Structural Studies of Group 5B–Halide–Dithio-ligand Complexes. Part 6.† Crystal Structures of Dichloro(*NN*-diethyldithiocarbamato)tris(pyridine)-bismuth(III)–Pyridine (1/1) and its Di-iodo-analogue

By **Colin L. Raston, Graham L. Rowbottom,** and **Allan H. White,** Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia 6009

Recrystallization of $[Bi(S_2CNEt_2)X_2]$, X = Cl, Br, or I, from pyridine solution has been shown to yield adducts $Bi(S_2CNEt_2)X_2(py)_4$. Single-crystal *X*-ray structure determinations have shown the three compounds to be isomorphous within a monoclinic unit cell ($P2_1/c$) with *a ca.* 13.7, *b ca.* 14.4, *c ca.* 16.0 Å, β *ca.* 93—101°, *Z* = 4, and to comprise $[Bi(S_2CNEt_2)X_2(py)_3]$ molecules with a further pyridine solvate molecule in the lattice. The bismuth environment is pseudo-seven-co-ordinate, the pyridine ligands being rather loosely bound, and the stereochemistry pseudo-pentagonal bipyramidal, with axial halogen substituents (Bi–Cl ,2.6_9; Bi–I, 3.0_6 Å).

IN a recent paper,[1] we have described the preparation of a 2 : 1 adduct between tris(*O*-ethyl dithiocarbonato)-antimony(III) and 4,4′-bipyridyl. The crystal structure was determined in the anticipation that the substance might comprise a binuclear system $(EtOCS_2)_3Sb(4,4'\text{-bipyridyl})Sb(S_2COEt)_3$, as the structure determinations of $[Sb,Bi(S_2CNEt_2)_3]$[2] had exhibited some tendency toward an increase in co-ordination number above six. In the event, it was found that the structure was simply a lattice adduct of a new isomer of $[Sb(S_2COEt)_3]$ with 4,4′-bipyridyl. In view of this result, it seemed reasonable to use pyridine as a possible solvent for recrystallization of the bismuth–halide–dithiocarbamate complexes described in the present series. However, it was found that when $[Bi(S_2CNEt_2)X_2]$ was recrystallized (X = Cl, Br, or I), a highly solvated crystalline form was obtained which rapidly lost pyridine on exposure to air. In order to establish the nature of one of these solvates, a single-crystal structure determination was carried out on the dichloro-derivative showing that the complex was $[Bi(S_2CNEt_2)Cl_2(py)_3]\cdot py$, and that some of the pyridine was indeed co-ordinated, albeit loosely. In view of the complexes throughout the series of halides, structure determinations were also undertaken on both the bromide and iodide analogues; the bromide, despite a number of attempts to gather satisfactory data, was found to degrade rapidly in the *X*-ray beam. Accordingly, as the three are isomorphous, albeit with wide variations in cell dimensions, we report in detail only the structures of the chloride $[Bi(S_2CNEt_2)Cl_2(py)_3]\cdot py$, (1), and the iodide, $[Bi(S_2CNEt_2)I_2(py)_3]\cdot py$, (2), in the present paper.

CRYSTALLOGRAPHY

Crystal Data.—(1). $C_{25}H_{30}BiCl_2N_5S_2$, $M = 744.3$, Monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 13.723(3)$, $b = 13.760(3)$, $c = 16.107(3)$ Å, $\beta = 100.30(1)°$, $U = 2\,993(1)$ Å^3, $D_c = 1.65$ g cm^{-3}, $Z = 4$, $F(000) = 1\,456$, $\mu(\text{Mo}) = 59.4$ cm^{-1}. Specimen size: 0.18 × 0.40 × 0.12 mm, $2\theta_{\text{max.}} = 50°$, $n = 5\,285$, $n_o = 2\,778$. Values of *R*, *R′*, *S* are 0.035, 0.038, 1.2 respectively.

(2). $C_{25}H_{30}BiI_2N_5S_2$, $M = 927.5$, symmetry as above, $a = 13.674(6)$, $b = 15.308(5)$, $c = 15.541(6)$ Å, $\beta = 92.74(3)°$, $U = 3\,249(2)$ Å^3, $D_c = 1.90$ g cm^{-3}, $F(000) = 1\,744$, $\mu(\text{Mo}) = 72$ cm^{-1}. Specimen size: 0.40 × 0.25 × 0.25 mm, $2\theta_{\text{max.}} = 50°$, $n = 5\,758$, $n_o = 2\,780$. Values of *R*, *R′*, *S* are 0.042, 0.049, 1.5 respectively.

Abnormal Features.—Both compounds (and the dibromo-analogue) lost solvent rapidly on exposure to the atmosphere. Data collection was carried out on specimens mounted in capillaries, the bromide ‡ undergoing degradation in the process. Thermal motion, especially in the iodide which has a more spacious packing array, was very high on some of the pyridine species and accordingly these were included in the refinement under appropriate con-

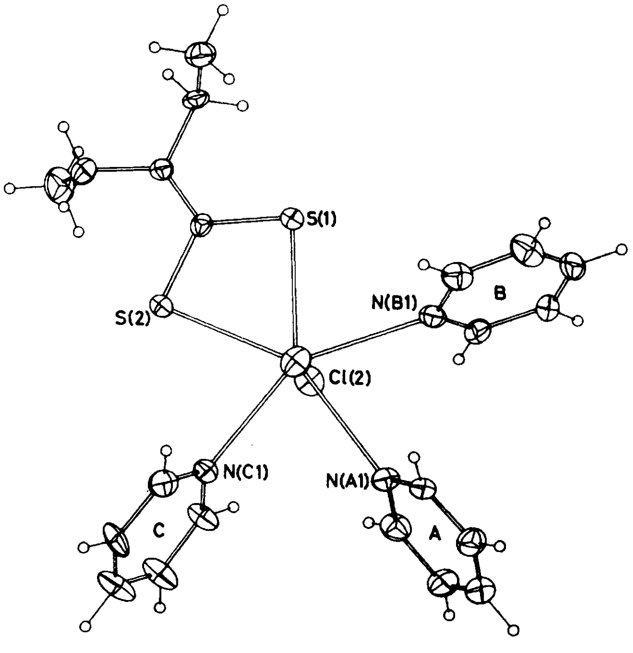

FIGURE 1 A single molecule of (1) projected down the Cl(1)–Bi bond, showing 20% thermal ellipsoids for the non-hydrogen atoms and segment labelling within the molecule

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† Part 5, C. L. Raston, G. L. Rowbottom, and A. H. White, preceding paper. Part 1 (ref. 9) contains general descriptive crystallographic and definitional detail.

‡ For the bromide, $C_{25}H_{30}BiBr_2N_5S_2$, $M = 833.2$, $a = 13.780(3)$, $b = 14.035(3)$, $c = 16.181(3)$ Å, $\beta = 101.13(2)°$, $U = 3\,071(1)$ Å^3, $D_c = 1.80$ g cm^{-3}, $F(000) = 1\,600$, $\mu(\text{Mo}) = 84$ cm^{-1}. Specimen size: 0.48 × 0.38 × 0.25 mm, $2\theta_{\text{max.}} = 45°$, $n = 4\,680$, $n_o = 2\,406$, *R*, *R′* values are 0.11, 0.13 respectively.

TABLE 1

Non-hydrogen atom fractional cell co-ordinates for (1) and (2)

	(1)			(2)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Bi	0.253 50(3)	0.048 80(2)	0.248 28(3)	0.249 94(4)	0.030 77(3)	0.242 41(3)
X(1)	0.162 5(2)	0.047 7(2)	0.385 2(2)	0.120 63(7)	0.034 67(6)	0.400 91(6)
X(2)	0.359 5(2)	0.074 3(2)	0.127 5(2)	0.385 79(8)	0.043 51(7)	0.095 25(6)
(*a*) Dithiocarbamate ligand						
S(1)	0.091 8(2)	−0.005 9(2)	0.133 4(2)	0.098 0(3)	−0.008 0(2)	0.132 1(2)
S(2)	0.235 3(2)	−0.147 7(2)	0.221 5(2)	0.225 7(3)	−0.142 9(2)	0.212 7(2)
C(1)	0.134 3(6)	−0.123 2(6)	0.144 2(5)	0.134 4(9)	−0.116 3(8)	0.139 3(7)
N(1)	0.089 6(5)	−0.194 8(5)	0.097 0(5)	0.089 2(7)	−0.176 8(6)	0.091 7(7)
C(2)	0.003 1(7)	−0.173 9(7)	0.028 2(5)	0.009 2(12)	−0.154 8(9)	0.028 6(8)
C(3)	−0.094 4(7)	−0.184 2(8)	0.058 6(7)	−0.092 6(12)	−0.164 2(12)	0.067 2(10)
C(4)	0.119 3(8)	−0.296 9(7)	0.106 5(7)	0.116 3(12)	−0.268 3(8)	0.093 6(10)
C(5)	0.191 1(10)	−0.323 6(9)	0.049 3(8)	0.188 6(15)	−0.291 2(12)	0.026 8(12)
(*b*) Pyridine A						
N(A1)	0.365 0(5)	0.208 0(6)	0.318 7(5)	0.365 6(8)	0.169 7(6)	0.316 6(7)
C(A2)	0.326 9(7)	0.259 8(7)	0.375 1(6)	0.323 4(11)	0.230 2(9)	0.361 3(9)
C(A3)	0.371 5(8)	0.342 3(8)	0.411 0(7)	0.371 2(15)	0.300 2(11)	0.396 5(11)
C(A4)	0.459 6(8)	0.371 1(9)	0.394 3(7)	0.466 6(13)	0.309 8(11)	0.383 3(11)
C(A5)	0.500 8(7)	0.320 3(8)	0.337 9(8)	0.511 1(11)	0.248 9(10)	0.341 0(11)
C(A6)	0.452 5(7)	0.238 7(8)	0.301 1(7)	0.461 0(10)	0.179 2(10)	0.303 5(10)
(*c*) Pyridine B						
N(B1)	0.152 2(5)	0.212 8(6)	0.197 9(5)	0.165 1(7)	0.184 9(7)	0.195 5(6)
C(B2)	0.063 4(7)	0.230 8(8)	0.215 3(7)	0.075 8(10)	0.205 7(10)	0.212 2(9)
C(B3)	0.008 3(8)	0.313 7(9)	0.187 7(7)	0.029 2(11)	0.284 4(9)	0.184 8(9)
C(B4)	0.047 9(8)	0.379 4(8)	0.138 1(8)	0.079 6(11)	0.338 4(9)	0.137 0(10)
C(B5)	0.140 5(8)	0.361 5(8)	0.119 9(8)	0.168 0(11)	0.315 4(9)	0.115 5(10)
C(B6)	0.188 9(7)	0.277 6(7)	0.151 7(7)	0.212 3(10)	0.239 1(8)	0.144 3(9)
(*d*) Pyridine C						
N(C1)	0.412 1(5)	−0.031 8(5)	0.343 2(5)	0.393 2(8)	−0.050 8(7)	0.339 5(7)
C(C2)	0.502 3(7)	−0.018 5(9)	0.325 1(7)	0.477 2(13)	−0.069 8(12)	0.307 9(10)
C(C3)	0.584 8(8)	−0.055 2(9)	0.372 2(8)	0.550 7(14)	−0.114 9(14)	0.355 5(11)
C(C4)	0.578 3(9)	−0.109 4(11)	0.441 6(8)	0.535 5(17)	−0.145 3(20)	0.430 8(14)
C(C5)	0.487 6(9)	−0.126 2(8)	0.461 3(7)	0.454 7(19)	−0.117 6(20)	0.465 9(14)
C(C6)	0.406 0(8)	−0.083 8(8)	0.411 2(7)	0.375 8(14)	−0.074 6(19)	0.415 6(13)
(*e*) Pyridine D (non-co-ordinated) *						
N(D1)	0.753 7(8)	0.065 8(9)	0.225 6(7)	0.787 7(—)	0.042 0(—)	0.281 9(—)
C(D2)	0.814 2(9)	0.047 8(9)	0.170 9(9)	0.843 5(—)	0.044 1(—)	0.219 0(—)
C(D3)	0.791 2(10)	0.068 1(10)	0.089 5(9)	0.791 8(—)	0.060 7(—)	0.126 9(—)
C(D4)	0.702 7(12)	0.111 0(11)	0.060 5(10)	0.701 8(—)	0.107 7(—)	0.126 8(—)
C(D5)	0.641 6(9)	0.126 2(11)	0.115 0(11)	0.645 0(—)	0.055 0(—)	0.190 0(—)
C(D6)	0.669 9(10)	0.104 1(10)	0.194 4(9)	0.699 7(—)	0.082 3(—)	0.262 4(—)

* All atoms in the iodine complex were refined as carbon atoms as the exceedingly high thermal motion renders it likely that the nitrogen is disordered. Refinement of atoms in (*x*,*y*,*z*) led to unrealistic positioning of some of the carbon atoms and the molecule was constrained at a reasonable geometry.

straint (see Table 1), where needful. Segment labelling is given in Figure 1.

Structure-factor amplitudes, thermal parameters, hydrogen-atom parameters, least-squares planes, and details of the pyridine geometries are given in Supplementary Publication No. SUP 22981 (37 pp.).*

DISCUSSION

The structure determinations delineate the stoicheiometry of the two compounds (1) and (2) (and their isomorphous bromine analogue) as being $[Bi(S_2CNEt_2)X_2(py)_3]\cdot py$, the asymmetric unit of the structure comprising one molecule of complex (containing three pyridine ligands), accompanied by one pyridine solvent molecule in the lattice. Thermal motion on the pyridine species becomes increasingly high as we progress from the chloride to the iodide derivative, and in the region of the structure affected (Figure 2), the precision of the determination is badly lowered. Although the compounds lose pyridine on exposure to the atmosphere, refinement details do not suggest that pyridine populations in the iodide (or the chloride for that matter) are less than unity.

The molecules of (1) and (2) are of interest. In the present series of complexes, they are the first species studied which are found to be mononuclear. The metal atom co-ordination environment (Table 2) is dominated by a pseudo-axial X–Bi–X array with conspicuous right angles to nearly all other ligating atoms, suggesting pentagonal-bipyramidal co-ordination geometry. The axial arrays are very nearly symmetrical and linear: Cl–Bi–Cl, 170.5(1)°, Bi–Cl, 2.721(3), 2.653(3) Å; I–Bi–I, 174.2(1)°, Bi–I, 3.101(2), 3.021(2) Å, the small but significant discrepancy in the two almost equal axial

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* For details see Notices to Anthors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

TABLE 2

Bismuth atom environments in (1) and (2): $r_{\mathrm{Bi-X}}$ in Å; the remaining entries in the matrices are the angles (°) subtended by the relevant atoms at the bismuth. Primed atoms are generated by the inversion operation

(*a*) Compound (1)

Atom	$r_{\mathrm{Bi-X}}$	Cl(2)	S(1)	S(2)	N(A1)	N(B1)	N(C1)
Cl(1)	2.721(3)	170.5(1)	96.47(9)	94.58(8)	88.5(2)	87.8(2)	88.8(2)
Cl(2)	2.653(3)		91.43(8)	93.51(8)	82.0(2)	89.4(2)	88.7(2)
S(1)	2.728(3)			65.27(7)	144.2(2)	73.4(2)	139.1(2)
S(2)	2.742(3)				149.8(2)	138.6(2)	73.9(2)
N(A1)	2.794(8)					71.4(2)	76.2(2)
N(B1)	2.698(8)						147.5(2)
N(C1)	2.668(7)						

(*b*) Compound (2)

Atom	$r_{\mathrm{Bi-X}}$	I(2)	S(1)	S(2)	N(A1)	N(B1)	N(C1)
I(1)	3.101(2)	174.2(1)	93.33(8)	94.84(9)	89.5(2)	86.8(2)	89.5(2)
I(2)	3.021(2)		90.91(9)	90.51(8)	84.8(2)	90.6(2)	89.8(2)
S(1)	2.695(4)			65.9(1)	144.5(4)	73.4(2)	139.9(2)
S(2)	2.715(4)				149.0(2)	139.3(2)	74.0(2)
N(A1)	2.86(1)					71.5(3)	75.4(3)
N(B1)	2.71(1)						146.7(3)
N(C1)	2.72(1)						

distances being preserved in both compounds. [For the undetailed bromide analogue, we find Br–Bi–Br, 172.9(2)°, Bi–Br, 2.906(6), 2.739(7) Å.] The 'equatorial' plane in each case comprises S(1, 2), N(A, B, C) and the bismuth, the disposition being highly reminiscent of that found in [Bi(S$_2$CNEt$_2$)I$_2$].[3] For (1), (2) the defining atom deviations respectively are −0.08, −0.04; 0.00, −0.04; −0.10, −0.10; 0.09, 0.08; 0.04, 0.08; 0.04, 0.03 (σ, 0.08, 0.07 Å). The dithiocarbamate S$_2$CNC$_2$ plane is inclined at a slight angle to the median plane [dihedral: 9.7(1), 9.1(2)°], while in (2) the pyridine ring C is somewhat more steeply inclined (A, 68.0, 55.5; B, 65.1, 65.5; C, 68.0, 89.8°). Interligand angles in the median plane are shown in Figure 3. The interligand angle sum is 360°.

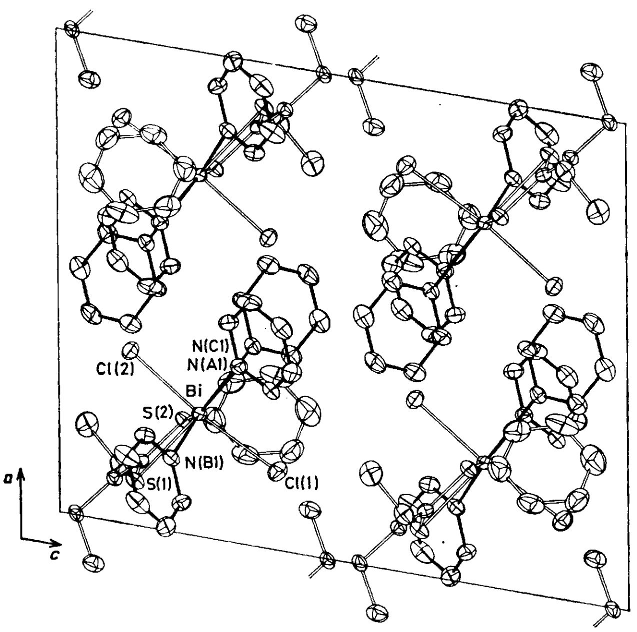

FIGURE 2 Unit-cell contents of (1) projected down *b*; showing 20% thermal ellipsoids for the non-hydrogen atoms. Co-ordinated pyridine ligands have solid bonds

In spite of the pseudo-seven-co-ordinate pentagonal-bipyramidal co-ordination array about the metal atom it is clear that the bismuth–pyridine nitrogen distances are very long; it is also of interest that the small but significant perturbation from linearity of the X–Bi–X system is directed so as to be with the halogen atoms slightly toward the central pyridine group. All of which suggests the presence of a stereochemically active lone pair still remains, in competition with the would-be co-ordinate-bonding propensity of the pyridine ligands.

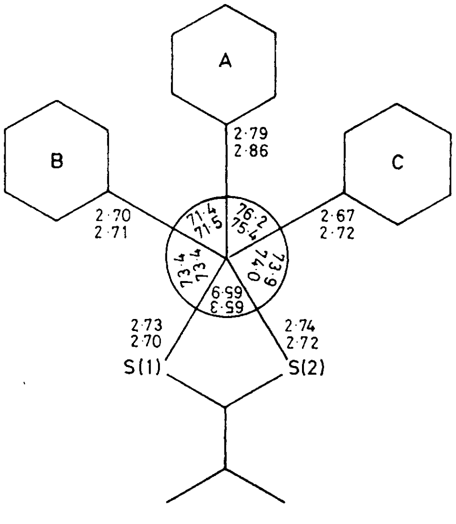

FIGURE 3 Median plane geometry; the two values in each case are for (1), (2) respectively: distances (Å) and angles (°)

Irrespective of this, the pentagonal-bipyramidal co-ordination sphere is highly unusual for the system [M(bidentate)(unidentate)$_5$], the only previously reported example being that of [W(Ph$_2$PCH$_2$PPh$_2$)I$_2$(CO)$_3$][4] which has the predicted pentagonal-bipyramidal seven-co-ordinate stereochemistry expected for a small biden-

TABLE 3

Pyridine α-hydrogen–chlorine contacts (Å) for (1)

Pyridine ring	Cl(1)	Cl(2)
A	2.96	3.05
B	3.14	3.00
C	3.07	2.91

tate ligand bite of 1.09, *cf.* the present 1.08. A similar decrease of the axial angle well below 180° is also observed in the tungsten complex, the angle between the pair of *trans* carbonyl groups being 172.8(5)°, the contraction lying opposite the bidentate ligand also. In regard to the presence or otherwise of a stereochemically active lone pair, it is also of interest to note that in the context of increasing co-ordination number, *e.g.* as in the complexes $[Te(S_2CNEt_2)_4]$[5] and $[Te(S_2CNC_4H_8O)_4]\cdot C_6H_6$,[6] stereochemically active lone pairs are not observed, the stereochemistry conforming to that predicted purely by electron-pair repulsion theory. {However, in $[NEt_4][Bi(S_2COEt)_4]$,[7] the co-ordination geometry does suggest the possible presence of a sterically active lone pair.}

TABLE 4

Dithiocarbamate ligand geometries. The two values in in each entry are for (1), (2) respectively

(*a*) Distances/Å	
C(1)–S(1)	1.715(9), 1.70(1)
C(1)–S(2)	1.724(8), 1.73(1)
S(1) · · · S(2)	2.950(4), 2.944(5)
C(1)–N(1)	1.33(1), 1.32(2)
N(1)–C(2)	1.50(1), 1.47(2)
N(1)–C(4)	1.46(1), 1.45(2)
C(2)–C(3)	1.51(1), 1.55(2)
C(4)–C(5)	1.51(2), 1.51(3)
(*b*) Angles/°	
Bi–S(1)–C(1)	88.3(3), 87.7(4)
Bi–S(2)–C(1)	87.7(3), 87.7(4)
S(1)–C(1)–S(2)	118.2(5), 118.2(7)
S(1)–C(1)–N(1)	121.9(6), 121.2(9)
S(2)–C(1)–N(1)	119.9(6), 120.6(9)
C(1)–N(1)–C(2)	120.3(7), 122(1)
C(1)–N(1)–C(4)	124.2(7), 124(1)
C(2)–N(1)–C(4)	115.5(7), 115(1)
N(1)–C(2)–C(3)	111.8(7) 112(1)
N(1)–C(4)–C(5)	111.7(9), 113(1)

The pyridine α-hydrogen–chlorine distances of (1) are given in Table 3. These lie at the van der Waals limit (3.0 Å)[8] and while the higher thermal motion present in the iodine derivative may simply be a consequence of the more spacious unit cell, equally, in consideration of the increased dihedral angles with the median plane, it may be a consequence also of relieved α-hydrogen–halogen repulsion. Regrettably, the precision of the determination of the pyridine groups in (2) does not permit a more precise test of this hypothesis.

The S_2CNC_2 fragment of the dithiocarbamate is almost planar [σ 0.03, 0.01 Å for (1), (2)]; the bismuth atom deviations are 0.29, 0.29 Å respectively. In both cases, the methyl groups lie on alternate sides of the ligand plane. The ligand is symmetrically bonded to the metal and its geometry close to that of the free ion (Table 4).[9]

[0/1050 *Received, 7th July,* 1980]

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