A Tris-Complex of 3-Mercapto-1,5-diphenylformazan: Structure of Bismuth Dithizonate*

By Margaret L. Niven,† Harry M. N. H. Irving and Luigi R. Nassimbeni

School of Chemical Sciences, University of Cape Town, Rondebosch 7700, South Africa

and Alan T. Hutton

Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT, England

Abstract

[Bi(C$_{13}$H$_{11}$N$_4$S)$_3$], C$_{39}$H$_{33}$BiN$_{12}$S$_3$, M_r = 974·56, m.p. 450–459 K, crystallizes in the triclinic space group $P\bar{1}$ with a = 15·599 (8), b = 14·042 (7), c = 13·461 (7) Å, α = 112·50 (2), β = 120·03 (2), γ = 55·96 (2)°, Z = 2, V = 2094 (2) Å^3, D_m = 1·52, D_c = 1·55 Mg m^{-3}, μ(Mo $K\alpha$) = 4·22 mm^{-1}, $F(000)$ = 958. Final R = 0·065 for 4830 observed reflections. There is a facial arrangement of the ligands around the Bi^{III}. Bi–S and Bi–N distances are in the ranges 2·613 (3)–2·606 (3) Å and 2·746 (10)–2·678 (9) Å respectively. The dithizone residues retain a marked planarity.

Introduction

X-ray structure determinations on metal complexes of dithizone (3-mercapto-1,5-diphenylformazan; H$_2$dz) are few in number, but in every case the ligand behaves as a bidentate chelating agent coordinating through both nitrogen and sulphur to give a five-membered ring of the type shown in Fig. 1.

Nickel dithizonate, Ni(Hdz)$_2$, is essentially square planar with angles S–Ni–S and N–Ni–N of 96 and 98° respectively, with a Ni–S bond of 2·19 Å and a

---

* IUPAC nomenclature: Tris(1,5-diphenylthiocarbazonato-*N*,*S*)-bismuth(III).

† Author to whom correspondence should be addressed.

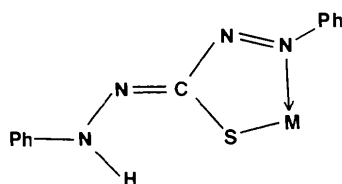Fig. 1. Coordination of dithizone.

© 1982 International Union of Crystallography

normal Ni–N distance of 1·87 Å (Laing & Alsop, 1970). The whole molecule including the distal phenyl rings is almost coplanar. It has been shown (Alsop, 1971) that the platinum and palladium Pt(Hdz)$_2$ and Pd(Hdz)$_2$ are isostructural. Primary zinc dithizonate, Zn(Hdz)$_2$, on the other hand, has been studied independently by two groups (Math & Freiser 1970; Mawby & Irving, 1971, 1972) and has been shown to contain two almost planar dithizonate groups acting as bidentate ligands and tetrahedrally coordinated to zinc through sulphur (Zn–S, 2·22 and 2·29 Å) and nitrogen (Zn–N, 2·11 and 2·03 Å). The orange orthorhombic crystals of mercury dithizonate have also shown (Harding, 1958; Alsop, 1971) a distorted tetrahedral configuration about mercury with two short Hg–S bonds (2·33 Å) and two long Hg–N bonds (2·56 Å). Unfortunately the crystals (from pyridine) retain about 2 mol of solvent for 1 mol of complex which are clearly not coordinated. When kept over concentrated sulphuric acid, crystals of Hg(Hdz)$_2$.2py lose pyridine, become optically opaque and show an X-ray powder pattern. In contrast, well-defined and solvent-free crystals of phenylmercury(II) dithizonate, PhHg(Hdz), (Hutton & Irving, 1979; Hutton, Irving & Nassimbeni, 1980) and methylmercury(II) dithizonate, CH$_3$Hg(Hdz), (Hutton, Irving & Nassimbeni, 1980; Hutton, 1980) show essentially the same features as far as the chelation is concerned and are interesting because of the irregular three-coordination about the mercury atom. A preliminary communication (Bryan & Knopf, 1961) indicates that copper(II) dithizonate, Cu(Hdz)$_2$, has a square-planar configuration about the central atom, but the structures of Cd(Hdz)$_2$ and Pb(Hdz)$_2$, and those of the 1:1 complexes such as Ag(Hdz), Tl(Hdz) and for example R_3Pb(Hdz) or R_2Tl(Hdz) (R = alkyl), are still unknown. Nickel dithizonate forms a 1:1 adduct with 2,2'-bipyridyl (Math & Freiser, 1970) and in the resulting octahedral complex Ni(Hdz)$_2$.bpy, the two chelated dithizone

moieties occur, somewhat surprisingly, with the two S atoms in a *cis* position.

Bismuth dithizonate Bi(Hdz)$_3$ is the only tris-complex which can be obtained by liquid–liquid extraction from an aqueous phase and its structure has therefore been investigated to see whether octahedral coordination is involved and whether a *mer* or *fac* configuration is favoured.

Experimental

Preparation

According to a previously reported method (Alsop, 1971) the complex was prepared by shaking a 0·5% solution of dithizone in chloroform with 0·05 M Bi^{3+}, which had been obtained by dissolving metallic bismuth in boiling concentrated H$_2$SO$_4$, diluting, complexing with KCN and adding ammonia to pH 5. After shaking, the chloroform layer was removed through filter paper, washed with water and refiltered, dried over anhydrous magnesium sulphate and finally evaporated under nitrogen. Bronze crystals were grown from CS$_2$ and, after grinding, were deemed suitable for X-ray analysis.

Crystal and intensity data

Preliminary photographs (Cu $K\alpha$ radiation, λ = 1·542 Å) showed no symmetry and no systematic absences, indicating one of the two triclinic space groups. Accurate cell dimensions were obtained by least squares from the settings of 25 high-order reflections measured on a Philips PW 1100 four-circle

Table 1. *Experimental and refinement parameters for the crystal structure of* Bi(Hdz)$_3$

Composition	
% C found (calc.)	47·85 (48·05)
% H	3·55 (3·40)
% N	16·95 (17·20)
Data collection	
Crystal dimensions (mm)	0·60 × 0·56 × 0·40
Scan mode	ω–2θ
Scan width ($^\circ\theta$)	1·3
Scan speed ($^\circ\theta$ s^{-1})	0·043
Range scanned (2θ) ($^\circ$)	6–46
Stability of standard reflections (%)	0·52
Number of reflections collected	5425
Number of observed reflections	4830 with $I_{(rel)} > 2\sigma I_{(rel)}$
Refinement	
Number of variables	243
$R = \sum \|\|F_o\| - \|F_c\|\|/\sum \|F_o\|$	0·065
$R_w = \sum w^{1/2}\|\|F_o\| - \|F_c\|\|/\sum w^{1/2}\|F_o\|$	0·066
Weighting scheme w	$(\sigma^2 F + 2 \times 10^{-3} F^2)^{-1}$
U_{iso} of H atoms in calculated positions	
Aromatic (Å^2)	0·087 (9)
Imino protons H [N(15),N(25),N(35)] (Å^2)	0·080 (6)

diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·7107 Å). Intensities were collected by the ω–2θ scan technique. The intensities of three reference reflections were monitored after every 68 measured reflections to ascertain stability of the crystal. Lorentz–polarization corrections were applied but no correction was made for absorption. Experimental details of the data collection are listed in Table 1.

Solution and refinement of the structure

The space group $P\bar{1}$ was chosen as the more likely, and the successful refinement of the structure vindicated this choice.

The Bi atom was located in a Patterson map and subsequent weighted difference syntheses yielded the positions of all the remaining non-hydrogen atoms. The final full-matrix least-squares refinement was carried out with the Bi and S atoms treated anisotropically and the remaining non-hydrogen atoms isotropically. The aromatic H atoms were constrained to ride at 1·00 Å from their respective parent C atoms, their positions being dictated by the geometry of the molecule. Their isotropic temperature factors were treated as a single parameter. No imino protons were revealed in difference maps; however, as justified later in the paper, they were placed in calculated positions and constrained to ride at 1·0 Å from N(15), N(25) and N(35) respectively, with a single temperature factor for all three. Details of the final refinements are given in Table 1. The weighting schemes were chosen to give the smallest systematic variation of $w\Delta^2$ with the magnitude of F_o, as shown by analyses of variance computed after the final cycles.* In the final cycle the mean e.s.d. in the parameters of the non-hydrogen atoms was >100 times the average parameter shift, while the final difference map was smooth except close to Bi where the largest residual peaks were 1·89 and 1·82 e Å^{-3}. Complex neutral-atom scattering factors were taken from Cromer & Mann (1968) for Bi, C, N and S and from Stewart, Davidson & Simpson (1965) for H, with dispersion corrections from Cromer & Liberman (1970). Table 2 lists the final fractional atomic coordinates and temperature factors for all the non-hydrogen atoms. All computations were performed at the Computer Centre of the University of Cape Town on a Univac 1100/81 computer with *SHELX* (data reduction, structure solution and refinement), *XANADU* (molecular geometry) and *PLUTO* (illustrations) (Sheldrick, 1976; Roberts & Sheldrick, 1975; Motherwell, 1974).

---

* The analyses of variance, lists of structure factors, hydrogen-atom coordinates, anisotropic temperature factors, least-squares-planes parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36792 (52 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates* $(\times 10^4)$ *and thermal parameters* $(\text{Å}^2 \times 10^3)$ *for non-hydrogen atoms*

	x	y	z	U_{eq} or U_{Iso}
Bi(1)	3019 (1)	574 (1)	476 (1)	39 (1)*
S(1)	4795 (2)	829 (2)	1942 (2)	41 (2)*
S(2)	4144 (3)	−1464 (3)	−497 (3)	44 (2)*
S(3)	2968 (3)	1559 (3)	−866 (2)	51 (2)*
N(11)	2505 (7)	2727 (7)	1712 (7)	35 (2)
N(12)	3186 (7)	3134 (8)	2280 (8)	39 (2)
C(13)	4290 (8)	2320 (9)	2457 (9)	33 (2)
N(14)	4960 (8)	2800 (8)	3092 (8)	42 (2)
N(15)	6039 (8)	2133 (8)	3337 (8)	40 (2)
C(111)	1354 (9)	3597 (9)	1497 (10)	40 (3)
C(112)	976 (11)	4762 (11)	1602 (11)	53 (3)
C(113)	−121 (11)	5526 (12)	1377 (12)	60 (4)
C(114)	−876 (13)	5128 (13)	1024 (13)	68 (4)
C(115)	−521 (13)	3971 (13)	876 (13)	73 (4)
C(116)	616 (11)	3192 (12)	1123 (12)	58 (3)
C(151)	6801 (9)	2586 (9)	4066 (9)	38 (3)
C(152)	7900 (10)	1860 (11)	4228 (11)	51 (3)
C(153)	8686 (12)	2266 (12)	4962 (12)	61 (4)
C(154)	8363 (12)	3346 (12)	5506 (13)	65 (4)
C(155)	7290 (13)	4077 (13)	5376 (13)	67 (4)
C(156)	6464 (12)	3700 (12)	4620 (12)	59 (3)
N(21)	4099 (8)	−1052 (8)	1829 (8)	40 (2)
N(22)	4757 (8)	−2104 (8)	1579 (8)	44 (2)
C(23)	4835 (9)	−2392 (10)	497 (10)	41 (3)
N(24)	5527 (9)	−3499 (9)	326 (9)	53 (3)
N(25)	5718 (9)	−3925 (9)	−638 (9)	51 (3)
C(211)	4023 (9)	−814 (9)	2914 (10)	40 (3)
C(212)	4363 (12)	−1672 (13)	3485 (13)	66 (4)
C(213)	4215 (13)	−1312 (14)	4560 (14)	73 (4)
C(214)	3792 (13)	−189 (14)	5002 (15)	77 (4)
C(215)	3448 (12)	676 (12)	4445 (12)	62 (4)
C(216)	3567 (11)	329 (11)	3392 (11)	52 (3)
C(251)	6340 (10)	−5110 (10)	−901 (10)	46 (3)
C(252)	6683 (12)	−5502 (12)	−1814 (12)	63 (4)
C(253)	7314 (14)	−6680 (14)	−2094 (15)	79 (5)
C(254)	7615 (15)	−7443 (16)	−1442 (16)	85 (5)
C(255)	7259 (13)	−7046 (14)	−549 (14)	76 (4)
C(256)	6616 (11)	−5885 (12)	−295 (12)	59 (4)
N(31)	1371 (8)	614 (8)	−1682 (8)	44 (2)
N(32)	1223 (8)	1024 (8)	−2464 (8)	45 (2)
C(33)	1902 (9)	1497 (9)	−2178 (10)	39 (3)
N(34)	1621 (8)	1942 (8)	−3087 (9)	47 (2)
N(35)	2171 (9)	2448 (9)	−2938 (9)	50 (3)
C(311)	662 (10)	169 (10)	−1987 (11)	48 (3)
C(312)	−224 (12)	245 (13)	−3018 (14)	68 (4)
C(313)	−896 (14)	−221 (14)	−3247 (15)	78 (4)
C(314)	−698 (13)	−780 (13)	−2502 (14)	72 (4)
C(315)	137 (15)	−889 (16)	−1480 (16)	88 (5)
C(316)	838 (14)	−370 (14)	−1168 (15)	80 (5)
C(351)	1890 (11)	3013 (11)	−3812 (11)	50 (3)
C(352)	991 (11)	3039 (11)	−4840 (12)	58 (3)
C(353)	731 (14)	3606 (13)	−5717 (14)	73 (4)
C(354)	1384 (14)	4098 (14)	−5466 (15)	79 (5)
C(355)	2232 (15)	4079 (15)	−4440 (15)	84 (5)
C(356)	2496 (12)	3528 (12)	−3602 (13)	65 (4)

* U_{eq} for anisotropic atoms calculated according to:

$$U_{eq} = \tfrac{1}{3}(U_{11}\sin^2\alpha + U_{22}\sin^2\beta + U_{33}\sin^2\gamma + 2U_{23}\sin\beta\sin\gamma\cos\alpha$$

$$+ 2U_{31}\sin\alpha\cos\beta\sin\gamma + 2U_{12}\sin\alpha\sin\beta\cos\gamma)/$$

$$(1 + 2\cos\alpha\cos\beta\cos\gamma - \cos^2\alpha - \cos^2\beta - \cos^2\gamma).$$

Results and discussion

Bond lengths and angles for the title complex are given in Tables 3 and 4 respectively. Relevant bond orders in the dithizone residues, calculated according to a previously reported method (Burke-Laing & Laing, 1976), are given in Table 5. The molecular structure is illustrated in Fig. 2. The crystals consist of discrete molecules, each containing three dithizone residues acting as bidentate ligands coordinating through S and N. The configuration of the molecule is all-*cis*, *i.e.* the three S atoms are facially arranged on one side of the bismuth coordination sphere; such a situation is to be expected from steric considerations of the ligand.

Bismuth coordination

The coordination about the Bi^{3+} ion may be described as pseudo octahedral, distortions from the regular structure evidenced by deviations from 90 and 180° of the *cis*- and *trans-L—Bi—L* bond angles ($L =$ coordinating ligand atom). It has been reported (Myers, 1967, 1968) that for Bi^{III} the lone pair is only slightly if at all stereochemically active, in which case the distortions in this structure would presumably arise from 'bite' limitations of the dithizonate ligands. However, later works indicate that the lone electron

Table 3. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

Bi(1)—S(1)	2·607 (3)	C(211)—C(212)	1·38 (2)
Bi(1)—S(2)	2·606 (3)	C(212)—C(213)	1·43 (2)
Bi(1)—S(3)	2·613 (3)	C(213)—C(214)	1·34 (2)
Bi(1)—N(11)	2·706 (8)	C(214)—C(215)	1·38 (2)
Bi(1)—N(21)	2·678 (9)	C(215)—C(216)	1·38 (2)
Bi(1)—N(31)	2·746 (10)	C(216)—C(211)	1·37 (2)
S(1)—C(13)	1·75 (1)	N(25)—C(251)	1·39 (2)
S(2)—C(23)	1·72 (1)	C(251)—C(252)	1·38 (2)
S(3)—C(33)	1·73 (1)	C(252)—C(253)	1·39 (2)
N(11)—N(12)	1·25 (1)	C(253)—C(254)	1·37 (2)
N(12)—C(13)	1·39 (1)	C(254)—C(255)	1·37 (2)
C(13)—N(14)	1·32 (1)	C(255)—C(256)	1·37 (2)
N(14)—N(15)	1·32 (1)	C(256)—C(251)	1·36 (2)
N(11)—C(111)	1·45 (1)	N(31)—N(32)	1·25 (1)
C(111)—C(112)	1·37 (2)	N(32)—C(33)	1·38 (2)
C(112)—C(113)	1·36 (2)	C(33)—N(34)	1·35 (2)
C(113)—C(114)	1·38 (2)	N(34)—N(35)	1·30 (1)
C(114)—C(115)	1·36 (2)	N(31)—C(311)	1·38 (2)
C(115)—C(116)	1·40 (2)	C(311)—C(312)	1·37 (2)
C(116)—C(111)	1·36 (2)	C(312)—C(313)	1·38 (2)
N(15)—C(151)	1·41 (1)	C(313)—C(314)	1·32 (2)
C(151)—C(152)	1·37 (2)	C(314)—C(315)	1·33 (2)
C(152)—C(153)	1·39 (2)	C(315)—C(316)	1·45 (2)
C(153)—C(154)	1·32 (2)	C(316)—C(311)	1·40 (2)
C(154)—C(155)	1·34 (2)	N(35)—C(351)	1·42 (2)
C(155)—C(156)	1·42 (2)	C(351)—C(352)	1·39 (2)
C(156)—C(151)	1·36 (2)	C(352)—C(353)	1·44 (2)
N(21)—N(22)	1·27 (1)	C(353)—C(354)	1·38 (2)
N(22)—C(23)	1·40 (2)	C(354)—C(355)	1·35 (2)
C(23)—N(24)	1·32 (2)	C(355)—C(356)	1·37 (2)
N(24)—N(25)	1·31 (1)	C(356)—C(351)	1·36 (2)
N(21)—C(211)	1·42 (2)		

Table 4. Angles (°) with e.s.d.'s in parentheses

S(1)–Bi(1)–S(2)	93·5 (1)	N(21)–N(22)–C(23)	115·6 (9)
S(2)–Bi(1)–S(3)	90·0 (1)	S(2)–C(23)–N(22)	126·5 (8)
S(3)–Bi(1)–S(1)	84·8 (1)	S(2)–C(23)–N(24)	123·1 (9)
S(1)–Bi(1)–N(11)	68·0 (2)	N(22)–C(23)–N(24)	110·4 (10)
S(2)–Bi(1)–N(11)	160·1 (2)	C(23)–N(24)–N(25)	119·1 (10)
S(3)–Bi(1)–N(11)	81·6 (2)	N(24)–N(25)–C(251)	120·3 (10)
S(1)–Bi(1)–N(21)	77·4 (2)	N(21)–C(211)–C(212)	123·1 (11)
S(2)–Bi(1)–N(21)	68·9 (2)	N(21)–C(211)–C(216)	117·5 (10)
S(3)–Bi(1)–N(21)	151·0 (2)	C(212)–C(211)–C(216)	119·5 (12)
N(11)–Bi(1)–N(21)	111·6 (3)	C(211)–C(212)–C(213)	117·4 (14)
S(1)–Bi(1)–N(31)	152·4 (2)	C(212)–C(213)–C(214)	120·8 (15)
S(2)–Bi(1)–N(31)	81·8 (2)	C(213)–C(214)–C(215)	122·6 (16)
S(3)–Bi(1)–N(31)	68·1 (2)	C(214)–C(215)–C(216)	116·6 (14)
N(11)–Bi(1)–N(31)	111·1 (3)	C(211)–C(216)–C(215)	123·2 (12)
N(21)–Bi(1)–N(31)	124·8 (3)	N(25)–C(251)–C(252)	118·3 (11)
Bi(1)–S(1)–C(13)	104·8 (4)	N(25)–C(251)–C(256)	122·2 (12)
Bi(1)–S(2)–C(23)	105·6 (4)	C(252)–C(251)–C(256)	119·6 (12)
Bi(1)–S(3)–C(33)	105·6 (4)	C(251)–C(252)–C(253)	119·8 (14)
Bi(1)–N(11)–N(12)	123·3 (7)	C(252)–C(253)–C(254)	119·5 (17)
Bi(1)–N(11)–C(111)	120·7 (6)	C(253)–C(254)–C(255)	120·2 (17)
N(12)–N(11)–C(111)	113·8 (9)	C(254)–C(255)–C(256)	119·9 (16)
N(11)–N(12)–C(13)	114·7 (9)	C(251)–C(256)–C(255)	121·0 (14)
S(1)–C(13)–N(12)	126·7 (8)	Bi(1)–N(31)–N(32)	122·0 (7)
S(1)–C(13)–N(14)	121·9 (8)	Bi(1)–N(31)–C(311)	122·6 (7)
N(12)–C(13)–N(14)	111·4 (9)	N(32)–N(31)–C(311)	115·4 (10)
C(13)–N(14)–N(15)	118·5 (9)	N(31)–N(32)–C(33)	116·7 (10)
N(14)–N(15)–C(151)	120·9 (9)	S(3)–C(33)–N(32)	127·5 (8)
N(11)–C(111)–C(112)	124·7 (10)	S(3)–C(33)–N(34)	122·4 (9)
N(11)–C(111)–C(116)	115·9 (10)	N(32)–C(33)–N(34)	110·1 (10)
C(112)–C(111)–C(116)	119·4 (11)	C(33)–N(34)–N(35)	117·3 (10)
C(111)–C(112)–C(113)	121·2 (13)	N(34)–N(35)–C(351)	121·7 (11)
C(112)–C(113)–C(114)	119·9 (13)	N(31)–C(311)–C(312)	124·9 (12)
C(113)–C(114)–C(115)	119·6 (15)	N(31)–C(311)–C(316)	117·7 (12)
C(114)–C(115)–C(116)	119·9 (15)	C(312)–C(311)–C(316)	117·3 (13)
C(111)–C(116)–C(115)	119·9 (13)	C(311)–C(312)–C(313)	121·0 (15)
N(15)–C(151)–C(152)	117·7 (10)	C(312)–C(313)–C(314)	121·8 (17)
N(15)–C(151)–C(156)	121·5 (11)	C(313)–C(314)–C(315)	121·3 (17)
C(152)–C(151)–C(156)	120·8 (12)	C(314)–C(315)–C(316)	119·4 (17)
C(151)–C(152)–C(153)	119·6 (12)	C(311)–C(316)–C(315)	119·0 (16)
C(152)–C(153)–C(154)	119·8 (14)	N(35)–C(351)–C(352)	118·8 (12)
C(153)–C(154)–C(155)	122·1 (15)	N(35)–C(351)–C(356)	118·8 (12)
C(154)–C(155)–C(156)	119·7 (14)	C(352)–C(351)–C(356)	122·4 (13)
C(151)–C(156)–C(155)	118·0 (13)	C(351)–C(352)–C(353)	117·7 (13)
Bi(1)–N(21)–N(22)	123·3 (7)	C(352)–C(353)–C(354)	117·5 (15)
Bi(1)–N(21)–C(211)	123·3 (7)	C(353)–C(354)–C(355)	122·7 (17)
N(22)–N(21)–C(211)	113·5 (9)	C(354)–C(355)–C(356)	120·3 (17)
		C(351)–C(356)–C(355)	119·4 (15)

Fig. 2. Perspective view of the molecular structure of Bi(Hdz)₃.

Table 5. Relevant bond orders in the dithizone residues

Bond	Order		Sum of bond orders around N atom
N(11)–C(111)	1·01	N(11)	2·81
N(11)–N(12)	1·80		
N(12)–C(13)	1·25	N(12)	3·05
C(13)–N(14)	1·58		
N(14)–N(15)	1·44	N(14)	3·02
N(15)–C(151)	1·11	N(15)	2·55 + 1(N–H) = 3·55
N(21)–C(211)	1·07	N(21)	2·82
N(21)–N(22)	1·75		
N(22)–C(23)	1·16	N(22)	2·91
C(23)–N(24)	1·69	N(24)	2·97
N(24)–N(25)	1·28		
N(25)–C(251)	1·20	N(25)	2·48 + 1(N–H) = 3·48
N(31)–C(311)	1·25	N(31)	3·03
N(31)–N(32)	1·78		
N(32)–C(33)	1·39	N(32)	3·17
C(33)–N(34)	1·50	N(34)	3·05
N(34)–N(35)	1·55		
N(35)–C(351)	1·11	N(35)	2·66 + 1(N–H) = 3·66

pair in Bi^{III} is stereochemically active resulting in distortions not only of coordination bond angles but also in the relevant bond lengths. In the crystal structure of Bi^{III} O,O'-diisopropylphosphorodithioate (Lawton, Fuhrmeister, Haas, Jorman & Lohmeyer, 1974) lone-pair–bond-pair repulsions in the Bi coordination sphere result in larger bond lengths for those bonds adjacent to the lone pair [Bi–S = 2·89 (1), 2·88 (1), 2·86 (1) Å; av. r.m.s. = 2·87 (2) Å], and shorter lengths for those more remote [Bi–S = 2·71 (1), 2·70 (1), 2·69 (1) Å; av. r.m.s. = 2·70 (1) Å], as well as an opening of the bond angles straddling the lone pair. In the crystal structure of tris(diethyl-dithiocarbamato)bismuth(III) (Raston & White, 1976), a stereochemically active lone pair is again suggested by three short Bi–S bonds fac, one from each ligand [Bi–S 2·60 (1)–2·78 (1) Å], and three long bonds [Bi–S 2·91 (1)–2·96 (1) Å].

Concerning the structure reported here, one long Bi–S [2·613 (3) Å, cf. 2·606 (3), 2·607 (3) Å] and two long Bi–N [2·746 (10), 2·706 (8) Å, cf. 2·678 (9) Å] imply that the lone pair on Bi^{III} is situated in the region encompassed by S(3), N(11) and N(31). However, its stereochemical activity is presumably overridden by the strength and rigidity of the ligand, no significant opening of the bond angles straddling the lone pair being evidenced.

Bi–S and Bi–N bond distances of this order of magnitude have been observed previously (Battaglia, Bonamartini Corradi, Nardelli & Vidoni Tani, 1978) in the structure of μ_4-chloro-{tris[trichloro(thiosemi-carbazide)bismuth(III)]}[tris(thiosemicarbazide)bis-muth(III)] hexachlorobismuthate(III) chloride [Bi–S in the range 2·60 (1)–2·64 (1) Å; Bi–N in the range 2·54 (4)–2·71 (4) Å].

Generally, however, Bi–S distances appear to be slightly longer. Bi–S covalent bond distances in various other six-coordinate Bi^{III} structures are in the range 2·68 (1)–2·79 (1) Å (Battaglia, Bonamartini Corradi,

Pelizzi & Vidoni Tani, 1975), 2·69 (1)–2·87 (1) Å (Lawton *et al.*, 1974), 2·74 (1)–2·79 (1) Å (Battaglia & Bonamartini Corradi, 1981), and in *catena-μ*-chloro-dichlorobis(ethylenethiourea)bismuth(III) (Battaglia *et al.*, 1978), Bi–S is 2·706 (5) Å. A single low value of 2·60 (1) Å for one Bi–S distance in the structure of tris(diethyldithiocarbamato)bismuth(III) [as compared with the range 2·70 (1)–2·96 (1) for other Bi–S in that structure] (Raston & White, 1976) is attributed to a weak dimerization interaction with a neighbouring molecule and is hence not representative of 'normal' Bi–S covalent bond distances. Even a reduction in coordination number from 6 to 5 does not appear to enhance Bi–S bond strengths as shown in the structure of bis(1-oxopyridine-2-thiolato)phenylbismuth (Curry & Jandacek, 1972) in which Bi–S bonds are 2·64 (1) and 2·71 (1) Å.

A Bi–N length of 2·90 (1) Å in trichlorotris(3-sulphanilamido-6-methoxypyridazine)bismuth(III) (Belicchi Ferrari, Calzolari Capacchi, Cavalca & Fava Gasparri, 1972) is also longer than those found in this work. However, the Bi^{III} in that structure is nine coordinate, a factor which may be contributing to the weakening of Bi–N bonds.

The therefore relative shortening of Bi–S in Bi(Hdz)$_3$ may be attributed to the coordinating strength of the dithizonate ligand which is of course to be expected from the high Lewis basicity of the S atom, its being the strong base of the weak acid dithizone (p$K_a \simeq 5$) (Irving, 1977). The strength of the ligand is further evidenced in its coordination with Zn^{II} for which extremely short strong Zn–S bonds (2·22 and 2·29 Å) are obtained (Math & Freiser, 1971; Mawby & Irving, 1971, 1972).

The dithizone residue

Single-bonded :N–N: and :C–N: normally have a length of 1·47 Å, while double-bonded ·N=N· and :C=N are 1·25 and 1·27 Å respectively. Hence N(11)–N(12), N(21)–N(22) and N(31)–N(32) are largely double bond in character, having lengths 1·25 (1), 1·27 (1) and 1·25 (1) Å respectively: these correspond to bond orders (Burke-Laing & Laing, 1976) of *ca* 1·7–1·8. Remaining N–N bond distances in the dithizone residues are significantly longer [N(14)–N(15) 1·32 (1), N(24)–N(25), 1·31 (1), N(34)–N(35) 1·30 (1)] indicating greater single-bond character. C–N distances between the phenyl rings and the N–N–C–N–N chains are in the range 1·38 (1)–1·45 (1) Å which yield bond orders of ~1·0–1·2 while the remaining C–N distances are shorter, somewhat intermediate between single and double character, implying delocalization of π electrons within the N–N–C–N–N chain. It has been found (Burke-Laing & Laing, 1976) that the sum of the bond orders for an N atom bonded to only *two* other atoms is close to 3,

but for an N atom bonded to three atoms (one being H for which the N–H bond order is 1) it is well above 3, between 3·4 and 3·7. On this basis the geometrical placement of H atoms such that they bond to N(15), N(25) and N(35) is well justified (see Table 5).

The three S–C bond lengths [1·75 (1), 1·72 (1) and 1·73 (1) Å] are of the expected magnitude and yield bond orders ~1·0 (Laing, 1977). The S–C bond order is probably decreased by donation of electron density to the Bi acceptor upon coordination, for the S–C bond order in crystalline dithizone is given as 1·2. Bond lengths and angles pertaining to the phenyl rings are as expected. The parameters for several least-squares planes and a list of torsion angles have been deposited.*

In previously studied metal dithizonate structures (Alsop, 1971; Mawby & Irving, 1972; Hutton, Irving & Nassimbeni, 1980), a marked planarity of the dithizonate ligands is observed. However, in these structures no more than two dithizonate ligands were coordinated and hence it was expected that in the tris-Bi^{III} complex the ligands might experience distortions owing to steric interactions. Quite remarkably, this does not appear to be the case, and the ligands are once again relatively planar. The maximum deviation of any of the atoms in the N–N–CS–N–N chains from the mean planes they describe is 0·03 (2) Å. As expected, the phenyl rings are also markedly planar [maximum deviation of a C(phenyl ring) from the plane of the phenyl ring = 0·02 (2) Å]. Examination of the angles between the normals to the N–N–CS–N–N planes and the normals to the relevant phenyl rings show that they are all small [in the range 3·9 (2)–18·3 (2)°] implying only slight twisting of the phenyl rings presumably to avoid steric interaction. The overall planarity of each dithizone moiety allows extensive delocalization of electrons; that this occurs is evidenced by the relevant bond lengths discussed previously. Geometric placement of imino protons 1·00 (1) Å from N(15), N(25) and N(35) according to sp^2 hybridization of those nitrogens does not allow linearity of the N(15)–H–S(1), N(25)–H–S(2) and N(35)–H–S(3) angles, implying that any intramolecular N–H···S bonding cannot be strong. N–H distances of 1·0 Å give H[N(15)]–S(1), H[N(25)]–S(2) and H[N(35)]–S(3) distances of 2·40 (1), 2·45 (1) and 2·38 (1) Å respectively. The N···S separations are only 2·89 (1), 2·91 (1) and 2·89 (1) Å for N(15)–S(1), N(25)–S(2) and N(35)–S(3) respectively.

According to the criteria of a special study of the NH···S bond (Donohue, 1969) and a very recent work (Kuleshova & Zorkii, 1981) intramolecular hydrogen bonding of this nature is most definitely occurring in the Bi(Hdz)$_3$ complex. The concomitant orientation of one of the lone pairs on each of the S atoms towards

---

* See deposition footnote.

the respective H atoms then effectively locks the dithizone residues in *anti, s-trans* configurations. These configurations of the N—N—C—N—N chains are the same as those found in other $M(Hdz)_x$ complexes and in crystals of the free ligand itself.

References

ALSOP, P. A. (1971). *The Structure and Properties of Dithizone and the Metal Dithizonates.* PhD Thesis, Univ. of London.

BATTAGLIA, L. P. & BONAMARTINI CORRADI, A. (1981). *J. Chem. Soc. Dalton Trans.* pp. 23–26.

BATTAGLIA, L. P., BONAMARTINI CORRADI, A., NARDELLI, M. & VIDONI TANI, M. E. (1978). *J. Chem. Soc. Dalton Trans.* pp. 583–587.

BATTAGLIA, L. P., BONAMARTINI CORRADI, A., PELIZZI, G. & VIDONI TANI, M. E. (1975). *Cryst. Struct. Commun.* 4, 399–402.

BELICCHI FERRARI, M., CALZOLARI CAPPACCHI, L., CAVALCA, L. & FAVA GASPARRI, G. (1972). *Acta Cryst.* B28, 1169–1173.

BRYAN, R. F. & KNOPF, P. M. (1961). *Proc. Chem. Soc.* p. 203.

BURKE-LAING, M. & LAING, M. (1976). *Acta Cryst.* B32, 3216–3224.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.

CURRY, J. D. & JANDACEK, R. J. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1120–1123.

DONOHUE, J. (1969). *J. Mol. Biol.* 45, 231–241.

HARDING, M. M. (1958). *J. Chem. Soc.* pp. 4136–4143.

HUTTON, A. T. (1980). PhD Thesis, Univ. of Cape Town.

HUTTON, A. T. & IRVING, H. M. N. H. (1979). *J. Chem. Soc. Chem. Commun.* pp. 1113–1114.

HUTTON, A. T., IRVING, H. M. N. H. & NASSIMBENI, L. R. (1980). *Acta Cryst.* B36, 2064–2070.

IRVING, H. M. N. H. (1977). *Dithizone. Analytical Sciences Monographs* No. 5, pp. 20–22. London: The Chemical Society.

KULESHOVA, L. N. & ZORKII, P. M. (1981). *Acta Cryst.* B37, 1363–1366.

LAING, M. (1977). *J. Chem. Soc. Perkin Trans.* 2, pp. 1248–1252.

LAING, M. & ALSOP, P. A. (1970). *Talanta*, 17, 242–244.

LAWTON, S. L., FUHRMEISTER, C. J., HAAS, R. G., JORMAN, C. S. JR & LOHMEYER, F. G. (1974). *Inorg. Chem.* 13(1), 135–143.

MATH, K. S. & FREISER, H. (1970). *J. Chem. Soc. Chem. Commun.* pp. 110–111.

MATH, K. S. & FREISER, H. (1971). *Talanta*, 18, p. 435.

MAWBY, A. & IRVING, H. M. N. H. (1971). *Anal. Chim. Acta*, 55, 269.

MAWBY, A. & IRVING, H. M. N. H. (1972). *J. Inorg. Nucl. Chem.* 34, 109.

MOTHERWELL, W. D. S. (1974). Private communication.

MYERS, E. A. (1967). *J. Phys. Chem.* 71, 3531.

MYERS, E. A. (1968). *J. Phys. Chem.* 72, 532, 3117.

RASTON, C. L. & WHITE, A. H. (1976). *J. Chem. Soc. Dalton Trans.* pp. 791–794.

ROBERTS, P. & SHELDRICK, G. M. (1975). Private communication.

SHELDRICK, G. M. (1976). *SHELX.* Program for crystal structure determination, Univ. Chemical Laboratory, Cambridge.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

Bis(3-aminopyridine)copper Cyanate Monohydrate*

BY FEDOR VALACH AND MICHAEL DUNAJ-JURČO

Faculty of Chemical Technology, Slovak Technical University, 880 37 Bratislava, Czechoslovakia

Abstract

The structure of $Cu(NCO)_2(3\text{-ampy})_2(H_2O)$ (3-ampy: 3-aminopyridine, $C_5H_6N_2$), $C_{12}H_{14}CuN_6O_3$, $M_r = 353\cdot8$, was determined from 2029 independent reflec-
tions using a single crystal and Mo $K\alpha$ radiation. Crystals are triclinic, space group $P\bar{1}$, with $a = 8\cdot487$ (3), $b = 8\cdot349$ (3), $c = 12\cdot346$ (4) Å, $\alpha = 102\cdot44$ (3), $\beta = 82\cdot69$ (3), $\gamma = 120\cdot84$ (3)°, $V = 733\cdot3$ Å^3, $Z = 2$, $D_m = 1\cdot61$, $D_x = 1\cdot60$ g cm^{-3}. The structure was refined by block-diagonal least-squares techniques to $R = 0\cdot054$ and $R_w = 0\cdot040$ for 2029 independent reflections. It consists of infinite chains mutually linked by hydrogen bonds. One half of the