Structural Studies of Group 5B–Halide–Dithio-ligand Complexes. Part 8.† Crystal Structure of *N'N'*-Diethylthiocarbamoylpyridinium Pentachloropyridinebismuthate(III)

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The crystal structure of the title compound, $[C_5H_5NCSNEt_2]_2[BiCl_5(C_5H_5N)]$, has been determined by single-crystal *X*-ray diffraction methods at 295(1) K and refined by least-squares procedures to a conventional residual of 0.031 for 1 633 'observed' reflections. Crystals are orthorhombic, space group *Pbcn*, with a = 16.089(4), b = 14.852(4), c = 14.130(3) Å, and Z = 4. The anion lies on a crystallographic two-fold axis; Bi–N is 2.615(8) Å. The Bi–Cl distance *trans* to the Bi–N bond is shorter [2.637(3) Å] than the remainder [2.692(2), 2.700(3) Å]. The N–Bi–Cl(*cis*) angles are appreciably less than 90° [84.65(6), 84.91(6°)].

In a previous paper[1] in the present series we have described the preparation of the complex $[Bi(S_2CNEt_2)Cl_2(py)_3]\cdot py$ by recrystallizing $[Bi(S_2CNEt_2)Cl_2]$ from pyridine; in one preparation, it was noticed that a specimen preserved under pyridine for some weeks was heterogeneous, containing not only $[Bi(S_2CNEt_2)Cl_2(py)_3]\cdot py$ but also a small quantity of another crystalline phase. A crystal of this substance was isolated and characterized by a single-crystal structure determination, since the quantity available did not permit exhaustive characterization by more conventional means, and was shown to be the title compound $[C_5H_5NCSNEt_2]_2[BiCl_5(py)]$ (Found: C, 34.9; H, 4.2; Bi, 26.2; Cl, 21.4; N, 7.8; S, 7.4. Calc. for $C_{25}H_{35}BiCl_5N_5S_2$: C, 35.4; H, 4.1; Bi, 25.4; Cl, 20.8; N, 8.2; S, 7.4%).

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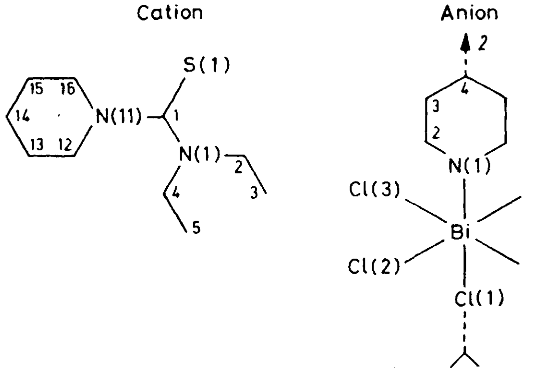
Crystal Data.—$C_{25}H_{35}BiCl_5N_5S_2$, M = 855.9, Orthorhombic, space group *Pbcn* (D_{2h}^{14}, no. 60), a = 16.089(4), b = 14.852(4), c = 14.130(3) Å, U = 3 376(1) Å^3, D_m = 1.70(1), Z = 4, D_c = 1.68 g cm^{-3}, $F(000)$ = 1 680, μ(Mo) = 55 cm^{-1}. Specimen size: 0.25 × 0.20 × 0.17 mm, $2\theta_{max.}$ = 50°, n = 2 990, n_o = 1 633. Values of R, R', S are 0.031, 0.034, 1.38 respectively.



Special Features.—Pyridinium hydrogen atoms were refined in (x, y, z); others were constrained in (x, y, z, U). Atom labelling is as shown.

Table 1 gives the non-hydrogen atom fractional co-ordinates and Figure 1 shows the unit-cell contents. Structure factor amplitudes, thermal parameters, and hydrogen-atom parameters are given in Supplementary Publication No. SUP 22983 (11 pp.).‡

TABLE 1

Non-hydrogen atom fractional co-ordinates

Atom	x	y	z
(*a*) Anion			
Bi	0.000 00(—)	0.158 78(2)	0.250 00(—)
Cl(1)	0.000 0(—)	0.336 4(2)	0.250 0(—)
Cl(2)	0.160 2(1)	0.141 9(1)	0.198 1(2)
Cl(3)	−0.050 7(2)	0.142 7(2)	0.068 7(2)
(*b*) Co-ordinated pyridine			
N(1)	0.000 0(—)	−0.017 3(5)	0.250 0(—)
C(2)	−0.036 7(5)	−0.062 5(5)	0.318 7(6)
C(3)	−0.037 4(6)	−0.155 5(5)	0.321 5(6)
C(4)	0.000 0(—)	−0.202 4(7)	0.250 0(—)
(*c*) Cation			
C(1)	0.827 0(5)	0.499 5(5)	0.225 1(5)
S(1)	0.882 0(2)	0.566 7(2)	0.159 2(2)
N(1)	0.828 0(4)	0.486 0(4)	0.316 4(5)
C(2)	0.894 7(5)	0.529 3(6)	0.374 7(7)
C(3)	0.871 8(7)	0.619 1(7)	0.410 3(8)
C(4)	0.760 8(6)	0.443 3(6)	0.372 0(6)
C(5)	0.784 3(8)	0.357 8(7)	0.420 4(7)
N(11)	0.765 8(4)	0.440 3(4)	0.175 4(4)
C(12)	0.700 9(5)	0.475 2(5)	0.128 3(6)
C(13)	0.648 9(5)	0.421 4(6)	0.076 7(6)
C(14)	0.666 4(6)	0.329 5(6)	0.073 5(6)
C(15)	0.731 9(6)	0.295 1(6)	0.122 5(6)
C(16)	0.784 7(6)	0.350 3(5)	0.171 6(6)

DISCUSSION

The structure determination characterizes the unknown complex as having the stoicheiometry $[C_5H_5NCSNEt_2]_2[BiCl_5(C_5H_5N)]$; the quality of the data was sufficiently good to allow definition and refinement of the positional parameters of all hydrogen atoms that could in any sense be regarded as critical to assignment of stoicheiometry (*i.e.* all except the ethyl), and the result is consistent with the presence of trivalent bismuth. All atoms of the cation occupy crystallographic general positions; the anion lies with the bismuth atom sited on a crystallographic two-fold axis and thus has

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† Part 7 is ref. 2. Part 1 (ref. 4) contains general descriptive crystallographic and definitional detail.

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

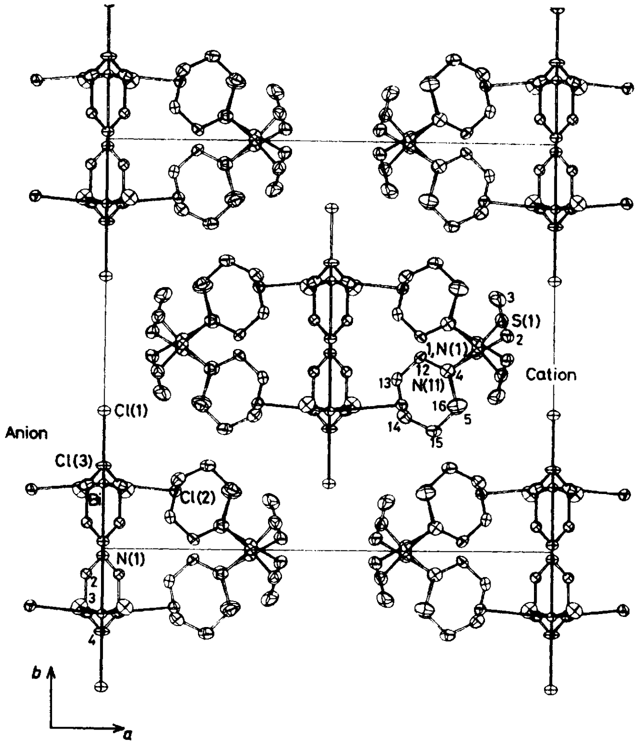


FIGURE 1 Unit-cell contents projected down *c*

overall *2* point symmetry. Both species are of interest and will be discussed separately.

(*a*) *The Anion.*—This appears to be the first occasion on which an anion of the type [MX$_5$(base)]$^{2-}$ has been reported and structurally substantiated for a Group 5B element. The bismuth environment is six-co-ordinate and pseudo-octahedral; four of the chlorine atoms lie in an equatorial plane and have distances which are only trivially different from each other [2.692(2), 2.700(3) Å]; the angles in this plane differ, being 91.29(9) and 87.76(9)°, the total of the plane being 358.1° (Table 2). The bismuth atom lies out of the plane of the four chlorine atoms (σ 0.01 Å) by 0.24 Å, directed toward the axial chlorine rather than the axial pyridine. The angles subtended by axial/equatorial chlorine pairs at the bismuth are substantially greater than 90°, being 95.36(5), 95.09(6)°, and the bismuth–axial chlorine distance is shorter than the bismuth–equatorial chlorines, being 2.637(3) Å. The *trans*-Cl–Bi–Cl angles in the equatorial plane are much less than 180°, being 169.29(8), 169.83(11)°. The bismuth–pyridine distance is shorter than those observed in the complexes [Bi(S$_2$CNEt$_2$)Cl$_2$(py)$_3$] [1] and [Bi(S$_2$CNEt$_2$)I$_2$(py)$_3$] [1] and comparable with those found in [Bi(S$_2$CNEt$_2$)I$_2$(terpy)]; [2] this is only to be expected, as the co-ordination number is lower. It is, nevertheless, comparable with the Bi–Cl distances, indicating that the Bi–N bond must be quite weak, a belief which is reinforced by the geometry about the axial chlorine. The reason for this weakness may arise from (*i*) electronic effects, one possibility (a) being that the pyridine is confronted by the lone pair of the bismuth which thus manifests stereochemical activity; another possibility (b) lies in the relative *trans* effects of the chlorine *versus* nitrogen ligands of different donor capacity. (*ii*) Steric effects, resulting from the effective bulk of the pyridine ligand, in particular consequent upon the disposition or presence of the *ortho*-hydrogen atoms. Figure 2(*a*) suggests this hypothesis to be highly tenable in view of the disposition of the pyridine ring plane midway between the projection of the equatorial chlorine atoms. Examination of the contacts H(2) . . . Cl(2,3) shows these to lie at 3.18(7), 3.30(7) Å respectively. The van der Waals sum for (Cl + H) is (1.8 + 1.2) Å = 3.0 Å,[3] suggesting that somewhat tighter co-ordination *is* sterically possible and that the effect most likely is electronic in origin.

TABLE 2

Non-hydrogen atom cation and anion geometry. Primed atoms are generated by the intra-anion two-fold rotor ($\bar{x}$, y, $\frac{1}{2} - z$)

(*a*) Anion

(*i*) Distances/Å

Bi–N(1)	2.615(8)	N(1)–C(2)	1.320(9)
Bi–Cl(1)	2.637(3)	C(2)–C(3)	1.382(11)
Bi–Cl(2)	2.692(2)	C(3)–C(4)	1.367(10)
Bi–Cl(3)	2.700(3)		

(*ii*) Angles/°

Bi–N(1)–C(2)	120.6(4)	N(1)–Bi–Cl(3)	84.91(6)
C(2)–N(1)–C(2)	118.8(8)	Cl(1)–Bi–Cl(2)	95.36(5)
N(1)–C(2)–C(3)	122.2(8)	Cl(1)–Bi–Cl(3)	95.09(6)
C(2)–C(3)–C(4)	119.0(8)	Cl(2)–Bi–Cl(3)	91.29(9)
C(3)–C(4)–C(3′)	118.7(9)	Cl(2)–Bi–Cl(3′)	87.76(9)
N(1)–Bi–Cl(1)	180.00(—)	Cl(2)–Bi–Cl(2′)	169.29(8)
N(1)–Bi–Cl(2)	84.65(5)	Cl(3)–Bi–Cl(3′)	169.83(11)

(*b*) Cation

(*i*) Distances/Å

N(11)–C(12)	1.34(1)	C(1)–S(1)	1.626(8)
N(11)–C(16)	1.37(1)	C(1)–N(1)	1.306(10)
N(11)–C(1)	1.50(1)	N(1)–C(2)	1.50(1)
C(12)–C(13)	1.37(1)	N(1)–C(4)	1.48(1)
C(13)–C(14)	1.40(1)	C(2)–C(3)	1.47(1)
C(14)–C(15)	1.36(1)	C(4)–C(5)	1.49(1)
C(15)–C(16)	1.37(1)		

(*ii*) Angles/°

C(12)–N(11)–C(16)	122.0(7)	N(11)–C(1)–S(1)	116.7(5)
C(12)–N(11)–C(1)	121.2(6)	N(11)–C(1)–N(1)	112.4(6)
C(16)–N(11)–C(1)	116.5(6)	S(1)–C(1)–N(1)	130.8(6)
N(11)–C(12)–C(13)	121.0(7)	C(1)–N(1)–C(2)	119.0(7)
C(12)–C(13)–C(14)	117.7(8)	C(1)–N(1)–C(4)	125.6(7)
C(13)–C(14)–C(15)	120.5(8)	C(2)–N(1)–C(4)	114.5(6)
C(14)–C(15)–C(16)	120.9(8)	N(1)–C(2)–C(3)	113.4(8)
C(15)–C(16)–N(11)	117.8(8)	N(1)–C(4)–C(5)	115.1(8)

In view of the observations of earlier papers in the series,[4] the stereochemically active lone pair is the most attractive alternative. The pyridine ring is very closely planar, no atom deviating by more than 0.004 Å.

(*b*) *The Cation.*—This, too, is novel. The NCSNC$_2$ fragment of the cation is rather less precisely planar than is usual in dithiocarbamate species, atom deviations being [N(11), C(1), S(1), N(1), C(2), C(4) respectively] −0.15, 0.00, 0.15, −0.05, −0.13, 0.19 Å (σ 0.14 Å) with C(3), C(5) lying on either side (deviations 1.19, −0.98 Å), all of which is indicative that the prime component of the distortion is torsion about C(1)–N(1); this may have some origin in the S . . . H(2B) contact (2.8 Å, *cf.* van der Waals, 3.05 Å),[3] which, unlike the dithiocarbamate

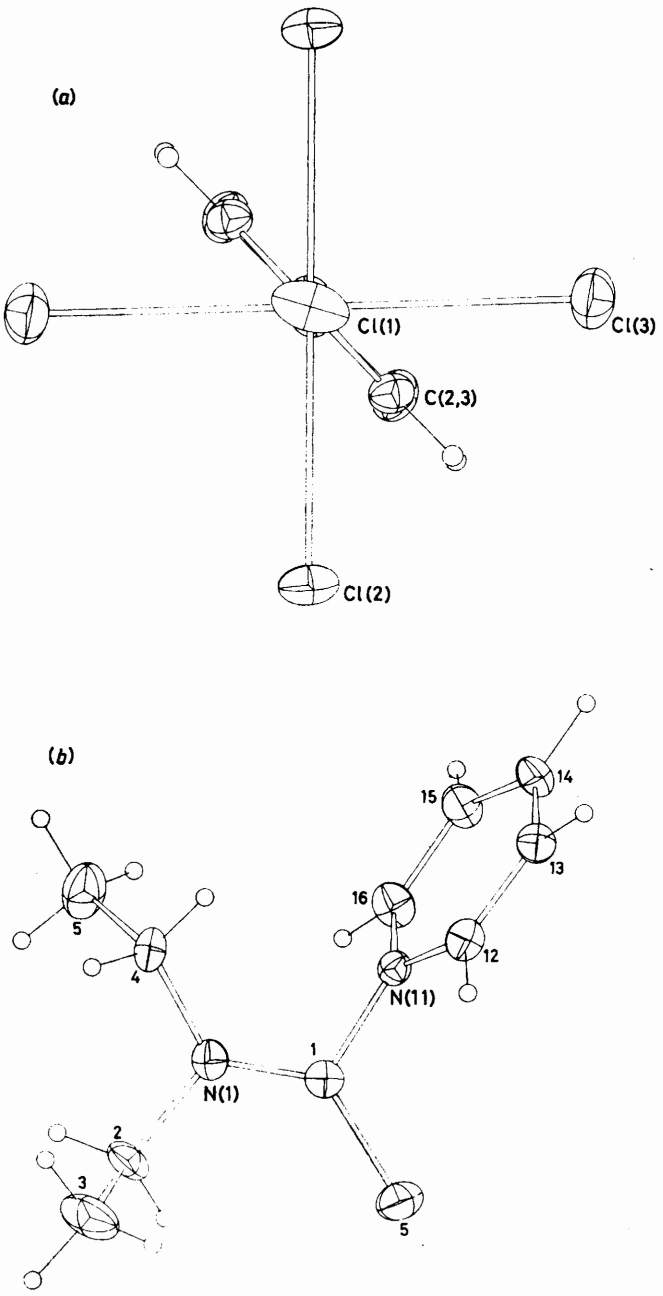
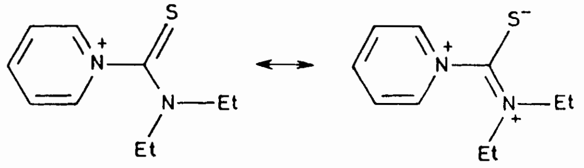


FIGURE 2 (*a*) Projection of the anion down its two-fold axis. (*b*) Projection of the cation normal to the N(CS)NC_2 plane

analogue, has no counterpart on the other side of the ligand at ' S(2) '. [This must remain the subject of conjecture for the present, however, as the present implication would be that a similar contact to ' S(2) ' would reinforce the torque about C(1)–N(1), whereas the dithiocarbamate ligand S_2CNC_2 fragment is normally closely planar.] The cation pyridine ring shows no non-hydrogen deviation greater than 0.02 Å [σ (C_5N), 0.01 Å]; the C(1) deviation is 0.11 Å. The dihedral angle with the above thiocarbamoyl plane is 71.5°. The angle sums about N(11), C(1), N(1) respectively are 359.7, 359.9, 359.1° indicating that all may be considered essentially trigonal in character.

The bond lengths and angles about N(1) are as usual for the dithiocarbamate species, C(1)–N(1) having considerable double-bond character and the opposite angle C(2)–N(1)–C(4) being reduced well below 120° in consequence [114.5(6)°]. The C(1)–S(1) distance lies at the lower limit of observed C–S distances and must be considered to have very considerable double-bond character; this is borne out by the angular geometry about C(1) which varies considerably from regularity, N(11)–C(1)–N(1) in particular being 112.4(6)°, and S(1)–C(1)–N(1), 130.8(6)°, the latter being indicative of a low bond order in N(11)–C(1). This is borne out by the bond length [1.50(1) Å] and suggests that the positive charge of the cation must be firmly localized on the pyridine nitrogen, with little scope for delocalization by conjugation, this being reinforced by the large torsion about N(11)–C(1). The structure of the cation



is therefore as shown; S . . . H(12) is 2.99(6) Å. There is a close interspecies contact also, S . . . H(2B) ($2 - x$, y, $\frac{1}{2} - z$), 2.8_3 Å.

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