Synthesis and Crystal Structure of Bis(1-oxopyridine-2-thiolato)phenylbismuth

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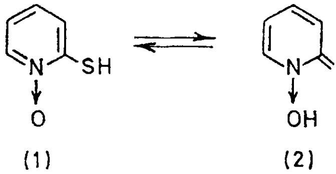
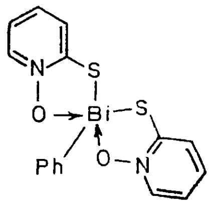
The title compound, a principal product of the reaction of acetato(diphenyl)bismuth and sodium 1-oxopyridine-2-thiolate, has been synthesised and its structure determined by *X*-ray crystallography from diffractometer data. Crystals are monoclinic, $a = 21{\cdot}157$, $b = 8{\cdot}813$, $c = 8{\cdot}944$ Å, all $\pm 0{\cdot}005$ Å, $\beta = 96{\cdot}74 \pm 0{\cdot}05°$, space-group $P2_1/a$, $Z = 4$. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to R 3·9% for 931 reflections. The co-ordination about the bismuth atom was found to be a distorted octahedron with a pair of electrons presumably occupying a co-ordination site. The sulphur and oxygen atoms are in a *cis*-configuration.

THE compound 1-oxopyridine-2-thiol (1) and its metal derivatives are of interest largely because of their potent antifungal and antibacterial properties.[1] However, relatively little is known about the manner in which (1), or its tautomer (2), bonds to metal atoms. Furthermore there is a lack of data which provide structural characterisation of organobismuth compounds.[2] We now describe the synthesis, isolation, and crystal structure of an organobismuth derivative (3) of the ligand (1).



(1) (2)



(3)

EXPERIMENTAL

Materials.—Diphenylbismuth acetate was obtained from the M & T Chemical Co. Phenylbismuth di-iodide was prepared according to a literature method.[3] All other chemicals were standard reagents. Melting points are corrected. I.r. spectra were obtained on a Perkin-Elmer model 621 or model 137 recording spectrophotometer for Nujol mulls.

Preparation of Compound (3).—Diphenylbismuth acetate

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[1] See, *e.g.*, A. Albert, C. W. Rees, and A. J. H. Tomlinson, *Brit. J. Exptl. Pathol.*, 1956, **37**, 500; A. Kaars Sijpesteijn and M. T. Janssen, *Nature*, 1958, **182**, 1313; U.S.P. 2,809,971; B.P. 761,171.

[2] G. O. Doak and L. D. Freedman, 'Organometallic Derivatives of Arsenic, Antimony, and Bismuth,' Wiley, New York, 1970.

[3] J. F. Wilkinson and F. Challenger, *J. Chem. Soc.*, 1924, **125**, 854.

(164·7 g, 0·39 mol) and sodium 1-oxopyridine-2-thiolate (59·7 g, 0·39 mol, 97·3% active) were added to dimethylformamide (3900 ml), stirred for 15 min (32°), and heated with stirring for 1·25 h (65°). The yellow solution was then filtered, and the filtrate mixed with dichloromethane and water (1 : 1 : 2). The bottom layer was separated and cooled in an ice bath. Crystals of the crude yellow product were washed with ether and water, and then dissolved in warm *NN*-dimethylacetamide (*ca.* 60°). When the warm solution was filtered, a small amount of solid was normally observed and was shown to be largely tris(1-oxopyridine-2-thiolato)bismuth (4) by comparison of its *X*-ray powder pattern with that of a prepared sample (see later).

The product was precipitated by the addition of water and was washed (water and ether). The purification procedure was repeated three more times. The crystals were dried, washed (ether), and redried *in vacuo* over P_4O_{10} [42%, m.p. (decomp.) 215—218 °C]. Traces of bright yellow crystals of the tris-product were observed in the light yellow sample viewed through a microscope (Found: C, 35·6; H, 2·5; Bi, 38·7; N, 5·2; S, 11·6. $C_{16}H_{13}BiN_2O_2S_2$ requires C, 35·7; H, 2·4; Bi, 38·8; N, 5·2; S, 11·9%).

This product was also prepared from phenylbismuth di-iodide and sodium 1-oxopyridine-2-thiolate in dimethylformamide, sodium iodide being removed by washing with water. Samples were re-precipitated four times as before, [m.p. (decomp.) 216—218 °C] (Found: C, 35·5; H, 2·4; Bi, 39·2; N, 5·3; S, 12·0%). Samples prepared by either method were shown to be identical from elemental analyses, *X*-ray powder photographs, and i.r. spectroscopy: ν(Bi–C) 442 and ν(Bi–O) 330 and 350 cm^{-1} (consistent with a *cis*-oxygen configuration).

Preparation of Compound (4).—$Bi(NO_3)_3,5H_2O$ (19·4 g, 0·04 mol) was dissolved in nitric acid (84 ml) and diluted with water to 2 l. Sodium 1-oxopyridine-2-thiolate (22·0 g, 0·143 mol, 96·8%) was dissolved in water (200 ml) and added to the solution and stirred for several minutes. The bright yellow product was washed with water and ethanol, air-dried, and washed with ether, hot dimethyl sulphoxide, hot *NN*-dimethylacetamide, and dried *in vacuo*; yield, 89% [m.p. (decomp.) 266—267·5°] (Found: C, 30·5; H, 2·0; Bi, 35·1; N, 7·0; S, 16·2. $C_{15}H_{12}BiN_3O_3S_3$ requires C, 30·7; H, 2·1; Bi, 35·6; N, 7·2; S, 16·4%).

Crystal Data.—$C_{16}H_{13}BiN_2O_2S_2$, Monoclinic, $a = 21{\cdot}157$, $b = 8{\cdot}813$, $c = 8{\cdot}944$ Å, all ±0·005 Å, $\beta = 96{\cdot}74 \pm 0{\cdot}05°$, $U = 1655{\cdot}7$ Å^3, $D_m = 2{\cdot}15$ (by flotation), $Z = 4$, $D_c = 2{\cdot}17$. Space-group $P2_1/a$ from systematic absences Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 95·0 cm^{-1}.

Determination of the Crystal Structure of (1).—Preliminary oscillation, Weissenberg, and precession photographs were used to determine the space-group. The unit-cell data were determined from diffractometer (Mo-K_α) measurements. Almost all reflections with indices $(h + k)$ odd were absent, but there were a few exceptions which eliminated the c centred unit cell from consideration. The bismuth atom was found to occupy a position with its y co-ordinate *ca.* 0·0, and thus the bismuth atoms are related by the translations of a c centred cell and cause the approximate $(h + k)$ odd absences. The crystal used for data collection was 0·23 × 0·23 × 0·10 mm. The intensity data were measured on a Siemens automatic diffractometer with five-step intensity measurements for each reflection. The intensity of the background was measured with stationary counts at the beginning and the end of a θ—2θ scan measurement across the peak, and two half scans across the peak were also measured. The reflections were measured up to $2\theta \leqslant 40°$ zirconium-filtered Mo-K_α radiation. 1534 Reflections were obtained of which 931 were > 3 times the standard deviation of the background intensity, and were considered observed (most $h + k$ odd reflections were unobserved). The intensities were converted to structure amplitudes by applying Lorentz and polarisation factors and approximately correcting absorption as a function of the diffractometer ϕ setting.

The bismuth atom position was identified in the Patterson map and used to calculate a Fourier map. An approximate spurious mirror plane at $y = 0$ resulted, but a sulphur atom, S(1), was identified out of the mirror plane and used with successive difference density maps to locate all the non-hydrogen atoms in the molecule. The R value, with only the bismuth atom used in the calculated structure-factors, was 22·6%. Least-squares refinement with all non-hydrogen atoms was carried out with isotropic temperature factors, and R was 4·9%. Anisotropic temperature factors were calculated for the bismuth and two sulphur atoms and varied for two cycles of full-matrix least-squares along with all positional parameters. The final R is 3·9% with the weighted value, 3·1% $[R' = \sqrt{\Sigma w(F_o - F_c)^2}/\sqrt{\Sigma w F_o^2}]$. The scattering factors used were those of Hanson *et al.*[4] with an anomalous dispersion correction of −4·8 e for the real component of the bismuth atomic scattering factor.[5] The weighting scheme is based upon counting statistics and has been described elsewhere.[6,*]

RESULTS AND DISCUSSION

Formation of Compound (3).—That the monophenyl derivative is formed is consistent with the earlier observations made concerning the reaction of diphenylbismuth chloride and sodium dimethyldithiocarbamate to give a monophenyl product.[7] Triphenylbismuth, identified by i.r. spectroscopy and m.p., is also observed in the product derived from the diphenylbismuth acetate. This, together with (3) may arise from a redistribution of diphenylbismuth acetate with subsequent reaction of the phenylbismuth diacetate. The tris complex (4), on the other hand, could be formed from any bismuth triacetate impurity in the diphenylbismuth acetate.

Crystal Structure (3).—The atomic positions and thermal parameters are listed in Table 1, and a perspective drawing of the molecule is shown in Figure 1. The molecular shape may be described as the intersection of two nearly perpendicular planes, the plane of the phenyl group and the approximate plane of the bismuth atom and the two bidentate ligands. The bismuth, sulphur, and oxygen atoms form a nearly planar moiety from which no atom deviates by $>0{\cdot}021$ Å.

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[*] Observed and calculated structure-factors are listed in Supplementary Publication No. SUP 20354 (2 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. sent as full size copies).

[4] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

[5] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[6] G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination,' Macmillan, New York, 1968.

[7] E. J. Kupchik and C. T. Theisen, *J. Organometallic Chem.*, 1968, **11**, 627.

TABLE 1

Full atomic and thermal parameters

Atom	x	y	z	B/Å^2
Bi	0·0506(1)	−0·0040(2)	0·2677(1)	*
S(1)	0·1154(3)	−0·0140(15)	0·0237(6)	*
S(2)	0·0329(3)	0·2594(7)	0·1298(6)	*
O(1)	0·1084(7)	−0·251(2)	0·248(2)	5·2(5)
O(2)	−0·0217(6)	0·158(2)	0·411(1)	4·1(4)
N(1)	0·1333(8)	−0·294(2)	0·128(2)	4·0(6)
N(2)	−0·0358(8)	0·302(2)	0·366(2)	3·5(5)
C(1)	0·153(1)	−0·445(2)	0·133(2)	4·6(8)
C(2)	0·182(1)	−0·495(5)	0·005(2)	5·6(7)
C(3)	0·192(1)	−0·401(3)	−0·120(3)	4·6(7)
C(4)	0·170(1)	−0·249(3)	−0·113(3)	5·0(8)
C(5)	0·141(1)	−0·194(2)	0·012(2)	3·6(7)
C(6)	−0·073(1)	0·384(3)	0·457(3)	4·0(7)
C(7)	−0·086(1)	0·537(3)	0·424(3)	5·5(9)
C(8)	−0·062(1)	0·602(3)	0·296(3)	4·4(7)
C(9)	−0·024(1)	0·520(3)	0·210(2)	4·7(7)
C(10)	−0·012(1)	0·366(3)	0·241(2)	3·7(7)
C(11)	0·134(1)	0·095(2)	0·417(2)	3·2(6)
C(12)	0·137(9)	0·072(2)	0·571(2)	3·4(7)
C(13)	0·187(1)	0·142(3)	0·672(2)	4·6(7)
C(14)	0·235(1)	0·228(3)	0·607(3)	5·0(8)
C(15)	0·228(1)	0·253(3)	0·447(3)	5·7(9)
C(16)	0·180(1)	0·176(3)	0·346(2)	4·0(7)

* Anisotropic parameters in the form:

$$\exp -\{\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl\}$$

	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Bi	14(2)	84(12)	102(12)	−3(17)	2(4)	12(34)
S(1)	41(20)	124(130)	129(91)	11(83)	34(35)	38(169)
S(2)	29(22)	133(116)	121(102)	13(45)	19(38)	45(101)

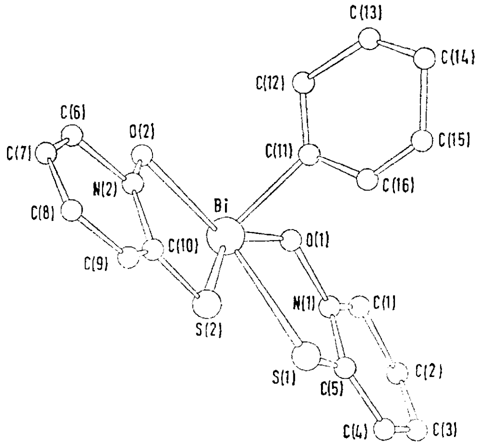

FIGURE 1 A drawing of the molecule showing the atom numbering

The phenyl group plane forms an angle of 85·1° with this plane.

The co-ordination about the bismuth atom may be described as a distorted octahedron with an electron pair presumably occupying one of the six co-ordination sites. The distortion to a square array about the bismuth atom is shown in Figure 2. The long oxygen–oxygen distance suggests either an electrostatic repulsion from partial negative charges on the oxygen atoms or an attractive sulphur–sulphur interaction.

The bond distances and angles are listed in Tables 2 and 3, respectively. Because of the dominance of the bismuth atom scattering, the standard deviations in light atom positions are large. The interatomic distances in the rings are reasonable in light of these estimated errors. The carbon–sulphur distances are between the mean carbon–sulphur thione distance of 1·673 Å reported for purine and pyrimidine thione derivatives[8] and the mean carbon–sulphur distance of 1·81 Å for paraffinic thiol compounds.[9] The oxygen–bismuth distances are in the intermediate range of bismuth(III)–oxygen bonds reported in bismuth(III) formate.[10]

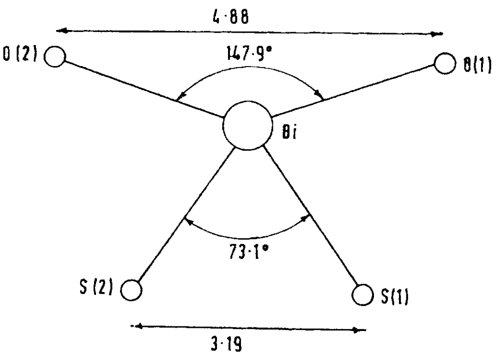

FIGURE 2 The Bi–O and Bi–S bonds

TABLE 2

Bond distances (Å)

Bi–S(1)	2·712(6)	C(3)–C(4)	1·42(3)
Bi–S(2)	2·635(9)	C(4)–C(5)	1·43(3)
Bi–O(1)	2·51(2)	N(2)–C(6)	1·40(3)
Bi–O(2)	2·54(1)	C(6)–C(7)	1·40(3)
Bi–C(11)	2·26(2)	C(7)–C(8)	1·42(3)
O(1)–N(1)	1·31(2)	C(8)–C(9)	1·38(3)
O(2)–N(2)	1·36(2)	C(9)–C(10)	1·41(4)
S(1)–C(5)	1·68(2)	C(11)–C(12)	1·39(3)
S(2)–C(10)	1·72(2)	C(12)–C(13)	1·46(3)
C(5)–N(1)	1·39(3)	C(13)–C(14)	1·44(3)
C(10)–N(2)	1·41(3)	C(14)–C(15)	1·44(3)
N(1)–C(1)	1·40(3)	C(15)–C(16)	1·44(3)
C(1)–C(2)	1·43(3)	C(16)–C(11)	1·42(3)
C(2)–C(3)	1·43(3)		

TABLE 3

Bond angles (°)

S(1)–Bi–S(2)	73·1(2)	C(4)–C(5)–N(1)	118(2)
O(1)–Bi–O(2)	147·9(5)	S(2)–C(10)–N(2)	121(2)
S(1)–Bi–C(11)	93·1(5)	C(9)–C(10)–N(2)	117(2)
S(2)–Bi–C(11)	89·7(5)	S(2)–C(10)–C(9)	122(2)
O(1)–Bi–C(11)	91·3(5)	Bi–O(1)–N(1)	124(1)
O(2)–Bi–C(11)	87·8(5)	Bi–S(1)–C(5)	106(1)
O(1)–Bi–S(1)	71·3(3)	Bi–O(2)–N(2)	120(1)
O(1)–Bi–S(2)	144·4(3)	Bi–S(2)–C(10)	106(1)
O(2)–Bi–S(1)	140·7(3)	N(1)–C(1)–C(2)	115(1)
O(2)–Bi–S(2)	67·7(3)	C(1)–C(2)–C(3)	125(3)
C(16)–C(11)–C(12)	124(2)	C(2)–C(3)–C(4)	116(2)
Bi–C(11)–C(16)	118(2)	C(3)–C(4)–C(5)	122(2)
Bi–C(11)–C(12)	118(2)	N(2)–C(6)–C(7)	119(2)
C(1)–N(1)–O(1)	113(2)	C(6)–C(7)–C(8)	119(2)
C(1)–N(1)–C(5)	125(2)	C(7)–C(8)–C(9)	121(2)
O(1)–N(1)–C(5)	122(2)	C(8)–C(9)–C(10)	121(2)
O(2)–N(2)–C(6)	116(2)	C(11)–C(16)–C(15)	116(2)
O(2)–N(2)–C(10)	121(2)	C(16)–C(15)–C(14)	122(2)
C(6)–N(2)–C(10)	123(2)	C(15)–C(14)–C(13)	119(2)
S(1)–C(5)–C(4)	123(2)	C(14)–C(13)–C(12)	118(2)
S(1)–C(5)–N(1)	119(2)	C(13)–C(12)–C(11)	120(2)

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[8] G. Lin, M. Sundaralingam, and S. K. Arora, *J. Amer. Chem. Soc.*, 1971, **93**, 1235.

[9] *Chem. Soc. Special Publ.*, No. 12, 1958.

[10] C. Stalhandske, *Acta Chem. Scand.*, 1969, **23**, 1525.

The packing in the unit cell is shown in a projection along the *b* axis in Figure 3. The closest bismuth–bismuth interaction is Bi · · · Bi^{I} 4·89 Å; the shortest intermolecular distance is Bi · · · O(2)^{I} 3·37 Å (atom I is at $-x$, $-y$, $1 - z$), which suggests an attraction between the two atoms. A bismuth–oxygen distance of 3·15 Å has been described as part of a secondary co-ordination sphere in tris(3-sulphanilamido-6-methoxypyridazine)-bismuth chloride.[11] The molecules are packed so as to leave a void on the side of the bismuth atom opposite the phenyl group. A final difference density map disclosed a peak of 1·5 eÅ^{-3} between the bismuth atom and S(1), however, it is probably a spurious peak since it is only 1·33 Å from the bismuth atom. A bismuth–hydrogen distance is reported to be 1·81 Å.[9] No other peaks appear in this difference density map in this void. Another example of a similarly exposed side of a Group VA atom is found in the recently reported structures of the potassium and ammonium tris(oxalato)antimonate(III) tetrahydrates, in which an electron lone-pair occupies an axial position of a pentagonal bipyramid.[12]

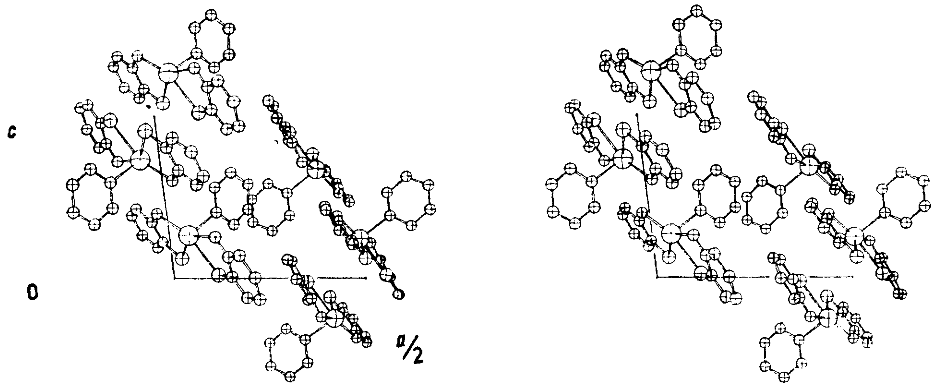

FIGURE 3 A stereo-projection along the *b* axis

We thank M. R. Becker, H. J. Steinnecker, and L. C. Strickland for technical assistance.

[1/1770 *Received, 27th September,* 1971]

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[11] L. Cavalca, M. Nardelli, G. Fava, and G. Giraldi, *Acta Cryst.*, 1963, **16**, *A*, 69.

[12] M. C. Poore and D. R. Russell, *Chem. Comm.*, 1971, 18.