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COMMUNICATION

AZAMACROCYCLIC COMPLEXATION OF BISMUTH(III): FORMATION AND STRUCTURE OF *fac*-($BiCl_3 \cdot Me_3$[9]aneN_3) WHERE Me_3[9]aneN_3 = 1,4,7-TRIMETHYL-1,4,7-TRIAZACYCLONONANE

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Abstract—Addition of bismuth(III) chloride and the triaza macrocyclic ligand Me_3[9]aneN_3 provided the dark yellow 1 : 1 adduct whose structure has been determined by X-ray diffraction. In the resulting half-sandwich arrangement the tridentate N-donor macrocycle and the three chlorine atoms occupy opposite faces of an octahedral bismuth(III) ion.

Crown ether complexation of the Group 15 halides MX_3 (M = As, Sb, Bi; X = halogen) dates from 1987 when Nicholson and co-workers[1] reported $SbCl_3 \cdot$15-crown-5 in which a pyramidal $SbCl_3$ unit is bonded to all five oxygen atoms of the macrocyclic ether in a half-sandwich structure. Since then a range of such Group 15–oxacrown complexes incorporating typically 12–crown–4, 15–crown–5 and 18–crown–6 and their derivatives has been reported.[2] In subsequent studies we have established a similar pattern of complexation for M^{III} with the crown thioether analogues, e.g. [9]aneS_3, [12]aneS_4, [15]aneS_5 and [18]aneS_6.[3] As a typical example $BiCl_3 \cdot$[18]aneS_6 features the thiacrown wrapped around the central bismuth atom of a pyramidal $BiCl_3$ unit leaving the metal in a nine-coordinate tricapped trigonal prismatic geometry.[4]

Turning to possible complexation of these M^{III} halides by azamacrocycles our first attempts using tetramethylcyclam (tmc) tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) were unsuccessful in terms of direct N-donation to the metal. Instead of simple adduct formation, complex μ-oxo-bridged polynuclear anionic species, e.g. $[As_4O_2Cl_{10}]^{2-}$, $[Sb_2OCl_6]^{2-}$ were obtained.[5] Incorporation of arsenic(III) into the parent ligand cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane) has been achieved by Lattman and co-workers.[6] The neutral compound [As(cyclamH)] exhibits a *trans*-annulated structure in which the arsenic atom has a distorted pseudo-trigonal bipyramidal geometry with two of the ring nitrogens and a lone-pair of electrons in an equatorial location and the remaining two ring nitrogen atoms in the axial positions.

In this communication we report the isolation and structural characterisation of the 1 : 1 adduct of bismuth(III) chloride and the triazamacrocyclic ligand Me_3[9]aneN_3. Although this particular ligand forms complexes with a variety of *d*-block metals[7] there is only one previous example involving a *p*-block element, namely the 1 : 1 adduct with $InCl_3$.[8] No structural details are available.

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Dropwise addition of $Me_3[9]aneN_3$ (0.55 g, 0.321 mmol) in acetonitrile (20 cm^3) to an ice-cold solution of $BiCl_3$ (0.10 g, 0.317 mmol) in acetonitrile (25 cm^3) produced a white cloudy suspension which was stirred for 12 h at 50°C. Removal of solvent gave a yellow solid which was washed with hexane (4×20 cm^3) and diethylether (2×20 cm^3). Recrystallisation from acetonitrile/dichloromethane gave the title product as pale yellow block crystals (0.14 g, 90.3%) suitable for X-ray diffraction studies. M.p. 246–248°C(decomp.). Found: C, 22.4; H, 4.4; N, 8.8; Cl, 21.6. Calc. for $C_9H_{21}N_3BiCl_3$: C, 22.2; H, 4.3; N, 8.6; Cl, 21.9%.

X-RAY CRYSTALLOGRAPHY

Crystal data are given in Table 1 together with refinement details. Data were collected with Mo-K_α radiation using the MAR research Image Plate System. The crystals were positioned at 75 mm from the Image Plate. Ninety-five frames were measured at 2° intervals with a counting time of 2 mins. Data analysis was carried out with the XDS program.[9] The structure was solved from the Patterson function and remaining atoms were located in a difference Fourier map. Refinement was attempted in both space groups *Pnma* and *Pna*2_1.[10] It was soon obvious that the structure though superficially able to fit in *Pnma*, in practice did not; for example all three methyl groups showed two distinct positions. Refinement led to $R = 0.07$ but unsatisfactory dimensions. Refinement was therefore attempted in *Pna*2_1. It proved necessary to include constraints on macrocycle bond lengths in order to obtain an acceptable structure but these constraints were lifted in the later stages of refinement. An empirical absorption correction was applied using the DIFABS program.[11] The bismuth and chlorine atoms were refined anisotropically and nitrogen and carbon atoms isotropically. Hydrogen atoms were included in calculated positions. Methyl groups were refined as rigid groups. Refinement using SHELXL[12] gave $R = 0.047$. While the structure shows reasonable dimensions, it is possible that this structure is disordered and indeed the SHELXL program suggested that all three chlorine atoms could be split over two positions. However attempts to refine disordered models proved unsuccessful.

All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. Bond lengths and angles are given in Table 2.

Table 1. Crystal data and structure refinement for **1**

Identification code	$BiCl_3L$
Empirical formula	C_9H_{21} $BiCl_3N_3$
Formula weight	486.62
Temperature (K)	293 (2)
Wavelength (Å)	0.71070
Crystal system	Orthorhombic
Space group	*Pc*2_1*n* (No. 33)
Unit cell dimensions (Å)	$a = 7.42(1)$ $b = 12.74(1)$ $c = 16.05$
Volume (Å^3)	1517.5
Z	4
Density (calculated) (g m^{-3})	2.130
Absorption coefficient (mm^{-1})	12.13
F(000)	920
Crystal size (mm)	$0.2 \times 0.2 \times 0.15$
θ range for data collection (°)	3.00–25.78
Index ranges	$0 \leq h \leq 7$, $-15 \leq k \leq 15$, $-19 \leq l \leq 19$
Reflections collected	4555
Independent reflections	2485 [*R*(int) = 0.0712]
Refinement method	Full-matrix least-squares on F^2
Data/parameters	2485/92
Goodness-of-fit on F^2	1.201
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0468$, $wR2 = 0.1117$
R indices (all data)	$R1 = 0.648$, $wR2 = 0.1240$
Largest diff. peak and hole (e Å^{-3})	1.679 and -1.159

Table 2. Bond lengths (Å) and angles (°) for **1**

(a) *Metal coordination sphere*	
Bi—N(14)	2.44(3)
Bi—N(11)	2.45(2)
Bi—N(17)	2.47(2)
Bi—Cl(3)	2.643(8)
Bi—Cl(1)	2.665(5)
Bi—Cl(2)	2.656(8)
N(14)—Bi—N(11)	70.5(7)
N(14)—Bi—N(17)	71.4(5)
N(11)—Bi—N(17)	72.0(7)
N(14)—Bi—Cl(3)	91.7(7)
N(11)—Bi—Cl(3)	89.7(5)
N(17)—Bi—Cl(3)	158.2(5)
N(14)—Bi—Cl(1)	91.7(7)
N(11)—Bi—Cl(1)	158.0(3)
N(17)—Bi—Cl(1)	90.6(6)
Cl(3)—Bi—Cl(1)	103.9(6)
N(14)—Bi—Cl(2)	154.9(6)
N(11)—Bi—Cl(2)	90.1(6)
N(17)—Bi—Cl(2)	87.8(6)
Cl(3)—Bi—Cl(2)	104.3(3)
Cl(1)—Bi—Cl(2)	102.8(6)
(b) *Macrocycle dimensions*	
N(11)—C(19)	1.36(3)
N(11)—C(100)	1.47(2)
N(11)—C(12)	1.57(3)
C(12)—C(13)	1.45(3)
C(13)—N(14)	1.36(3)
N(14)—C(15)	1.54(3)
C(15)—C(16)	1.49(3)
N(14)—C(200)	1.54(3)
C(16)—N(17)	1.28(3)
N(17)—C(300)	1.56(3)
N(17)—C(18)	1.58(3)
C(18)—C(19)	1.47(3)
C(19)—N(11)—C(100)	114(2)
C(19)—N(11)—C(12)	110(2)
C(100)—N(11)—C(12)	108(2)
C(19)—N(11)—Bi	109(2)
C(100)—N(11)—Bi	108(2)
C(12)—N(11)—Bi	109(2)
C(13)—C(12)—N(11)	116(2)
C(12)—C(13)—N(14)	111(2)
C(13)—N(14)—C(15)	115(2)
C(13)—N(14)—C(200)	112(2)
C(15)—N(14)—C(200)	103(2)
C(13)—N(14)—Bi	111(2)
C(15)—N(14)—Bi	108(2)
C(200)—N(14)—Bi	108(2)
C(16)—C(15)—N(14)	116(2)
N(17)—C(16)—C(15)	116(2)
C(16)—N(17)—C(300)	117(2)
C(16)—N(17)—C(18)	115(2)
C(300)—N(17)—C(18)	100(2)
C(16)—N(17)—Bi	108(2)
C(300)—N(17)—Bi	108(2)
C(18)—N(17)—Bi	108(2)
C(19)—C(18)—N(17)	116(2)
N(11)—C(19)—C(18)	116(2)

Supplementary material includes atomic coordinates, anisotropic thermal parameters, hydrogen positions, remaining dimensions and structure factor tables and has been deposited at the Cambridge Crystallographic Data Centre.

DISCUSSION

The ^{1}H NMR spectrum shows both the N—Me protons (δ 3.03) and the backbone CH_2 protons (δ 3.50) as sharp singlets with relative intensities 9 : 12 respectively; these values point to a pronounced downfield shift of 0.73 and 0.86 ppm, respectively, following ligand coordination to bismuth(III). Similarly the ^{13}C NMR spectrum consisting of two singlets confirms the equivalence of the N—Me groups (δ 48.39) and of the ring CH_2 linkages (δ 57.65) consistent with the observed half-sandwich structure.

The structure of the title compound consists of a pyramidal $BiCl_3$ unit directly bonded to the three nitrogen atoms of the Me_3[9]aneN_3 macrocycle and is shown in Fig. 1 together with the atomic numbering scheme. The central bismuth atom has a distorted octahedral environment with Bi—Cl bond

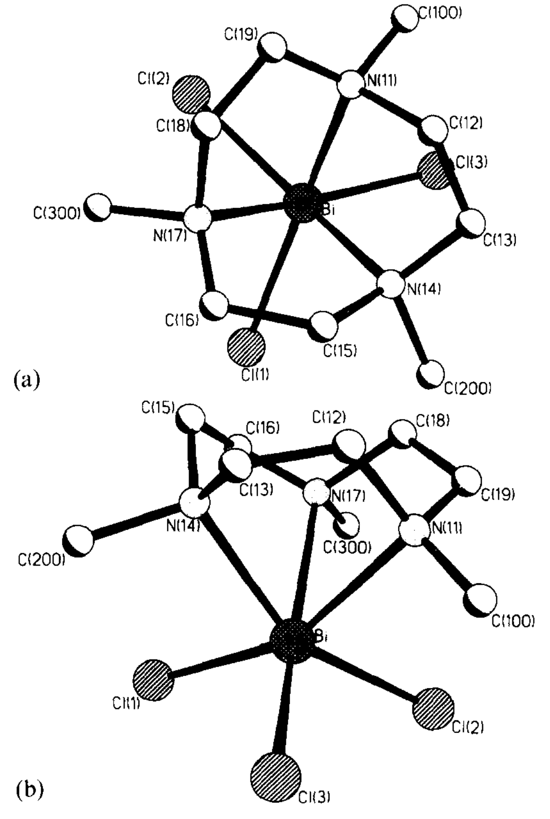

Fig. 1. The molecular structure of *fac*-($BiCl_3 \cdot Me_3$[9]aneN_3), including the atomic numbering, as viewed (a) down the approximate three-fold axis and (b) perpendicular to this axis.

Table 3. Torsions angles (°) in **1**

C(12)—C(13)—N(14)—C(15)	−68.7(30)
C(13)—N(14)—C(15)—C(16)	126.4(26)
N(14)—C(15)—C(16)—N(17)	−37.9(35)
C(15)—C(16)—N(17)—C(18)	−69.9(3)
C(16)—N(17)—C(18)—C(19)	125.4(26)
N(17)—C(18)—C(19)—N(11)	−37.7(31)
C(18)—C(19)—N(11)—C(12)	−69.4(23)
C(19)—N(11)—C(12)—C(13)	132.0(19)
N(11)—C(12)—C(13)—N(14)	−45.0(33)

distances [2.643(8), 2.665(5), 2.656(8) Å] and Bi—N bond distances [2.44(3), 2.45(2) and 2.47(2) Å]; it lies at a distance of 1.82 Å from the plane defined by the nitrogen atoms of the ring and at 1.11 Å from the plane containing the three halogen atoms. With N—Bi—N = 71.3° (mean) and Cl—Bi—Cl = 103.7° (mean) the considerable angular constriction imposed by the tridentate azamacrocycle is counterbalanced by a corresponding angular dilation amongst the chlorine atoms. The macrocycle exhibits the expected endodentate conformation with an approximate three-fold symmetry axis as demonstrated by the torsion angles listed in Table 3. This conformation is commonplace in metal complexes containing either one or two [9]aneN_3 and [9]aneS_3 macrocycles.[13] All three methyl groups are directed towards the plane of the three chlorine atoms.

Further investigations of the coordination chemistry of MCl_3 (M = As, Sb, Bi) with Me_3[9]aneN_3 and other azamacrocycles are now in progress.

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