.524(3) | S(2)–Te–Br | 81.39(7) |
| Te–S(2) | 2.471(2) | S(1)–Te–S(2) | 71.03(8) |
| Te–Te' | 3.797(1) | Te–Br'–Te' | 79.31(3) |

' (–x, ½ + y, ½ – z).

aspect of the structure is that the tellurium and bromine atoms adopt a helical structure, with two pairs of bromine and tellurium atoms forming the repeat unit. This helix is shown in Fig. 2, viewed along the $[\bar{3}01]$ direction. The helices which are situated around the two-fold screw axes, (0, y, ¼) and (0, y, ¾), extend indefinitely along the y axis with a periodicity of *b* [6.030(1) Å]; within the crystal there are left- and right-handed helices which alternate throughout the structure.

The separation of the tellurium atoms within the helix is 3.797(1) Å, compared to 4.12 Å for the sum of the van der Waals radii [4], and separations of 2.84 Å and 3.47 Å found in tellurium metal [5], attributed to the single bond and metallic interactions respectively. This suggests that there is a substantial interaction between the tellurium atoms, which would occur throughout the helix. Other atom contacts, both within the helix and between helices, are in excess of 3.7 Å, which is greater than the sum of the van der Waals radii of the atoms involved.

The four coordinating atoms form a trapezoid, similar to that observed for $Te(S_2COC_2H_5)_2$ [6], with all five atoms being coplanar. Some bond lengths and angles are given in Table II, the others are similar to those previously reported for $Te(S_2COC_2H_5)_2$ [6] and $[Et_4N][Te(S_2COC_2H_5)_3]$ [7]. The similarities between the two Te–Br distances, and between the two Te–S distances, suggest that the lone pairs of electrons, contained in the valence shell of the tellurium atom, lie approximately perpendicular to the $Br_2TeS_2$ plane. One of the lone pairs seems to point in the direction of a bromine atom in the same helix 4.4 Å away, while the other seems to occupy a cavity between the helices.

Only a few inorganic materials are known to possess helical structures. These include elemental tellurium [5], modifications of sulphur [8] and selenium [9], and the mercury(II) 1,1-dithiolate complexes, $Hg[(i\text{-}C_3H_7O)_2PS_2]_2$ [10] and $Hg[S_2CO(i\text{-}C_3H_7)]_2$ [11].

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