Crystal and Molecular Structure of Polymeric Tetraphenylarsonium Bis(1,2-dicyanoethene-1,2-dithiolato)bismuthate(III) †

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The crystal and molecular structure of the title compound, $[AsPh_4][Bi\{S_2C_2(CN)_2\}_2]$, has been determined by single-crystal *X*-ray diffraction methods at ambient temperature and refined by least-squares procedures to a conventional residual of 0.085 for 2 648 observed reflections. Crystals are monoclinic, space group $P2_1/n$, with a = 16.06(4), b = 28.11(4), c = 7.389(6) Å, β = 98.16(10)°, and Z = 4. The structure comprises an infinite linear polymeric chain in which successive bismuth atoms are bridged by two dithiolene ligands, each ligand providing one bridging sulphur atom. The stereochemistry at the bismuth atom is either highly distorted octahedral with a stereochemically inactive lone pair or, more likely, distorted pentagonal bipyramidal with a stereochemically active lone pair occupying an equatorial position.

According to the valence-shell electron-pair repulsion model of Sidgwick and Powell[1] and of Gillespie and Nyholm[2] the stereochemistry of non-transition elements is governed by repulsions between pairs of valence electrons, although it has been found[3] that soft donors generally lead to a stereochemically inactive lone pair in seven-electron-pair AX_6E type complexes (A = non-transition element, X = ligand atom, E = lone pair). However, bidentate ligands may prevent the attainment of local octahedral symmetry, and one objective of structural studies of dithiolato complexes of bismuth(III) is to detect whether a stereochemically active lone pair occupies a seventh co-ordination position. The presence of a stereochemically active lone pair is inferred from deviations from local octahedral or approximate octahedral symmetry about the central atom. Considerable distortion from octahedral symmetry, implying the presence of a stereochemically active lone pair, has been found[4] in the structure of the 1,1-dithiolato complex $[Bi\{S_2P(OCHMe_2)_2\}_3]$ whereas $[Bi(tu)_6]^{3+}$ (tu = thiourea) has been found[5] to have a regular octahedral structure and hence a stereochemically inactive lone pair. There are two reports of the structure of the 1,1-dithiolato complex $[Bi(S_2CNEt_2)_3]$. One[6] describes it as being pseudo-pentagonal bipyramidal with a stereochemically active lone pair occupying one of the axial positions, the other[7] describes it as being a centrosymmetric sulphur-bridged dimer in which the metal is pseudo-eight-co-ordinate with a less stereochemically active lone pair. Recent publications by the latter authors[8] have described structural studies for a series of mixed 1,1-dithiolato–halogeno–bismuth(III) complexes, and they observe that the general features for the series are 'complexes of variable and irregular stereochemistries, the implied presence of lone pairs on the metal atom of variable stereochemistry, and copious potential for the formation of polymeric and oligomeric systems by way of bridging halide and dithiocarbamate groups.'

We have previously described[9] the syntheses and electrochemical properties of the tetraethylammonium salts of a series of anionic bismuth(III) complexes of dicyanoethene-1,2-dithiolate formulated as $[NEt_4]_2[Bi_2\{S_2C_2(CN)_2\}_2X_4]$, $[NEt_4]_2[Bi_2\{S_2C_2(CN)_2\}_3X_2]$, and $[NEt_4]_4[Bi_2\{S_2C_2(CN)_2\}_5]$ (X = Cl, Br, or I). Crystals suitable for *X*-ray crystallographic analysis could not be obtained for any of these complexes but they were speculatively considered to have a common binuclear structural unit in which two bismuth atoms were bridged by two dithiolene ligands. We now report the isolation and crystal and molecular structure of the complex $[AsPh_4][Bi\{S_2C_2(CN)_2\}_2]$, which in addition to its intrinsic interest, and although it is not one of our original series, we consider provides a more convincing alternative structural model for the 1,2-dithiolene complexes $[Bi_2\{S_2C_2(CN)_2\}_2X_4]^{2-}$ and $[Bi_2\{S_2C_2(CN)_2\}_3X_2]^{2-}$.

Experimental

Tetraphenylarsonium Bis(1,2-*dicyanoethene*-1,2-*dithiolato*)-*bismuthate*(III).—Bismuth trichloride (10 mmol) was treated with $Na_2[S_2C_2(CN)_2]$ (20 mmol) in acetone. The dark red mixture was filtered into aqueous tetraphenylarsonium chloride. The precipitate consisted of a mixture of complexes, which were separated by fractional crystallisation from ethanol. A small quantity of the title complex was obtained as black laths, which were recrystallised from ethanol. These proved suitable for *X*-ray crystallographic analysis, although none of the other complexes separated gave crystals of sufficiently high quality for such study.

Crystal data. $C_{32}H_{20}AsBiN_4S_4$, M = 872.7. Monoclinic, space group $P2_1/n$, a = 16.06(4), b = 28.11(4), c = 7.389(6) Å, β = 98.16(10)°, U = 3 301 Å^3, Z = 4, D_c = 1.754 g cm^{-3}, $F(000)$ = 1 680; Cu-K_α radiation, λ = 1.5418 Å, μ = 141 cm^{-1}.

Equi-inclination multi-film Weissenberg photographs of reciprocal lattice layers 0—3*kl*, *h*0—1*l*, and *hk*0—5 were scanned by the S.E.R.C. Microdensitometer Service, Daresbury Laboratory. Because spot intensities fell off rapidly with increasing diffraction angle, only 2 648 unique reflections out of *ca.* 5 500 scanned were classified as observed. Data reduction was repeated with inclusion of absorption corrections after the elemental composition of the crystal had become apparent. The approximate co-ordinates of the Bi atoms were readily obtained from a Patterson synthesis, and the other non-hydrogen atoms were located by difference syntheses alternating with cycles of full-matrix least-squares refinement. In the later stages, the Bi, As, and S atoms were refined with anisotropic thermal parameters, and the phenyl rings were constrained as regular hexagons with a C–C bond length of 1.395 Å. After the removal of 21 reflections which appeared to have been badly measured, refinement converged at R = 0.085 (2 627 data, 151 parameters, unit weights for all parameters). The final difference synthesis contained no evidence of any lattice solvent molecules. The SHELX76 program[10] was used in all calculations. Atomic parameters are listed in Table 1.

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† *Supplementary data available* (No. SUP 23563, 17 pp.): thermal parameters, structure factors. See Notice to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Non-hydrogen atom co-ordinates (× 10^4) for $[AsPh_4][Bi\{S_2C_2(CN)_2\}_2]$

Atom	*x*	*y*	*z*
Bi	132(1)	121(1)	2 516(2)
As	931(2)	3 477(1)	391(5)
S(1)	−768(5)	710(3)	−4(12)
S(2)	1 310(5)	485(3)	657(10)
S(3)	466(5)	861(3)	4 752(10)
S(4)	1 423(5)	−200(3)	5 268(11)
N(1)	−582(20)	1 934(12)	−1 412(45)
N(2)	1 829(21)	1 729(12)	−496(47)
N(3)	2 480(22)	1 506(13)	5 659(47)
N(4)	3 530(22)	298(12)	6 587(47)
C(1)	−264(19)	1 574(11)	−976(42)
C(2)	14(19)	1 111(11)	−362(41)
C(3)	829(21)	1 026(12)	−141(45)
C(4)	1 379(20)	1 396(11)	−439(43)
C(5)	2 039(22)	1 186(13)	5 461(48)
C(6)	1 539(17)	762(10)	5 350(39)
C(7)	1 928(18)	313(10)	5 580(39)
C(8)	2 823(23)	340(12)	6 034(48)
C(11)	66(13)	3 625(8)	8 430(26)
C(12)	212(13)	3 944(8)	7 065(26)
C(13)	−435(13)	4 057(8)	5 661(26)
C(14)	−1 226(13)	3 850(8)	5 623(26)
C(15)	−1 372(13)	3 530(8)	6 989(26)
C(16)	−726(13)	3 418(8)	8 392(26)
C(21)	1 213(13)	4 016(6)	1 899(26)
C(22)	1 745(13)	3 963(6)	3 551(26)
C(23)	1 954(13)	4 357(6)	4 672(26)
C(24)	1 629(13)	4 804(6)	4 143(26)
C(25)	1 096(13)	4 857(6)	2 491(26)
C(26)	888(13)	4 463(6)	1 370(26)
C(31)	1 841(13)	3 294(8)	9 216(31)
C(32)	1 751(13)	2 911(8)	8 006(31)
C(33)	2 398(13)	2 796(8)	7 008(31)
C(34)	3 136(13)	3 064(8)	7 220(31)
C(35)	3 226(13)	3 448(8)	8 430(31)
C(36)	2 579(13)	3 563(8)	9 428(31)
C(41)	638(15)	2 983(8)	1 957(31)
C(42)	−29(15)	3 056(8)	2 944(31)
C(43)	−248(15)	2 703(8)	4 116(31)
C(44)	202(15)	2 277(8)	4 302(31)
C(45)	870(15)	2 204(8)	3 315(31)
C(46)	1 088(15)	2 557(8)	2 143(31)

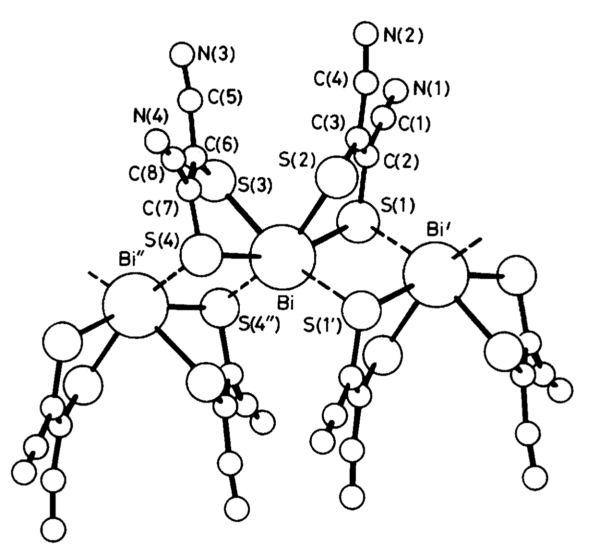

Figure 1. Basic structural unit for anion in $[AsPh_4][Bi\{S_2C_2(CN)_2\}_2]$

Table 2. Cation geometry in $[AsPh_4][Bi\{S_2C_2(CN)_2\}_2]$

(*a*) Bond lengths (Å)	
As−C(11)	1.91(2)
As−C(21)	1.90(2)
As−C(31)	1.88(2)
As−C(41)	1.91(2)
(*b*) Angles (°)	
C(11)−As−C(21)	111(1)
C(11)−As−C(31)	104(1)
C(11)−As−C(41)	114(1)
C(21)−As−C(31)	111(1)
C(21)−As−C(41)	107(1)
C(31)−As−C(41)	111(1)

Discussion

The basic structural unit (Figure 1) is part of an infinite linear polymeric chain (Figure 2) in which adjacent bismuth atoms are doubly bridged by two dithiolene ligands, each ligand providing one bridging sulphur atom. Alternate bismuth–bismuth spacings are 3.744(2) and 3.816(2) Å. Two parallel strands of the polymer are aligned along *c* and there are no close significant interchain interactions. The cation is well ordered and its geometry (Table 2) conventional.

Within the anion, the bismuth environment is six-co-ordinate, each metal atom having a pair of dithio-chelate ligands attached and bridged by them to two adjacent bismuth atoms. The bonding to the dithiolene ligand is unsymmetrical [Bi−S(1,2,3,4) 2.746(9), 2.693(7), 2.664(7), 2.836(8) Å], with the longer of the two bonds within each chelate being that to the sulphur atom which bridges to the next bismuth. The bridging sulphur links are quite long [Bi−S-(1′,4″) 3.238(10), 3.182(10) Å] but significantly shorter than that reported [8b] [3.462(5) Å] for the corresponding linkage in polymeric (*NN*-diethyldithiocarbamato)bismuth(III). Although the bismuth atoms do not occupy special positions in the unit cell, the metal point symmetry approximates to C_2, with the two-fold axis bisecting a line joining the two non-bridging sulphur atoms S(2) and S(3). Despite the pseudo C_2 axis, the array about the bismuth atom does not quite fit any idealised structure. It might be described as pseudo-octahedral, although great distortion is required, particularly in the angular geometry. Such distortion might, however, be imposed merely by the angular requirements for the bite of the 1,2-dithiolene ligands rather than by the presence of a stereochemically active lone pair. Alternatively, we consider a more attractive description is that of a distorted pentagonal bipyramidal array about the bismuth with one of the equatorial positions occupied by a stereochemically active lone pair, a ' 1 : 5 : 1 ' stereochemistry originally predicted by Gillespie [2b] for seven-electron-pair AX_6E type complexes. The sulphur atoms S(1) and S(4) occupy the axial positions of the pentagonal bipyramid with the equatorial positions occupied by S(1′), S(2), S(3), S(4″) and the lone pair, presumably directed along the C_2 axis between S(1′) and S(4″) (Figure 3). The sum of the angles subtended by the equatorial atoms at the bismuth is 364.2°; the deviations of the atoms from a least-squares plane through them are: S(1′), 0.27; S(2), −0.45; S(3), 0.44; S(4″), −0.26 Å, with the bismuth deviation being −0.02 Å. It may be significant that in the equatorial positions the distance between a bridge sulphur and its neighbouring

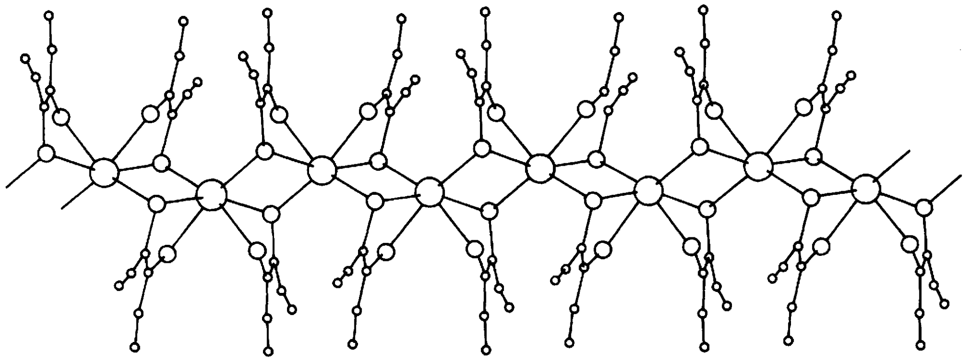

Figure 2. Single polymeric strand of $[Bi\{S_2C_2(CN_2)_2\}]^-$

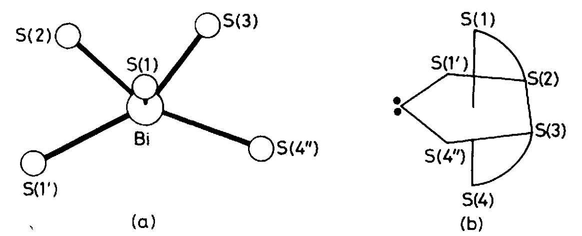

Figure 3. (a) Projection of the bismuth environment in $[Bi\{S_2C_2(CN)_2\}_2]^-$ down the S(1),S(4) axis; (b) schematic representation of the corresponding idealised co-ordination environment

Table 3. Bismuth co-ordination environment in $[AsPh_4][Bi\{S_2C_2(CN)_2\}_2]$

(*a*) Distances (Å)			
Bi–S(1)	2.746(9)	Bi–S(4)	2.836(8)
Bi–S(1′)	3.238(10)	Bi–S(4″)	3.182(10)
Bi–S(2)	2.693(7)	Bi–S(3)	2.664(7)
S(1) ··· S(2)	3.36(2)	S(3) ··· S(4)	3.35(2)
S(1) ··· S(1′)	4.72(2)	S(4) ··· S(4″)	4.67(2)
S(1) ··· S(3)	3.81(2)	S(4) ··· S(2)	3.90(2)
S(1) ··· S(4″)	4.06(2)	S(4) ··· S(1′)	4.06(2)
S(2) ··· S(3)	3.64(2)	S(1′) ··· S(4″)	5.50(2)
(*b*) Angles (°)			
S(1)–Bi–S(1′)	103.0(2)	S(4)–Bi–S(4″)	101.5(6)
S(1)–Bi–S(2)	76.4(2)	S(4)–Bi–S(3)	75.0(2)
S(1)–Bi–S(3)	89.4(2)	S(4)–Bi–S(2)	89.5(2)
S(1)–Bi–S(4″)	86.0(4)	S(4)–Bi–S(1′)	85.6(1)
S(1′)–Bi–S(2)	71.3(3)	S(3)–Bi–S(4″)	74.3(3)
S(3)–Bi–S(1′)	161.4(6)	S(2)–Bi–S(4″)	161.2(6)
S(1)–Bi–S(4)	159.8(6)	S(1′)–Bi–S(4″)	132.8(3)
S(2)–Bi–S(3)	85.7(2)	Bi–S(1)–Bi′	77.0(4)
Bi–S(4)–Bi″	78.5(4)		

Symmetry code: *X*′: $-x, -y, -z$; *X*″: $-x, -y, 1 - z$.

Table 4. Dithiolene ligand geometry in $[AsPh_4][Bi\{S_2C_2(CN)_2\}_2]$

(*a*) Distances (Å)			
S(1)–C(2)	1.74(3)	S(4)–C(7)	1.66(3)
S(2)–C(3)	1.77(3)	S(3)–C(6)	1.74(3)
C(2)–C(3)	1.32(4)	C(6)–C(7)	1.41(4)
N(1)–C(1)	1.16(4)	N(3)–C(5)	1.14(4)
N(2)–C(4)	1.19(4)	N(4)–C(8)	1.16(4)
C(1)–C(2)	1.43(4)	C(7)–C(8)	1.43(4)
C(3)–C(4)	1.40(4)	C(5)–C(6)	1.44(4)
(*b*) Angles (°)			
Bi–S(1)–C(2)	100(1)	Bi–S(4)–C(7)	97(1)
Bi–S(2)–C(3)	101(1)	Bi–S(3)–C(6)	98(1)
S(1)–C(2)–C(3)	126(3)	S(4)–C(7)–C(6)	124(2)
S(2)–C(3)–C(2)	125(3)	S(3)–C(6)–C(7)	126(2)
S(1)–C(2)–C(1)	116(2)	S(4)–C(7)–C(8)	122(2)
S(2)–C(3)–C(4)	116(2)	S(3)–C(6)–C(5)	114(2)

chelate sulphur [S(1′) ··· S(2), 3.486; S(4″) ··· S(3), 3.556 Å] is close to the van der Waals radius sum (3.70 Å) for two sulphur atoms. The bismuth co-ordination environment is recorded in Table 3.

The geometry of the dithiolene ligand is conventional (Table 4) and deviations from planarity for the ligand are small, the maximum deviations from the mean planes of the ligands being for ligand atoms C(4) (−0.06 Å) and N(4) (+0.08 Å). However, the chelate rings are not planar but folded, the dihedral angles made by the BiS_2 and $S_2C_2(CN)_2$ planes being 31.6° [BiS(1)S(2) : S(1)S(2)C(2)C(3)] and 43° [BiS(3)S(4) : S(3)S(4)C(6)C(7)]. Such large degrees of folding are unusual but not unprecedented for the chelate rings of metal 1,2-dithiolene complexes; the TiS_2 plane has been found[11] to be folded out of the $S_2C_2H_2$ plane at an angle of 46.1° in the complex $[Ti(\eta^5\text{-}C_5H_5)_2(S_2C_2H_2)]$. Other unusual parameters of $[Bi\{S_2C_2(CN)_2\}_2]^-$, compared with typical values reported[12] for 1,2-dithiolene complexes, are the long intra-ligand (chelate bite) distances [S(1) ··· S(2), 3.364(16), S(3) ··· S(4), 3.350(16 Å] and the small S–Bi–S intra-ring angles [S(1)–Bi–S(2), 76.4(2); S(3)–Bi–S(4), 75.0(2)°]. These parameters are, however, similar to those found[13] for $[NEt_4]_3[In\{S_2C_2(CN)_2\}_3]$ (S ··· S, 3.39 Å; S–In–S, 80°). It appears that the large deviation from planarity in the chelate ring of the bismuth complex is required to provide for the relief of steric strain.

The bismuth–chelate sulphur distances are, if anything, slightly longer than those reported for 1,1-dithiolato-complexes of bismuth(III).[6–8] This is the reverse of what might be expected[12] and suggests that the extent of metal–ligand π-bonding in $[Bi\{S_2C_2(CN)_2\}_2]^-$ is small, despite the unsaturated ligand π-system [mean C–S distance, 1.73 Å, mean C–C (chelate ring) distance, 1.36 Å].

Finally, the polymeric structure found for $[Bi\{S_2C_2(CN)_2\}_2]^-$ suggests similar structures for the related anionic complexes $[Bi_2\{S_2C_2(CN)_2\}_2X_4]^{2-}$ and $[Bi_2\{S_2C_2(CN)_2\}_2X_2]^{2-}$, for which crystals suitable for *X*-ray analysis have so far evaded isolation. These two proposed structures are shown in Figure 4 and require both sulphur and halogen bridges between adjacent bismuth atoms.

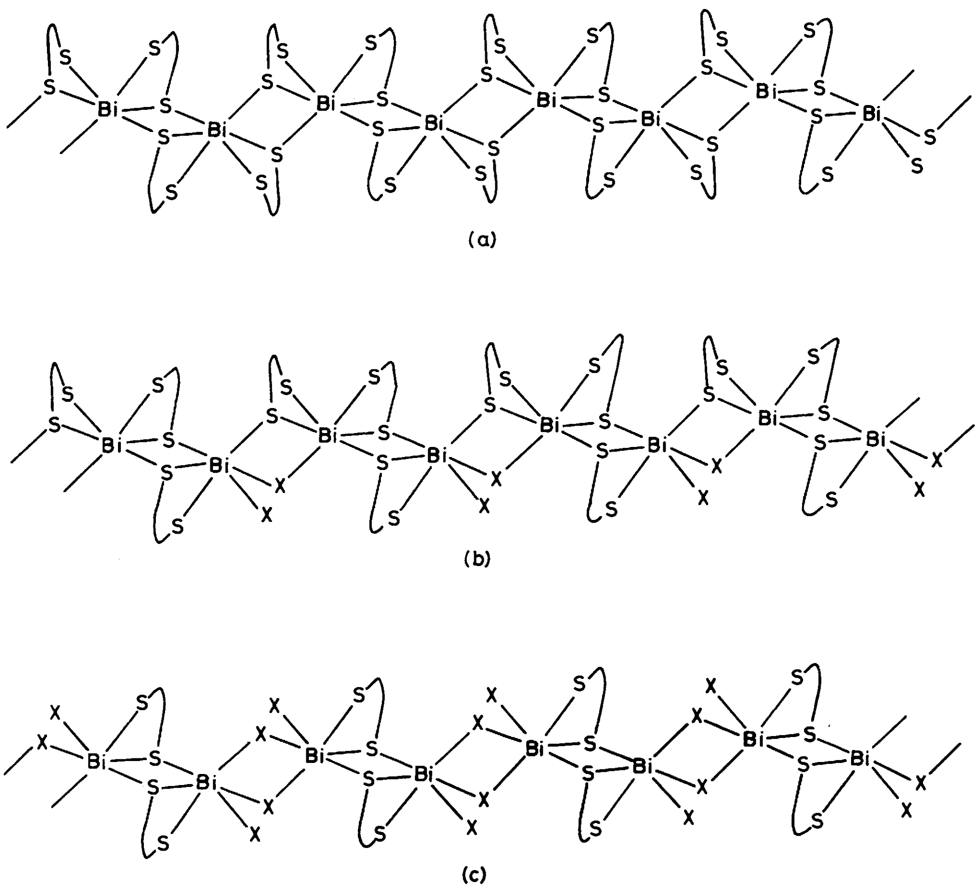

Figure 4. Idealised representations of (a) polymeric structure found for $[Bi\{S_2C_2(CN)_2\}_2]^-$; (b) polymeric structure proposed for $[Bi_2\{S_2C_2(CN)_2\}_3X_2]^{2-}$; (c) polymeric structure proposed for $[Bi_2\{S_2C_2(CN)_2\}_2X_4]^{2-}$

Acknowledgements

We thank Stella Denholm for experimental assistance.

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Received 13*th September* 1982; *Paper* 2/1571