Crystal Structures of Tris(diethyldithiocarbamato)-antimony(III) and -bismuth(III)

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The crystal structures of the title compounds, $[Sb(S_2C{\cdot}NEt_2)_3]$, (I), and $[Bi(S_2C{\cdot}NEt_2)_3]$ (II) have been determined from *X*-ray diffractometer data by the heavy-atom method and refined by least squares to R 0.07 (I), 3 [332 reflections] and 0.09 (II) [6 029 reflections]. Crystals of both are monoclinic, $Z = 4$, space group $P2_1/a$; (I): $a = 14.665(5)$, $b = 13.619(5)$, $c = 12.642(4)$ Å, $\beta = 99.86(4)$°; (II): $a = 14.825(4)$, $b = 13.640(2)$, $c = 12.605(3)$ Å, $\beta = 100.01(3)$°.

(I) and (II) are isostructural; the symmetry of the $M(S_2C)_3$ unit resembles the C_3 symmetry of the arsenic derivative, with three short M–S bonds *fac*, one from each ligand [M–S 2.487(4)—2.631(4) (I); 2.595(5)—2.775(5) Å (II)], and three long bonds [M–S 2.886(4)—2.965(4) (I); 2.956(5)—2.964(4) Å (II)], with a considerable gap in the co-ordination about the pseudo-C_3 axis suggesting a stereochemically active lone-pair. The inversion image of the molecule approaches near this direction also, with a weak intermolecular metal–sulphur interaction [$M \cdots S^I$, 3.389(4) (I), 3.210(4) Å (II)].

PREVIOUS studies on $[As(S_2C{\cdot}NEt_2)_3]$ [1,2] have established the symmetry of the molecule as being approximately C_3, rather than the more usual D_3 associated with $[M(S_2C{\cdot}NEt_2)_3]$ derivatives, because of the presumed presence of a stereochemically active lone-pair. In association with our investigation of structural types among $[M(dtc)_3]$ derivatives [dtc = $(S_2C{\cdot}NEt_2)^-$], we examined samples of the antimony and bismuth derivatives recrystallized from benzene solution. *X*-Ray examination showed these to be examples of a previously unknown phase. The structure of this new phase exemplified by the antimony (I) and bismuth (II) derivatives has accordingly been established by *X*-ray diffraction and is reported here. Crystals used for the crystallographic work were 0.10 × 0.10 × 0.10 (I) and 0.22 × 0.21 × 0.26 mm (II).

EXPERIMENTAL

Unit cells were calibrated by a least-squares fit of the angular parameters of 15 reflections centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer. A unique data set was gathered for each compound by a conventional 2θ—θ scan, that for (I) being in the range $2\theta < 50°$, yielding 4 423 independent reflections, 3 332 having $I > 2\sigma(I)$ considered 'observed' and used in the structure solution and refinement. For (II), with a larger crystal, data were gathered to $2\theta < 60°$; much of the extra data, however, were weak and resulted in a rather higher residual. 7 308 Reflections were gathered, 6 029 having $I > 2\sigma(I)$. Data for (II) were corrected for absorption.

Crystal Data.—[Data given for (I); data for (II) in square brackets.] $C_{15}H_{30}N_3S_6Sb$ $[C_{15}H_{30}BiN_3S_6]$, $M = 566.5$ [653.8], Monoclinic, $a = 14.665(5)$ [14.825(4)], $b = 13.619(5)$ [13.640(2)], $c = 12.642(4)$ [12.605(3)] Å, $\beta = 99.86(4)$ [100.01(3)]°, $U = 2\,488(1)$ [2 510(1)] Å^3, $D_m = 1.52(1)$ [1.73(1)], $Z = 4$, $D_c = 1.513$ [1.730] g cm^{-3}, $F(000) = 1\,152$ [1 280]. Mo($K_{\bar{\alpha}}$) monochromatic radiation, $\lambda = 0.710\,69$ Å, $\mu = 16.11$ [71.65] cm^{-1}. Space group $P2_1/a$ (C^5_{2h}, No. 14). Neutral atom scattering factors,[3] those for Sb, Bi, S corrected for anomalous dispersion effects ($\Delta f'$, $\Delta f''$).[4]

The structures were solved by the heavy-atom method and refined by 9 × 9 block-diagonal least-squares, the parameters of the $M(S_2CN)_3$ molecular cores being refined as a single block in the final stages to approximate a full matrix procedure, anisotropic thermal parameters of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ being employed for all atoms. Hydrogen atoms were not located in either structure. At convergence, no parameter shift in either structure exceeded 0.3σ, the R being 0.069 and 0.092 and $R' \{= [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ being 0.071 and

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[1] M. Colapietro, A. Domenicano, L. Scaramuzza, A. Vaciago, and L. Zambonelli, *Chem. Comm.*, 1968, 302.

[2] C. L. Raston and A. H. White, *J.C.S. Dalton*, 1975, 2425.

[3] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[4] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 7.

0.098; a weighting scheme of the form $w = [\sigma^2(F_o) + n \times 10^{-4}(F_o)^2]^{-1}$ was used, values of $n = 6$ and 3 being found appropriate.

Ligand atoms are labelled as in ref. 2; the atoms S(*n*1) are associated with the long M–S bonds in all ligands in the present structures as in the arsenic structure.[2] Final atomic parameters are listed in Table 1, interatomic distances and angles in Table 2.

TABLE 1

Atomic fractional cell ($\times 10^5$ for Sb or Bi; others $\times 10^4$), with least-squares in estimated standard deviations in parentheses. Values for (II) follow those for (I)

Atom	*x*	*y*	*z*
Sb	04 441(6)	01 017(6)	16 409(7)
Bi	04 793(4)	00 687(4)	16 396(5)
Ligand (1)			
S(1)	−1 451(2)	−0 112(3)	0 580(3)
	−1 429(3)	−0 080(3)	0 463(4)
S(2)	−0 385(2)	1 739(3)	0 910(3)
	−0 365(3)	1 778(3)	0 781(4)
C(1)	−1 407(9)	1 152(9)	0 471(11)
	−1 409(10)	1 174(11)	0 386(11)
N	−2 164(7)	1 667(9)	0 014(9)
	−2 135(9)	1 684(11)	0 017(2)
C(2)	−3 068(9)	1 167(12)	−0 399(12)
	−3 063(11)	1 219(13)	−0 388(17)
C(3)	−3 664(10)	1 101(12)	0 480(15)
	−3 634(15)	1 114(17)	0 581(20)
C(4)	−2 122(9)	2 746(9)	−0 095(11)
	−2 110(12)	2 789(12)	−0 093(17)
C(5)	−1 807(12)	3 010(12)	−1 151(12)
	−1 857(15)	3 090(14)	−1 199(14)
Ligand (2):			
S(1)	−0 112(3)	−1 788(3)	2 507(3)
	−0 116(3)	−1 773(3)	2 543(4)
S(2)	−0 275(2)	0 257(2)	3 278(3)
	−0 316(3)	0 279(3)	3 304(4)
C(1)	−0 607(9)	−0 995(9)	3 270(11)
	−0 612(11)	−0 981(11)	3 276(12)
N	−1 232(7)	−1 251(8)	3 861(8)
	−1 257(9)	−1 235(10)	3 863(10)
C(2)	−1 695(9)	−0 537(9)	4 462(10)
	−1 724(12)	−0 569(12)	4 475(13)
C(3)	−2 601(10)	−0 187(13)	3 764(13)
	−2 616(14)	−0 192(16)	3 795(19)
C(4)	−1 529(8)	−2 278(9)	3 914(10)
	−1 541(11)	−2 294(11)	3 885(13)
C(5)	−0 958(10)	−2 783(11)	4 888(12)
	−0 969(12)	−2 804(12)	4 871(16)
Ligand (3):			
S(1)	2 190(3)	−0 518(3)	2 893(3)
	2 252(3)	−0 494(3)	2 860(4)
S(2)	1 591(2)	1 521(3)	2 376(3)
	1 638(3)	1 559(3)	2 414(4)
C(1)	2 460(9)	0 694(9)	2 854(11)
	2 531(14)	0 759(13)	2 853(16)
N	3 321(8)	1 043(9)	3 176(9)
	3 368(9)	1 072(11)	3 159(13)
C(2)	4 081(9)	0 382(12)	3 588(15)
	4 136(16)	0 401(19)	3 497(24)
C(3)	4 698(12)	0 217(18)	2 753(18)
	4 704(15)	0 268(25)	2 622(27)
C(4)	3 525(9)	2 134(10)	3 208(12)
	3 546(11)	2 146(13)	3 201(16)
C(5)	3 362(12)	2 565(11)	4 277(13)
	3 388(13)	2 549(14)	4 292(13)

Computation was carried out on a CDC 6200 machine using a variant of the '*X*-Ray '72' program system.[5] Tables of structure amplitudes and thermal parameters are deposited as a Supplementary Publication No. SUP 21617 (15 pp., 1 microfiche).*

DISCUSSION

The unit cells of (I) and (II) are isostructural; in each case the asymmetric unit is comprised of a metal atom near the origin and three closely associated diethyldithiocarbamate ligands.

Comparison with the structure of the arsenic analogue[2] is informative. In the latter, the metal atom is co-ordinated by the asymmetrically bidentate ligands and the molecular symmetry is close to C_3. There are three short As–S(2) distances, occupying a triangular face in the co-ordination polyhedron at similar distances [As–S(*n*2) **2.344(4)—2.354(4)** Å] and the longer As–S(*n*1) distances, although differing significantly, are also similar [As–S(*n*1) 2.812(4)—2.904(4) Å] [S(*n*1)–As–S(*n*′1) 98.1(1)—114.5(1), S(*n*2)–As–S(*n*′2) 88.4(1)—91.4(1)°]. This distortion from D_3 symmetry is attributed to the existence of a stereochemically active lone-pair along the pseudo-three-fold axis and opposed to the S(*n*2) triangular face, and the only significant intermolecular contact is an approach by a hydrogen atom from a neighbouring molecule along this axis toward the lone pair.

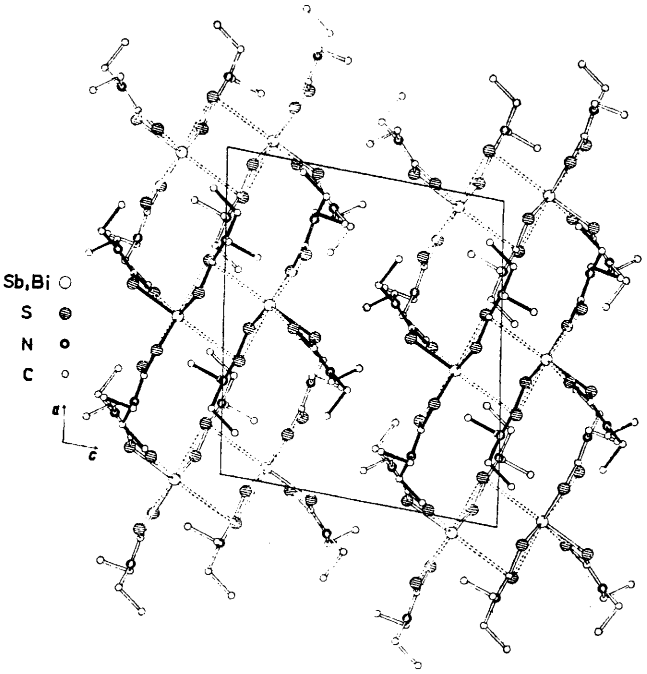

FIGURE 1 Unit-cell contents projected down *b*. Molecules centred at $y \sim \frac{1}{2}$ have solid bonds. The longer M–S bonds are dotted

Inasmuch as each ligand in the present structures is also asymmetrically co-ordinated to the metal, with the three short M–As(*n*2) distances occupying a triangular face of the co-ordination polyhedron [Sb,Bi–S(*n*2) 2.487(4)—2.631(4), 2.595(5)—2.775(5) Å], the antimony and bismuth derivatives resemble the arsenic. However, as will be apparent from Figure 1, the metal stereochemistry is appreciably different. Consideration of the deviation of the co-ordinated sulphur atoms from

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* For details, see Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

[5] '*X*-ray' program system, Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A., 1972.

Table 2

Interatomic distances (Å) and angles (°), with least-squares estimated standard deviations in parentheses; values for (II) follow those for (I)

(*a*) Molecular core

S(11)–M–S(21)	77.3(1), 79.1(1)	S(21)–M–S(31)	79.5(1), 82.8(1)
S(11)–M–S(22)	83.3(1), 83.3(1)	S(21)–M–S(32)	135.1(1), 135.0(1)
S(11)–M–S(31)	156.3(1), 160.5(1)	S(21)–M–S(11$^{\mathrm{I}}$)	119.7(1), 121.7(1)
S(11)–M–S(32)	138.3(1), 135.8(1)	S(31)–M–S(11$^{\mathrm{I}}$)	89.1(1), 87.3(1)
S(11)–M–S(11$^{\mathrm{I}}$)	97.9(1), 96.0(1)	M–S(11)–M$^{\mathrm{I}}$	82.1(1), 84.0(1)

(*b*) Ligands

	(1)	(2)	(3)
M–S(1)	2.886(4), 2.964(4)	2.965(4), 2.956(5)	2.895(4), 2.908(5)
M–S(2)	2.631(4), 2.775(5)	2.487(4), 2.595(5)	2.626(4), 2.730(4)
S(1)–M–S(2)	64.6(1), 62.4(1)	65.4(1), 64.8(1)	64.4(1), 63.4(1)
S(1)–C(1)	1.73(1), 1.71(2)	1.69(1), 1.67(2)	1.70(1), 1.76(2)
S(2)–C(1)	1.71(1), 1.75(2)	1.77(1), 1.77(2)	1.73(1), 1.73(2)
M–S(1)–C(1)	83.7(4), 86.3(5)	80.1(5), 81.6(6)	83.7(4), 86.1(6)
M–S(2)–C(1)	92.6(5), 91.8(5)	93.9(5), 91.3(6)	91.9(4), 92.5(6)
S(1)–C(1)–S(2)	118.9(8), 118.5(9)	118.2(8), 120.4(10)	118.7(7), 116.6(11)
C(1)–N	1.36(2), 1.30(2)	1.33(2), 1.35(2)	1.34(2), 1.31(2)
S(1)–C(1)–N	121(1), 122(1)	124(1), 124(1)	123(1), 122(1)
S(2)–C(1)–N	120(1), 119(1)	118(1), 116(1)	118(1), 121(1)
N–C(2)	1.50(2), 1.52(2)	1.47(2), 1.44(2)	1.46(2), 1.47(3)
N–C(4)	1.48(2), 1.51(2)	1.47(2), 1.51(2)	1.52(2), 1.49(2)
C(1)–N–C(2)	121(1), 123(1)	123(1), 126(1)	121(1), 122(2)
C(1)–N–C(4)	120(1), 122(1)	121(1), 118(1)	122(1), 119(1)
C(2)–N–C(4)	118(1), 114(1)	116(1), 116(1)	117(1), 119(1)
C(2)–C(3)	1.53(2), 1.61(3)	1.54(2), 1.53(3)	1.52(3), 1.51(4)
N–C(2)–C(3)	111(1), 110(2)	110(1), 111(1)	111(2), 112(2)
C(4)–C(5)	1.53(2), 1.56(3)	1.53(2), 1.54(2)	1.53(2), 1.54(3)
N–C(4)–C(5)	110(1), 111(2)	110(1), 109(1)	110(1), 109(2)
S(1) · · · S(2)	2.958(5), 2.975(6)	2.975(5), 2.990(6)	2.951(5), 2.968(6)

S(12)–M–S(21)	136.5(1), 136.0(1)	S(22)–M–S(31)	91.8(1), 95.6(1)
S(12)–M–S(22)	89.1(1), 89.1(1)	S(22)–M–S(32)	88.9(1), 88.6(1)
S(12)–M–S(31)	138.7(1), 137.1(1)	S(22)–M · · · S(11$^{\mathrm{I}}$)	174.9(1), 173.3(1)
S(12)–M–S(32)	74.3(1), 74.1(1)	S(32)–M · · · S(11$^{\mathrm{I}}$)	86.9(1), 87.3(1)
S(12)–M · · · S(11$^{\mathrm{I}}$)	86.9(1), 84.7(1)	M · · · S(11$^{\mathrm{I}}$)	3.389(4), 3.210(5)
M · · · M$^{\mathrm{I}}$	4.140(2), 4.135(2)		

Superscript I denotes atom at *x*, *y*, *z*.

Table 3

Least-squares planes in the form $pX + qY + rZ = s$; the orthogonal Å frame is defined by $X = ax + cz \cos \beta$, $Y = by$, $Z = cz \sin \beta$. σ (Å) is the estimated standard deviation of the defining atoms of the ligand planes, S_2CNC_2; χ^2 is given for 5° of freedom. Atom deviations are given in Å. Values for (II) follow those for (I). Sulphur atoms S(a1,2), S(b1,2) belong to the subsequent ligands in the cyclic permutation (1—3)

Ligand	(1)	(2)	(3)
10^4p	−4 241, −3 738	5 985, 5 854	−3 678, −3 358
10^4q	1 038, 0 781	−1 623, −1 616	0 944, 0 640
10^4r	8 997, 9 242	7 845, 7 945	9 251, 9 398
s	1.595, 1.362	2.454, 2.489	2.284, 2.346
σ	0.01, 0.02	0.03, 0.01	0.03, 0.03
χ^2	2.57, 6.48	45.4, 6.40	35.0, 20.0
S(1)	0.00, −0.01	−0.03, −0.02	0.03, 0.04
S(2)	−0.01, −0.01	−0.03, 0.01	−0.02, −0.03
C(1)	0.01, 0.02	0.01, 0.01	−0.01, 0.00
N	0.01, 0.02	0.01, 0.01	0.03, −0.01
C(2)	0.00, −0.01	−0.04, −0.02	−0.02, −0.03
C(3)	1.42, 1.48	−1.50, −1.46	−1.40, −1.41
C(4)	0.00, −0.01	0.03, 0.01	0.04, 0.04
C(5)	−1.44, −1.48	1.46, 1.47	1.50, 1.51
M	0.13, 0.40	−0.70, −0.68	−0.49, −0.55
S(a1)	1.26, 1.64	−3.21, −3.31	−0.08, −1.07
S(a2)	2.59, 2.90	−2.40, −2.53	−0.73, −1.04
S(b1)	0.48, 0.85	2.03, 2.03	0.63, 0.71
S(b2)	0.51, 0.86	0.62, 0.66	1.93, 1.93

Table 3 (*Continued*)

Plane (4):

M, S(21), S(22), S(11$^{\mathrm{I}}$)

(I) $0.8149X - 0.0784Y + 0.5743Z = 1.408$

(II) $0.8040X - 0.0709Y + 0.5903Z = 1.450$

Deviations:

M 0.00, 0.03; S(21) 0.00, 0.00; S(22) 0.00, −0.01; S(11$^{\mathrm{I}}$) 0.00, −0.01; S(11) −2.82, −2.89; S(31) 2.82, 2.87; S(32) 1.61, 1.70

Angles (°) between planes:

(1)—(2) 64.2, 59.8; (1)—(3) 3.6, 2.5; (2)—(3) 60.6, 57.3; (1)—(4) 80.6; 76.1; (2)—(4) 18.0, 18.0; (3)—(4), 77.0, 73.7

the ligand planes (Table 3) shows that for ligand (1) all other sulphur atoms are distributed on one side of the plane. As a result, a considerable gap exists in the co-ordination sphere. Part of this is accounted for by the close proximity of this part of the molecule to the inversion centre at the origin, and through this to the inversion image, so that one of the sulphur atoms of plane (1) [S(11)] approaches the related molecule quite closely. The strength of this interaction increases from the antimony to the bismuth derivative [M–S(11$^{\mathrm{I}}$) 3.389(4) and 3.210(5) Å], so that whereas in (I) the association must be rather weak, in (II) an apparent dimer is formed, at least in the solid state (the sum of the van der Waals radii in the two cases is 4.05 and >4.05 Å). The remainder of the co-ordination sphere on this side of the molecule is presumably occupied by the lone pair. If so, the closest description of the stereochemistry is that of a distorted dodecahedron. All ligands lie closely parallel to *b*. Ligands (1) and (3) are almost coplanar and although ligand (2) is not normal to them, the two sulphur atoms, the metal, and the inversion-related S(11) form a very good plane which is more nearly normal to them; it is clear from the associated angular geometry that the lone pair must be expected to be in this plane in the eight-co-ordination position between S(11) at $\bar{x},\bar{y},\bar{z}$ and S(21). If so, it will be approximately opposed to S(22) and it is notable that the distance M–S(22) in both structures is markedly shorter than the other M–S(n2) bonds.

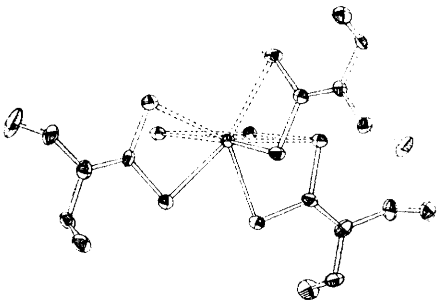

FIGURE 2 The molecule projected down *c*, showing the disposition of the ligands and the approach of the neighbouring molecule along *c*. 20% Thermal ellipsoids of the antimony derivative are shown

The ligand geometries are as expected, the S_2CNC_2 fragment conforming to a reasonable plane; the deviations of the metal atoms from the ligand planes, however, are substantial and, in the case of ligand (1) quite different, that of (I) being 0.13 as against 0.40 Å for (II). Since ligand (1) bridges the molecular pair, the greater distortion in the bismuth complex must be regarded as arising from the greater interaction with the inversion-related neighbour. Because of the dominance of the scattering by the heavy atoms, the sulphur geometries are not as well defined as in the arsenic derivative. However, within all ligands the expected correlation observed in the arsenic derivative between short C–S and long M–S bonds is found, albeit at a low level of significance, in all cases except ligand (1) in (I) where C(1)–S(11) is longer than expected, perhaps as a result of the intermolecular interaction, and ligand (3) in (II) where a similar effect appears to be a consequence of inaccuracy.

The foregoing complexes are reported to be monomeric[6] (in an unnamed solvent; $CHCl_3$ as in ref. 7?), and this is probably to be expected from the weak interaction between the molecules in the solid. Whereas in CCl_4 solution the ^1H n.m.r. spectrum of the diethyl derivatives is the usual quartet–triplet, indicating that the probable C_3 geometry of the monomer relaxes to a mean D_3 geometry on the ^1H n.m.r. time-scale, there is a pronounced solvent interaction with small quantities of added benzene, indicating formation of a 1 : 1 complex;[8] the nature of the interaction is in some doubt because equivalent protons of ligands are shielded equally. Moreover, in the dibenzyl derivatives, the phenyl proton signals are slightly split. A possible explanation of the latter phenomenon may lie in the possibility of the 1 : 1 associated complex being formed by approach of the benzene molecule with its six-fold axis coincident with the three-fold axis of the molecule in its distorted C_3 configuration, so as to interact with the lone pair; the lifetime of the distorted configuration in the 1 : 1 adduct would then become longer than the n.m.r. time-scale.

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