Synthesis and Molecular Structure of the Adduct Trichlorobismuth–1,4,7,10,13,16-hexathiacyclooctadecane (1/1)†

Gerald R. Willey,* Miles T. Lakin and Nathaniel W. Alcock
Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

The reaction (1:1) of $BiCl_3$ and [18]aneS_6 in acetonitrile provides colourless crystals of the adduct $BiCl_3$·[18]aneS_6. An X-ray crystal structure determination has revealed a $BiCl_3$ pyramidal unit bonded to all six sulfur atoms of the macrocyclic ring which adopts an unusual S-shaped conformation. The bismuth atom sits on a crystallographically imposed three-fold axis in a nine-co-ordinate [3:3:3] geometrical arrangement involving two sets of three sulfur atoms and the three chlorine atoms respectively. Crystals are cubic, space group *Pa*3 with $Z = 8$ and $a = 16.381(5)$ Å; 1312 independent reflections were measured of which 825 with $[I/\sigma(I) \geqslant 2.0]$ were used in the final refinement, $R = 0.044$ ($R' = 0.067$), Bi–S 3.146(4) and 3.225(4) Å, Bi–Cl 2.607(4) Å and Cl–Bi–Cl 89.0(1)°.

The ability of crown thioethers to bind transition-metal ions, particularly those in lower oxidation states, allows direct access to a wide range of stable metal thio complexes.[1] The catalogue of reported structures is enormous and provides a clear picture of the variety produced by subtle variations in ligand character (π acidity, conformation, denticity) and metal (geometry, co-ordination number).[2,3]

However, the co-ordination chemistry of these thioethers with non-transition-metal ions is still in a primitive stage of development as gauged by the mere handful of p-block complexes that have been synthesised and structurally characterised. Examples are limited to Pb^{II},[4] Al^{III},[5,6] In^{III}[7] and Tl^{I}.[8] In our current studies we are examining the reactions of MCl_3 (M = As, Sb or Bi) with a range of thiamacrocycles including 1,4,7-trithiacyclononane [9]aneS_3, 1,4,7,10-tetrathiacyclododecane ([12]aneS_4), 1,4,7,10,13-pentathiacyclopentadecane [15]aneS_5 and 1,4,7,10,13,16-hexathiacyclooctadecane ([18]aneS_6), in order to assess the co-ordination patterns of these Group 15/VB p-block metals. Previously we have reported the structures of $SbCl_3$·[9]aneS_3 and $2SbCl_3$·[18]aneS_6,[9] $BiCl_3$·[12]aneS_4 and $BiCl_3$·[15]aneS_5·0.5MeCN.[10] Herein we describe the nine-co-ordinate bismuth(III) compound $BiCl_3$·[18]aneS_6 in which the hexathia ligand shows an unusual S conformation.

Experimental

Manipulations of materials were carried out using a standard Schlenk system and/or a dinitrogen glove-box. Solvents were stored over CaH_2 and distilled under a dinitrogen atmosphere prior to use. The compounds $BiCl_3$ and [18]aneS_6 were used as obtained commercially (Aldrich). Details of the spectroscopic instrumentation have been previously described.[10]

Preparation of $BiCl_3$·[18]aneS_6.—A solution of [18]aneS_6 (0.28 g, 0.77 mmol) in acetonitrile (50 cm^3) was added dropwise to an ice-cold solution of $BiCl_3$ (0.24 g, 0.77 mmol) in acetonitrile (60 cm^3) and the resulting slurry was heated at 60 °C with stirring for 48 h. On cooling, the light yellow precipitate was filtered off *in vacuo*, washed with hexane (3 × 15 cm^3) and diethyl ether (2 × 20 cm^3) and redissolved in the minimum of hot acetonitrile. The resulting solution was layered with an equal volume of diethyl ether to provide slow deposition of the *product* as colourless blocks (0.41 g, 79%), m.p. 175–178 °C (decomp.) (Found: C, 21.95; H, 3.35; Cl, 15.15. $C_{12}H_{24}BiCl_3S_6$ requires C, 21.30; H, 3.60; Cl, 15.75%); ν_{max}(BiCl) 212, 240, (ligand) 832, 1140 and 1422 cm^{-1} (Nujol); δ_H(CD_3CN) 2.82 [24 H, s, CH_2 (ligand)]; λ_{max}(MeCN) 34 990 cm^{-1}.

X-Ray Crystallography.—*Crystal data.* $C_{12}H_{24}S_6$·$BiCl_3$, $M = 676.0$, cubic, space group *Pa*3, $a = 16.381(5)$ Å, $U = 4395.6$ Å^3, $Z = 8$, $D_c = 2.04$ g cm^{-3}, Mo-Kα radiation, $\lambda = 0.710\,69$ Å, μ(Mo-Kα) = 8.95 cm^{-1}, $F(000) = 2608$, $T = 290$ K.

A large colourless block crystal was mounted in a Lindemann tube to prevent hydrolysis. Data were collected with a Siemens R3m four-circle diffractometer in ω–2θ mode. Maximum 2θ was 50° with scan range ±0.7°(ω) around the Kα1–Kα2 angles, scan speed 2.5–15°(ω) min^{-1}, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. The *hkl* ranges were 0–19 on each axis.

Three standard reflections were monitored every 200 reflections, and showed no significant decrease during data collection. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($15 < 2\theta < 20°$). The 4357 reflections collected were processed using profile analysis to give 1312 unique reflections ($R_{int} = 0.063$), of which 825 were considered observed $[I/\sigma(I) \geqslant 2.0]$. These were corrected for Lorentz, polarisation and absorption effects (by the Gaussian method); minimum and maximum transmission factors were 0.10 and 0.27. Crystal dimensions were 0.36 × 0.33 × 0.36 mm.

Systematic reflection conditions 0*kl*, $k = 2n$, indicate space group *Pa*3. The structure was solved by direct methods using SHELXTL (TREF) to locate a probable position for the Bi atom, lying on the three-fold axis. The light atoms were then found by successive Fourier syntheses. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.08$ Å^2, and were inserted at calculated positions and not refined. Final refinement was on F by least-squares methods refining 67 parameters. Largest positive and negative peaks on a final Fourier difference synthesis were of height ±1.5 and −1.2 e Å^{-3}, the former apparently a bismuth diffraction ripple.

A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.005$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.044$, $R' = 0.067$, $S = 0.76$. Maximum

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

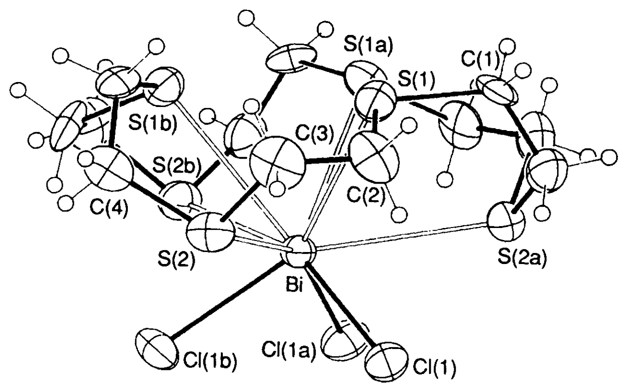

Fig. 1 View of the molecular structure of $BiCl_3{\cdot}[18]aneS_6$ showing the atomic numbering

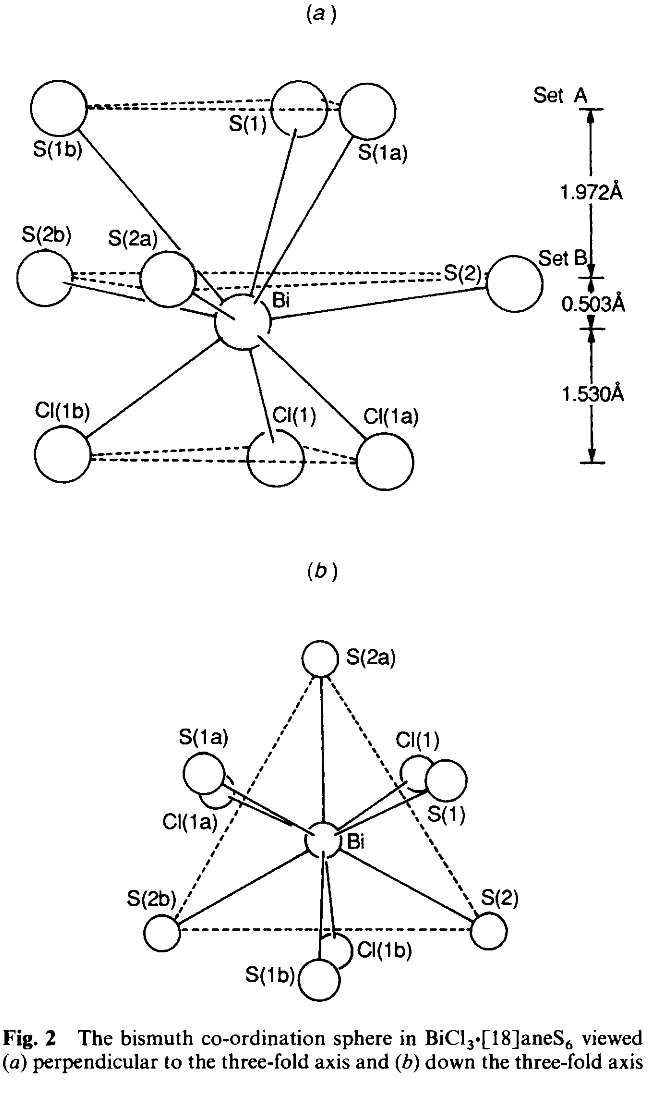

Fig. 2 The bismuth co-ordination sphere in $BiCl_3{\cdot}[18]aneS_6$ viewed (*a*) perpendicular to the three-fold axis and (*b*) down the three-fold axis

shift/error in final cycle 0.02:1. Computing with SHELXTL PLUS[11] on a DEC MicroVax-II. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 12. Final atomic coordinates are given in Table 1, and selected bond lengths and angles in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 1 Atom coordinates (× 10^4) of $BiCl_3{\cdot}[18]aneS_6$

Atom	*x*	*y*	*z*
Bi	3520.6(3)	3520.6(3)	3520.6(3)
S(1)	5126(2)	3399(2)	4654(2)
S(2)	3374(2)	2549(2)	5171(2)
Cl(1)	3817(3)	2011(2)	3116(2)
C(1)	6047(8)	3324(9)	4018(9)
C(2)	5048(9)	2366(10)	5003(10)
C(3)	4373(11)	2321(11)	5629(10)
C(4)	2918(10)	3197(9)	5940(9)

Table 2 Molecular dimensions (lengths in Å, angles in °) of $BiCl_3{\cdot}[18]aneS_6$*

Bi–S(1)	3.225(4)	Bi–S(2)	3.146(4)
Bi–Cl(1)	2.607(4)	S(1)–C(1)	1.838(14)
S(1)–C(2)	1.790(17)	S(2)–C(3)	1.838(18)
S(2)–C(4)	1.810(16)	C(1)–C(4a)	1.510(21)
C(2)–C(3)	1.510(23)		
S(1)–Bi–S(2)	62.4(1)	S(1)–Bi–Cl(1)	86.3(1)
S(2)–Bi–Cl(1)	75.7(1)	Cl(1)–Bi–Cl(1a)	89.0(1)
C(1)–S(1)–C(2)	100.1(7)	C(3)–S(2)–C(4)	101.7(7)
S(1)–C(1)–C(4a)	116.1(10)	S(1)–C(2)–C(3)	108.3(11)
S(2)–C(3)–C(2)	111.5(11)	S(2)–C(4)–C(1a)	114.9(11)

* Position a: *z*, *x*, *y*.

Results and Discussion

Direct addition (equimolar quantities) of $BiCl_3$ and $[18]aneS_6$ gives the stable colourless complex $BiCl_3{\cdot}[18]aneS_6$. The IR spectrum shows broad intense bands at 212 and 240 cm^{-1} associated with ν(BiCl) stretching modes and a distinctive trio of bands at 832, 1140 and 1422 cm^{-1} indicative of co-ordinated ligand. The ^1H NMR spectrum contains a singlet at δ 2.82 for the skeletal CH_2 protons of the crown ring.

The structure of $BiCl_3{\cdot}[18]aneS_6$ (Fig. 1) consists of a pyramidal $BiCl_3$ unit bonded to all six sulfur atoms of the crown thioether with the molecule showing a crystallographic three-fold symmetry. The co-ordination geometry around the bismuth atom can be viewed as nine-co-ordinate [3:3:3] involving two sets of sulfur atoms S(1), S(1a), S(1b), (set A) and S(2), S(2a), S(2b) (set B) and the three chlorine atoms, respectively. This arrangement is depicted in Fig. 2(*a*). As shown in Fig. 2(*b*) the three chlorine atoms are almost in an eclipsed position (7.3° stagger) with respect to the three sulfur atoms of set A, *i.e.* the nine-fold co-ordination approximates to a tricapped (rectangular faces) trigonal prism but with the bismuth atom displaced from the centre of the prism towards the halogen atoms. The metal lies at a distance of 2.475 Å below the plane defined by set A and only 0.503 Å below the plane defined by set B with the result that it is effectively tucked up inside the ring cavity in an unusual 'teepee' encapsulation. The Bi–S distances observed here, 3.225(4) and 3.146(4) Å, are similar to those in $BiCl_3{\cdot}[12]aneS_4$, 2.987(3)–3.206(3) Å, and $BiCl_3{\cdot}[15]aneS_5{\cdot}0.5MeCN$, 3.057(7)–3.433(7) Å.[10]

Interestingly, in the parent halide structure[13] the eight-co-ordinate bismuth atom also sits in a non-central position of a trigonal prism of chlorine atoms but with only two of the rectangular faces capped with bridging chlorine atoms. In the related structure of $PbCl_2$, trigonal-prismatic co-ordination with all three rectangular faces capped by halogen atoms, *i.e.* nine-co-ordinate Pb^{II}, is observed.[14]

Comparison of the dimensions of the $BiCl_3$ units [parent halide 2.513(7), 2.518(7), 2.468(3) Å, Cl–Bi–Cl 94.9(3), 93.2(3), 84.45(14)°; present structure Bi–Cl 2.607(4) Å, Cl–Bi–Cl 89.0(1)°] indicates retention of the basic trigonal-pyramidal shape (ψ-tetrahedral) observed in the parent halide; the bonds are somewhat lengthened and the angles are slightly decreased

Table 3 Torsion angles (°)

	[18]aneS_6		$BiCl_3$·[18]aneS_6	
-C-C-	−174.6	−78.9	60.6	
	179.2		55.8	
	anti (× 4)	*gauche* (× 2)	*gauche* (× 6)	
-C-S-	73.3		−138.5	80.4
	84.2		176.7	66.9
	−78.3			
	−99.8			
	−116.5			
	93.1			
	gauche (× 12)		*anti* (× 6)	*gauche* (× 6)

(and symmetrical) in the complex as a result of the steric/electronic effects induced by the bulky macrocyclic ligand. Whether or not this signifies retention of stereochemical activity of the lone pair of electrons associated with Bi^{III} is unclear; the stereochemical implications of the lone pair in analogous crown ether complexes of MCl_3 (M = As, Sb or Bi) have been discussed by Drew *et al.*[15]

The conformation adopted by the S_6 ring following complexation with Bi^{III} is remarkable, approximating to an S profile. Torsion angles are listed in Table 3. The parent ligand shows *gauche* geometry for all its C–S linkages[16] but the complex has an equal number of *gauche* (6/12) and *anti* (6/12) placements. For the C–C bonds the *anti* (4/6) and *gauche* (2/6) arrangements adopted in the parent ligand become uniformly (6/6) *gauche* in the complex, with torsion angles 60.6, 55.8° despite the repulsion from the unfavourable 1,4-(S ··· S) interactions. Evidently the strong Bi–S bonding interactions incorporating all six sulfur atoms of the ring more than compensate for this inhibiting effect.

It is pertinent to compare the present structure with that of the antimony(III) counterpart, $2SbCl_3$·[18]aneS_6. For the latter all the sulfur atoms of the thia crown are involved in chelation but as two terdentate sets bonding to separate $SbCl_3$ units positioned respectively above and below the S_6 cavity. The metal centres are six-co-ordinate with each of the three sulfur atoms *trans* to a chlorine atom in an irregular *fac* array. Presumably the combined effects of (*a*) larger size $Bi^{III} > Sb^{III}$, (*b*) stronger bond strength Bi–S > Sb–S ≫ As–S* and (*c*) increased tendency to high co-ordination number $Bi^{III} > Sb^{III}$ militate against symmetrical sexadentate chelation of a single $SbCl_3$ unit as observed in the present instance with $BiCl_3$.

Acknowledgements

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* We have been unable to isolate any adduct from the corresponding $AsCl_3$–[18]aneS_6–MeCN system.