The Crystal and Molecular Structure of Polymeric Tris(O-isopropylxanthato)bismuth(III)

BERNARD F. HOSKINS*, EDWARD R. T. TIEKINK and GEORGE WINTER

Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria, Australia 3052

Received August 25, 1983

In the course of a study concerning the asymmetry of sulphur co-ordination in xanthates of group V elements, we have isolated $Bi(^{i}Prxan)_3$ and determined its structure which shows noteworthy features. The complex was prepared by stirring $BiCl_3$ in an ethanol solution of $KS_2CO\text{-}i\text{-}C_3H_7$. Pale yellow crystals of $Bi(^{i}Prxan)_3$ were obtained from a benzene/light petroleum solution.

Crystal Data $Bi(S_2CO\text{-}i\text{-}C_3H_7)_3$, $C_{12}H_{21}O_3S_6Bi$, M = 614.7, orthorhombic, space group *Pnma* (D_{2h}^{16}, No. 62), a = 9.428(2), b = 11.003(3), c = 20.833(4) Å, U = 2161 Å^{-3} D_{meas} = 1.86 (aq. $ZnBr_2$ soln.), Z = 4, D_{calc} = 1.89 Mg m^{-3}, F(000) = 1184, μ(MoKα) = 16.18 mm^{-1}.

Preliminary photographic work indicated the crystal to be orthorhombic, intensity data were collected at room temperature on an Enraf-Nonius CAD-4 four-circle diffractometer up to a Bragg angle of

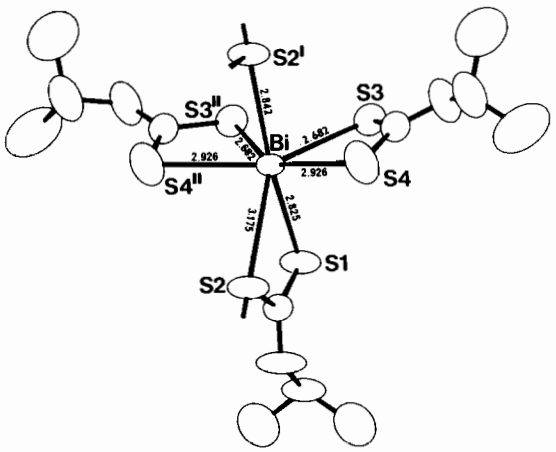

Fig. 1. Immediate environment of the Bi atom in the polymeric $Bi(^{i}Prxan)_3$ showing Bi–S bond distances (Å), which demonstrates the gross asymmetry in the co-ordination of the xanthate moieties; relevant angles are given in Table I.

TABLE I. Selected Bond Angles (°) for $Bi(^{i}Prxan)_3$. Estimated standard deviations in parentheses.

Atoms	Angle	Atoms	Angle
S(1)–Bi–S(2)	58.89(8)	S(3)–Bi–S(4)	63.66(7)
S(1)–Bi–S(3)	87.07(7)	S(3)–Bi–S(2^{I})	84.67(6)
S(1)–Bi–S(4)	100.76(6)	S(3)–Bi–S(3^{II})	83.82(6)
S(1)–Bi–S(2^{I})[a]	168.80(8)	S(3)–Bi–S(4^{II})	145.81(8)
S(2)–Bi–S(3)	127.53(4)	S(4)–Bi–S(2^{I})	82.19(7)
S(2)–Bi–S(4)	83.47(7)	S(4)–Bi–S(4^{II})	144.09(8)
S(2)–Bi–S(2^{I})	132.23(8)		

[a]I refers to the symmetry operation ½ + x, ½ − y, ½ − z; and II refers to x, ½ − y, z.

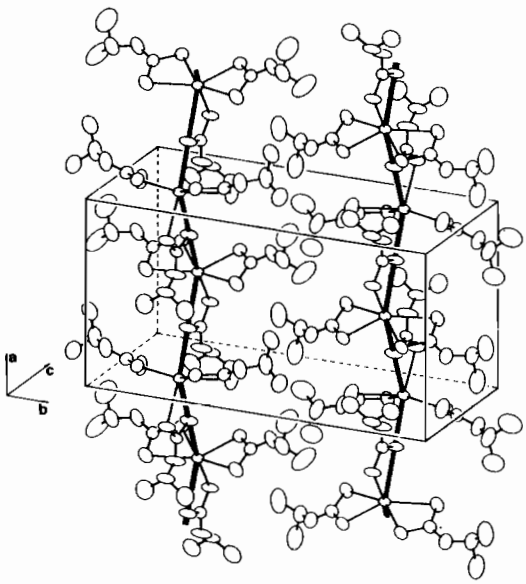

Fig. 2. Unit cell contents of the polymeric $Bi(^{i}Prxan)_3$; the –Bi–S–Bi interactions (highlighted) are reinforcing the OR Bi–S–C–S–Bi bridges.

27.5° using MoKα (graphite monochromator) radiation employing the ω:2θ scan technique. The $I \geqslant 2\sigma(I)$ criteria was used yielding 1796 unique reflections. No significant decomposition of the crystal occurred during the data collection. Successful refinement was achieved in the centrosymmetric space group *Pnma*. The position of the Bi atom was determined from the Patterson synthesis and the structure was refined using a full-matrix least squares method in which the function $\Sigma w \Delta^2$ was minimized [1]. Refinement was performed on all positional parameters, isotropic and then anisotropic thermal

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

parameters. Hydrogen atoms were included in the model in their calculated positions and a weighting scheme was applied. At convergence, conventional values of R and R_w were 0.042 and 0.039.

An ORTEP diagram of the immediate environment of the Bi atom is shown in Fig. 1 (Table I). The Bi atom is bonded to three bidentate xanthate ligands, two of which are related by a crystallographic mirror plane. Of particular interest is the co-ordination of the third xanthate ligand which displays gross asymmetry due to an additional interaction with a neighbouring Bi atom which leads to a linear polymeric structure. In fact this xanthate moiety may be considered as functioning both as a xanthate bridge and as a chelating ligand since the Bi–S(2) distance of 3.175(2) Å is well within the sum of the estimated van der Waal's radii of 3.8 Å [2], this also has the consequence that the bridging sulphur atom is three co-ordinate. A representation of the unit cell is shown in Fig. 2, where the –Bi–S–Bi– interactions have been highlighted These interactions appear to reinforce the xanthate bridges in the formation of the polymeric structure.

References

1 G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, Cambridge (1976).
2 A. Bondi, *J. Phys. Chem.*, *68*, 441 (1964). The van der Waal's radius for Pb was used.