Synthesis and Crystallographic Studies of Crown Thioether Complexes of Bismuth(III)†

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The pale yellow bismuth(III)–crown thioether complexes $BiCl_3\cdot[12]aneS_4$ **1** and $BiCl_3\cdot[15]aneS_5\cdot0.5MeCN$ **2** have been prepared and characterised. An X-ray crystal structure determination of **1** shows the central bismuth atom bonded to three chlorine atoms, Bi–Cl mean 2.571 Å, Cl–Bi–Cl 90.9(1)–94.3(1)°, and all four sulfur atoms of the $[12]aneS_4$ macrocycle, Bi–S 2.987(3)–3.206(3) Å, in an approximate half-sandwich structure. The four sulfur atoms are exactly coplanar and the bismuth atom sits in a central location over the ring at a distance of 1.87 Å from this plane. This is the first genuine example of *endo* complexation for $[12]aneS_4$ involving a p-block element. Compound **1** crystallises in the monoclinic space group $P2_1/n$ with $a = 7.985(4)$, $b = 12.956(7)$, $c = 15.278(9)$ Å, $\beta = 101.47(4)°$ and $Z = 4$. 2099 Observed reflections $[I/\sigma(I) \geqslant 2.0]$ gave in the final refinement $R = 0.037$. The structure of $BiCl_3\cdot[15]aneS_5\cdot0.5MeCN$ **2** shows full co-ordination of the $[15]aneS_5$ macrocycle to the $BiCl_3$ unit in a half-sandwich arrangement, with two independent identical molecules, Bi–Cl mean 2.565(7) Å, Bi–S 3.057(7)–3.433(7) Å, Cl–Bi–Cl 86.5(2)–93.0(2)°; acetonitrile is trapped as lattice solvate. The ligand undergoes a conformational change (exo- to endo-dentate) on complex formation. Compound **2** crystallises in the orthorhombic space group *Pbca* with $a = 16.972(9)$, $b = 15.418(8)$, $c = 30.60(2)$ Å, and $Z = 16$. 2951 Observed reflections $[I/\sigma(I) \geqslant 2.0]$ gave in the final refinement $R = 0.0545$. The resulting conformations of the macrocyclic ligands are discussed in terms of *gauche/anti* preferences and structural comparisons are drawn between **1** and **2** and their oxocrown counterparts.

The co-ordination chemistry of crown thioethers continues to attract attention; recent reviews by Cooper and Rawle[1] and Blake and Schröder[2] bear witness to the rapid advances in this particular sector of macrocyclic chemistry both in terms of the range of metal ions involved and the structural nuances and subtleties that have emerged. The majority of such crown thioether complexes involve transition-metal ions usually those with 'soft' or class (b) Lewis-acid characteristics. By contrast the examination of p-block metal ions is in its infancy and examples where main-group elements are bonded to S-donor macrocycles are limited to $[Pb([9]aneS_3)_2(OClO_3)_2]$($[9]aneS_3$ = 1,4,7-trithiacyclononane),[3] $[AlMe_3([12]aneS_4)]$($[12]aneS_4$ = 1,4,7,10-tetrathiacyclododecane),[4] $[(AlMe_3)_4([14]aneS_4)]$ ($[14]aneS_4$ = 1,4,8,11-tetrathiacyclotetradecane),[5] $[InCl_3([9]aneS_3)]$[6] (synthesis only) and the very recently reported $[Tl([9]aneS_3)][PF_6]$.[7]

In a prior communication[8] we have described the neutral Group 15 compounds $BiCl_3\cdot[9]aneS_3\cdot0.5MeCN$, $BiCl_3\cdot[18]aneS_6$ ($[18]aneS_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane) (synthesis) and $SbCl_3\cdot[9]aneS_3$ and $2SbCl_3\cdot[18]aneS_6$ (structures). The compound $SbCl_3\cdot[9]aneS_3$ has a chain structure in which each $SbCl_3$ unit is bonded unsymmetrically to the three sulfur atoms of the trithia crown (*endo* complexation) and to a further (bridging) sulfur atom of an adjacent one; in $2SbCl_3\cdot[18]aneS_6$ each of the $SbCl_3$ groups is separately bonded to three sulfur atoms of the ring in an irregular [2 + 1] *fac*-octahedral arrangement. The structural intricacies of these stable antimony(III)–crown thioether complexes has stimulated the search for further examples incorporating p-block elements and in this present study we describe the isolation and X-ray structural characterisation of bismuth(III) complexes with the $[12]aneS_4$ and $[15]aneS_5$(1,4,7,10,13-pentathiacyclopentadecane) crown macrocycles respectively.

Experimental

All manipulations were carried out under an inert atmosphere of N_2 using a glove-box and/or a conventional Schlenk system. Anhydrous $BiCl_3$ and the crown thioether ligands $[12]aneS_4$ and $[15]aneS_5$ were used directly as supplied commercially. Benzene, hexane, dichloromethane and acetonitrile were stored over CaH_2 and freshly distilled under N_2 prior to use. Infrared spectra were recorded on a Perkin-Elmer 580B spectrophotometer with samples as Nujol mulls placed between CsI plates, proton (^1H) NMR spectra (220 MHz, Perkin-Elmer R34) for CD_3CN solutions doped with $SiMe_4$ as internal reference, and UV/VIS spectra in sealed 1 cm quartz cells with MeCN solutions using a Shimadzu UV35 spectrophotometer. Microanalyses were carried out by Medac, Brunel University, Uxbridge, Middlesex.

Preparation of the Complexes.—$BiCl_3\cdot[12]aneS_4$ **1**. A solution of $[12]aneS_4$ (0.13 g, 0.52 mmol) in acetonitrile (50 cm^3) was added to an ice-cold solution of $BiCl_3$ (0.16 g, 0.52 mmol) in acetonitrile (50 cm^3) over a period of 30 min. The resulting solution was heated at 50 °C for 24 h and, following filtration, was allowed to cool slowly to room temperature. Small yellow needle crystals of the *product* (0.19 g, 66%) were obtained of suitable quality for X-ray diffraction studies, m.p. 193–194 °C (Found: C, 17.45; H, 2.95. $C_8H_{16}BiCl_3S_4$ requires C, 17.30; H, 2.90%); $\nu_{max}(BiCl)$ 228, 245; (ligand) 832, 919, 1404, and 1412 cm^{-1}; $\delta_H(CD_3CN)$ 2.76 [16 H, s, CH_2 (crown)]; $\lambda_{max}(MeCN)$ 35 075 cm^{-1}.

$BiCl_3\cdot[15]aneS_5\cdot0.5MeCN$ **2**. Dropwise addition of $[15]aneS_5$ (0.25 g, 0.84 mmol) in acetonitrile (50 cm^3) to an ice-cold solution of $BiCl_3$ (0.27 g, 0.84 mmol) in acetonitrile (50 cm^3) produced a white cloudy suspension which was stirred for 24 h at 50 °C. Removal of solvent gave a white solid which was washed with hexane (4 × 20 cm^3) and diethyl ether (2 × 20 cm^3). Recrystallisation from acetonitrile–dichloromethane provided the *product* as pale yellow lath crystals (0.44 g, 82%) suitable for X-ray diffraction studies, m.p. 172–174 °C (Found:

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

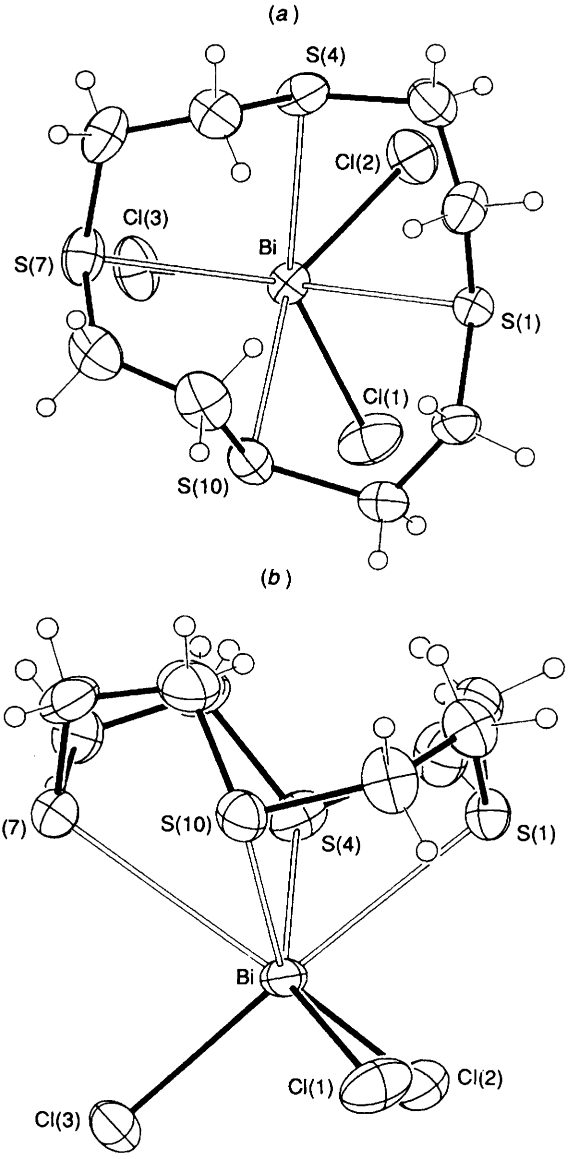

Fig. 1 Two views of $BiCl_3$·[12]aneS_4 **1**

C, 20.60; H, 3.45; N, 1.05; $C_{22}H_{43}Bi_2Cl_6NS_{10}$ requires C, 20.75; H, 3.40; N, 1.10%); ν_{max}(BiCl) 226, 254; (ligand) 1016, 1260, 1404, 1414; (CN) 2248 and 2290 cm^{-1}; $\delta_H(CD_3CN)$ 2.88 [20 H, s, CH_2 (crown)]; λ_{max}(MeCN) 35 137 cm^{-1}.

Crystal-structure Analyses.—Crystal data. $C_8H_{16}BiCl_3S_4$ **1**, $M = 555.82$, monoclinic, space group $P2_1/n$, $a = 7.985(4)$, $b = 12.956(7)$, $c = 15.278(9)$ Å, $\beta = 101.47(4)°$, $U = 1549$ Å^3, $Z = 4$, $D_c = 2.38$ g cm^{-3}, Mo-Kα radiation, $\lambda = 0.710\ 69$ Å, μ(Mo-Kα) = 123.6 cm^{-1}, $T = 290$ K, $F(000)$ 1048.0.

$C_{10}H_{20}BiCl_3S_5$·0.5MeCN **2**, $M = 636.4$, orthorhombic, space group *Pbca*, $a = 16.972(9)$, $b = 15.418(8)$, $c = 30.60(2)$ Å, $U = 8007$ Å^3, $Z = 16$, $D_c = 2.11$ g cm^{-3}, Mo-Kα radiation, $\lambda = 0.710\ 69$ Å, μ(Mo-Kα) = 96.8 cm^{-1}, $T = 290$ K, $F(000) = 4880.0$.

Both crystals were capillary mounted to avoid possible decomposition. Data for **2** are given in parentheses. Data were collected with a Syntex P2$_1$ four-circle diffractometer in ω–2θ mode. Maximum 2θ was 50° (45°) with scan range ±1.4 (2θ) around the Kα_1 – Kα_2 angles, scan speed 5–29° min^{-1} depending on the intensity of the 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. The *hkl* ranges were 0–9, 0–15, −18 to 18 (0–16, 0–18, 0–33).

Three standard reflections were monitored every 200 reflections and showed a slight decrease during data collection. The data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($15 < 2\theta < 18°$) ($18 < 2\theta < 20°$). Reflections were processed using profile analysis to give 2741 (4957) unique reflections (for **1**, R_{int} = 0.039); 2099 (2951) were considered observed [$I/\sigma(I) \geqslant 2.0$] and used in refinement. They were corrected for Lorentz, polarisation and absorption effects, the last by the Gaussian method; maximum and minimum transmission factors 0.58 and 0.28 (0.27 and 0.19). Crystal dimensions were 0.17 × 0.12 × 0.35 (0.36 × 0.33 × 0.12) mm.

Systematic absences: **1**, $h0l$ $h + l = 2n$, $0k0$ $k = 2n$, indicating space group $P2_1/n$; **2**, $0kl$ $k = 2n$, $h0l$ $l = 2n$, $hk0$ $h = 2n$, indicating space group *Pbca*.

Heavy atoms were located by the Patterson interpretation section of SHELXTL and the light atoms then found on successive Fourier syntheses. For compound **2** Fourier syntheses revealed one molecule of solvent MeCN per asymmetric unit. 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; H atoms of the solvent molecule in **2** were not included. Final refinement was on F by least-squares methods refining 146(366) parameters including an isotropic extinction parameter for **1** [final value 0.000 20(3)].

For compound **1** largest positive and negative peaks on a final Fourier difference synthesis were of height 1.5 and −1.1 e Å^{-3} with all significant peaks near Bi; for **2** final peaks were ±1.0 e Å^{-3}. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.000\ 50$ (0.0062) was used and shown to be satisfactory by a weight analysis. For **1**, final $R = 0.037$, $R' = 0.040$ and for **2** final $R = 0.055$, $R' = 0.051$. Maximum shift/error in a final cycle 0.1 (0.2). Computing with SHELXTL PLUS[9] on a DEC MicroVax-II computer. Scattering factors in the analytical form and anomalous dispersion factors taken from ref. 10. 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.

Results and Discussion

Reactions of $BiCl_3$ (1 mol) and the appropriate crown thioether (1 mol) in acetonitrile provide the corresponding monoadducts $BiCl_3$·[12]aneS_4 **1** and $BiCl_3$·[15]aneS_5·0.5MeCN **2** as pale yellow solids. These can be purified by recrystallisation from MeCN–CH_2Cl_2 but each one is quite sensitive to air/moisture and must be handled under dinitrogen.

Structure of $BiCl_3$·[12]aneS_4 **1**.—The single-crystal X-ray structure of compound **1** shows a half-sandwich arrangement in which the bismuth atom is co-ordinated to all four sulfur atoms of the crown (see Fig. 1 with atom labelling scheme). Selected bond lengths and angles are given in Table 2. The conformation of the ring approximates to C_4 symmetry with the four sulfur atoms coplanar; the maximum deviation from the mean plane defined by S(1)–S(4)–S(7)–S(10) is ±0.01 Å. The $BiCl_3$ unit sits centrally over the crown ring cavity, with the bismuth at 1.873 Å from the S(1)–S(4)–S(7)–S(10) plane.

The Bi–S bond distances show no substantial variation and have a mean of 3.065 Å, typical for co-ordinated bismuth(III) species, *e.g.* $Bi(MeCO_2)_3$·3S=C$(NH_2)_2$ [Bi–S 3.020(2)–3.124(2), mean 3.061 Å for nine-co-ordinate Bi^{III}][11] and $BiCl_3$·2Et_2NCSC-SNEt_2 [Bi–S 2.818(13)–3.042(12), mean 2.942Å for seven-coordinate Bi^{III}].[12] The parameters of the $BiCl_3$ unit change very little on complexation indicative of a weak interaction of the thiamacrocycle with the metal halide; the mean Bi–Cl bond distance is 2.571 Å and the mean Cl–Bi–Cl angle 92.3° compared to Bi–Cl 2.468(4)–2.517(7) (mean 2.496 Å) and Cl–Bi–Cl 84.5(3)–

Table 1 Atom coordinates (× 10^4)

Atom	x	y	z	Atom	x	y	z
(*a*) Compound **1**							
Bi	501.8(5)	2 332.3(3)	2 164.1(2)	C(2)	2 880(14)	4 318(8)	3 984(7)
Cl(1)	1 754(4)	2 394(2)	741(2)	C(3)	1 009(16)	4 422(7)	4 046(8)
Cl(2)	−1 449(4)	3 877(2)	1 623(2)	C(5)	724(15)	2 484(7)	4 822(7)
Cl(3)	−1 723(4)	974(2)	1 469(2)	C(6)	89(15)	1 396(8)	4 665(7)
S(1)	3 099(3)	3 953(2)	2 867(2)	C(8)	2 990(15)	479(8)	4 191(7)
S(4)	−245(3)	3 279(2)	3 889(2)	C(9)	4 188(15)	1 249(8)	3 931(8)
S(7)	737(4)	694(2)	3 756(2)	C(11)	5 354(14)	2 410(7)	2 608(8)
S(10)	3 942(4)	1 368(2)	2 742(2)	C(12)	5 223(13)	3 381(7)	2 094(7)
(*b*) Compound **2**							
Bi(1)	1 681.0(5)	2 940.3(5)	1 920.2(3)	C(19)	3 529(13)	4 599(15)	1 758(9)
Bi(2)	6 579.9(5)	1 430.2(5)	616.1(3)	C(110)	2 965(13)	5 097(15)	2 024(8)
Cl(11)	2 885(4)	2 221(4)	2 283(2)	S(21)	5 063(4)	2 244(5)	51(2)
Cl(12)	779(4)	1 886(4)	2 357(2)	S(22)	4 973(4)	1 281(4)	1 061(2)
Cl(13)	1 749(4)	1 934(4)	1 271(2)	S(23)	6 035(3)	3 112(4)	1 286(2)
Cl(21)	5 951(3)	151(4)	227(2)	S(24)	7 854(4)	2 626(5)	1 001(2)
Cl(22)	6 873(4)	540(4)	1 308(2)	S(25)	6 919(4)	2 918(5)	−23(3)
Cl(23)	7 878(4)	970(5)	245(3)	C(21)	4 405(13)	2 554(15)	495(7)
S(11)	2 591(3)	4 411(4)	2 462(2)	C(22)	4 193(14)	1 734(17)	759(9)
S(12)	604(3)	4 299(4)	2 471(2)	C(23)	4 968(16)	1 832(15)	1 573(8)
S(13)	−46(4)	3 116(4)	1 565(2)	C(24)	5 140(12)	2 815(16)	1 559(7)
S(14)	1 348(3)	4 499(4)	1 261(2)	C(25)	6 770(12)	2 763(15)	1 682(7)
S(15)	3 131(3)	3 659(4)	1 450(2)	C(26)	7 570(12)	3 057(16)	1 524(8)
C(11)	1 925(14)	5 166(15)	2 728(7)	C(27)	7 731(24)	3 612(20)	669(10)
C(12)	1 155(12)	5 273(12)	2 481(8)	C(28)	7 672(19)	3 541(21)	217(12)
C(13)	−178(14)	4 566(17)	2 110(9)	C(29)	6 032(18)	3 633(17)	21(13)
C(14)	−592(13)	3 760(16)	1 923(9)	C(210)	5 397(17)	3 237(20)	−138(16)
C(15)	−86(14)	3 808(15)	1 065(7)	N(001)	10 189(19)	−158(18)	768(11)
C(16)	724(15)	3 953(18)	905(9)	C(001)	9 834(25)	283(23)	992(11)
C(17)	2 187(18)	4 725(20)	953(9)	C(002)	9 331(26)	749(26)	1 258(13)
C(18)	2 814(16)	4 052(18)	932(10)				

Table 2 Selected bond lengths (Å) and angles (°)

(*a*) For $BiCl_3$·[12]aneS_4

Bi–Cl(1)	2.569(4)	Cl(1)–Bi–Cl(2)	90.9(1)
Bi–Cl(2)	2.569(3)	Cl(1)–Bi–Cl(3)	91.4(1)
Bi–Cl(3)	2.575(3)	Cl(2)–Bi–Cl(3)	94.3(1)
Bi–S(1)	2.996(3)		
Bi–S(4)	3.072(3)		
Bi–S(7)	3.206(3)		
Bi–S(10)	2.987(3)		

(*b*) For $BiCl_3$·[15]aneS_5, molecules A and B

	A	B
Bi–Cl(1)	2.576(7)	2.539(6)
Bi–Cl(2)	2.602(7)	2.571(7)
Bi–Cl(3)	2.522(7)	2.579(7)
Bi–S(1)	3.205(7)	3.346(8)
Bi–S(2)	3.251(7)	3.057(7)
Bi–S(3)	3.138(7)	3.433(7)
Bi–S(4)	3.187(7)	3.076(7)
Bi–S(5)	3.058(7)	3.068(8)
Cl(1)–Bi–Cl(2)	88.6(2)	93.0(2)
Cl(1)–Bi–Cl(3)	92.2(2)	86.5(2)
Cl(2)–Bi–Cl(3)	92.7(2)	92.9(2)

94.9(3)° (mean 90.9°) in the parent halide.[13] The key structural feature of compound **1** is the ligand reorganisation whereby [12]aneS_4 functions as a tetradentate S-donor. In the solid state [12]aneS_4 has all four sulfur atoms exodentate in a quadrangular array[14] an arrangement which, *a priori*, would favour its functioning as a bridging ligand between separate metal centres. Examples of both chelate and bridging bonding modes for this tetrathiamacrocycle are known: [$AlMe_3$([12]aneS_4)], exodentate (*trans*) bridging to two separate planar $AlMe_3$ units;[4] [Ni_2([12]aneS_4)$_3$]$^{4+}$, where both bridging and chelating bonding modes to octahedral nickel(II) centres are postulated;[15] [Re(CO)$_3$([12]aneS_4)]$^+$, with terdentate S-donation to the octahedral Re^I leaving the fourth sulfur atom unco-ordinated.[16] Examples where all four sulfur atoms are chelated to a metal ion include *cis*-[Ru(MeCN)(PPh_3)([12]aneS_4)]$^{2+}$ and *cis*-[Ru(CO)(PPh_3)([12]aneS_4)]$^{2+}$ for octahedral Ru^{II},[17] *cis*-[RhCl(PEt_2Ph)([12]aneS_4)]$^{2+}$ for octahedral Rh^{III},[17] [Pd([12]aneS_4)]$^{2+}$ for square-planar Pd^{II},[18] [Ni_2Cl_2([12]aneS_4)$_2$]$^{2+}$ for octahedral Ni^{II},[19] and [Cu([12]aneS_4)(H_2O)]$^{2+}$ for square-pyramidal Cu^{II}.[20] Compound **1** represents the first confirmed example of endodentate chelate formation incorporating a p-block metal.

Structure of $BiCl_3$·[15]aneS_5·0.5MeCN **2**.—In the structure of compound **2** (Fig. 2 with atom labelling) all five sulfur atoms of the pentathiamacrocyclic ring are bonded to a $BiCl_3$ unit in a half-sandwich arrangement. The acetonitrile is not co-ordinated to Bi^{III} but is simply trapped as lattice solvate. The crystallographic asymmetric unit contains two independent molecules. Neither has crystallographic symmetry but they have essentially identical $BiCl_3$·[15]aneS_5 half-sandwich geometries with identical metal co-ordination. Variations in the independent Bi–S and Bi–Cl bond distances are without chemical significance. Selected bond lengths and angles are listed in Table 2. The Bi–S bond distances, mean 3.182 Å, are longer than those in **1** consistent with the increase in co-ordination number of the central bismuth atom. In this instance the sulfur atoms are not coplanar and the bismuth atom sits in a central position over the macrocyclic ring at distances of 1.659 (molecule A) and 1.709 Å (molecule B) from the least-squares mean plane defined by the five sulfur atoms. Again, as in **1**, the $BiCl_3$ moiety has very similar dimensions to those of the parent halide, *viz*. Bi–Cl mean 2.565 Å and Cl–Bi–Cl angles

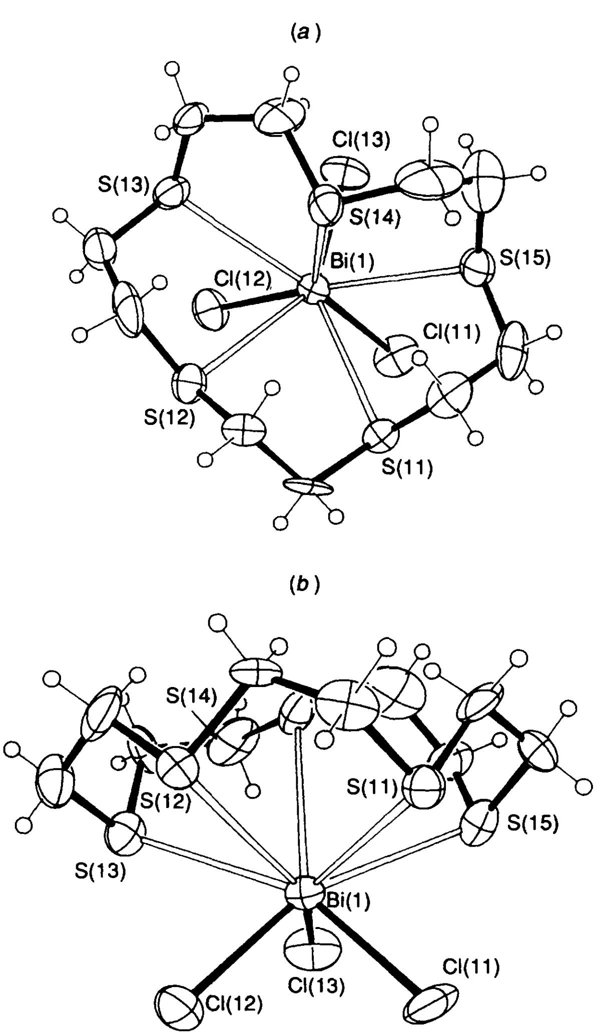

Fig. 2 Two views of one molecule of $BiCl_3$·[15]aneS$_5$ **2**. The second molecule is essentially identical

approximately 90°. Whereas the parent ligand [15]aneS$_5$ adopts an exodentate conformation with the sulfur atom lone pairs orientated out of the macrocyclic ring,[14] complexation with $BiCl_3$ has effected a conformational change exodentate to endodentate wherein all five sulfur atoms are bonded to the central Bi^{III}. The limited co-ordination chemistry previously established for this pentathiamacrocyclic ligand invariably features complexation with transition-metal ions, *e.g.* [ReBr(CO)$_3$([15]aneS$_5$)] containing octahedral Re^{I} linked to only two of the ligand sulfur atoms with the remainder unco-ordinated[21] and $[M([15]aneS_5)]^{2+}$ (M = Pd^{II}, distorted trigonal bipyramid;[22] Pt^{II}, square-based pyramid),[23] $[Cu([15]aneS_5)]^{2+}$ (square-based pyramid) and $[Cu([15]aneS_5)]^{+}$ (distorted tetrahedral) in each of which the ligand is tetradentate with one sulfur atom unco-ordinated.[24] More recently the novel binuclear silver(I) complex $[Ag_2([15]aneS_5)_2]^{2+}$ [25] in which individual sulfur atoms from each ring bridge asymmetrically between the two metal centres which themselves show separate and distinct co-ordination geometries, *viz.* distorted tetrahedral and distorted square pyramidal, and the mercury(II) complex $[Hg([15]aneS_5)][PF_6]_2$ [26] (distorted square pyramidal) have been described. Compound **2** is the first example of chelate formation by this ligand with a p-block metal.

From the viewpoint of [12]aneS$_4$ and [15]aneS$_5$ as the sulfur congeners of the oxacrowns 12-crown-4 (1,4,7,10-tetraoxacyclododecane) and 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) respectively, structural comparisons between **1** and $BiCl_3$·12-crown-4[27] and between **2** and $BiCl_3$·15-crown-5[28] indicate the macrocyclic binding characteristics of O *versus* S. Relevant bond length and angle data are collected in Table 3. These four complexes of bismuth(III) chloride share a common half-sandwich structure. In **1** and $BiCl_3$·12-crown-4 each set of four donor atoms (oxygen or sulfur) are precisely coplanar, with the bismuth atom located in each structure at *ca.* 1.85 Å from this plane. With **2** and $BiCl_3$·15-crown-5 which feature the larger penta-substituted macrocyclic rings the bismuth atom sits over the central cavity in each case at a shorter distance *ca.* 1.6–1.7 Å from the mean plane defined by the five donor (oxygen or sulfur) atoms. The steric requirements of the bulkier [12]aneS$_4$ in **1**, as reflected by the *trans* S–Bi–S angles (mean 104.4°), *versus* the smaller oxacrown in $BiCl_3$·12-crown-4, *trans* O–Bi–O angles (mean 93.8°), do not effect any significant variation in the respective $BiCl_3$ units whose mean Cl–Bi–Cl angles remain essentially the same *viz.*, 92.3° in **1** and 92.9° in $BiCl_3$·12-crown-4. A similar picture emerges from comparisons of **2** and $BiCl_3$·15-crown-5 where the mean Cl–Bi–Cl angles are 91.0 and 90.0° respectively.

For both complexes the Bi–S bonds are about 0.35 Å longer than the corresponding Bi–O bonds. This difference is close to the mean difference in covalent radius of divalent O and S (*ca.* 0.4 Å) indicating that the Bi–O and Bi–S bonds are of similar strength.

As outlined by Cooper and co-workers[14,30] thia- and oxamacrocyclic ligands show contrasting conformational preferences. In brief, thiacrowns have a preference for *gauche* placement at C–S bonds and for *anti* placement at C–C bonds, the reverse being true in the case of oxocrowns. Interestingly we can trace the same patterns in our bismuth(III) complexes. Torsion angles are listed in Table 3.

(*a*) **1** *and* $BiCl_3$·12-crown-4. In the parent [12]aneS$_4$ each of the eight C–S linkages adopts a *gauche* placement.[14] Following complexation to $BiCl_3$ four have retained this *gauche* placement and four have an *anti* placement in an incipient *exo* to *endo* conformational rearrangement. As a direct comparison this profile of *gauche* (4) and *anti* (4) placements is observed in both $BiCl_3$·12-crown-4 and in the parent 12-crown-4.[29] In both **1** and $BiCl_3$·12-crown-4 each of the four C–C bonds shows torsional angles *ca.* ±60° for *gauche* placement, *e.g.* there has been a significant reorganisation with respect to the thiacrown which originally shows all four C–C bonds in an *anti* placement. Despite this reorganisation the dimensions of [12]aneS$_4$ are virtually unchanged following complexation with $BiCl_3$: the mean C–S bond distance in **1** is 1.805 Å ([12]aneS$_4$ mean 1.815 Å) with mean bond angles at sulfur of 102.2° ([12]aneS$_4$ mean 101.3°).

(*b*) **2** *and* $BiCl_3$·15-crown-5. In the case of [15]aneS$_5$ there is a similar tendency toward *gauche* placement for C–S linkages, *i.e.* seven of the ten C–S bonds show torsional angles *ca.* ±60°.[14] Following complexation with $BiCl_3$ and internal reorganisation (*exo* to *endo*) five of these C–S bonds retain *gauche* placement; for the oxocrown analogue $BiCl_3$·15-crown-5 there is a preponderance of *anti* placements, *i.e.* seven of the ten C–O bonds exhibit torsional angles *ca.* ±180°. For both **2** and $BiCl_3$·15-crown-5 all five C–C bonds are *gauche* with torsional angles *ca.* ±60°. What we are witnessing in **2** is a dramatic change in conformation for the pentathiamacrocycle which in the uncomplexed form shows *anti* placement for four of the five C–C bonds with torsion angles in the range 166.6–174.4°. As in the case of **1**, complexation of [15]aneS$_5$ with $BiCl_3$ causes no drastic changes in the dimensions of the macrocyclic ring despite the rearrangement.

As a final comment we are tempted to suggest that the unusual mode of co-ordination of these thiamacrocycles arises from the inflexible character of the $BiCl_3$ unit. As noted above the dimensions and geometry of the $BiCl_3$ unit in structures **1** and **2** are similar to those of the parent halide molecule which is regarded as ψ-tetrahedral with an active lone pair.[13] The formation of $BiCl_3$·12-crown-4, $BiCl_3$·15-crown-5 and indeed $BiCl_3$·18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane),[31]

Table 3 Selected mean dimensions for $BiCl_3 \cdot L$ [L = tetra- or penta-substituted (X) macrocycle]

Compound	12-crown-4 (X = O)	[12]aneS$_4$ (X = S)	$BiCl_3$·12-crown-4 (X = O)	$BiCl_3$·[12]aneS$_4$ **1** (X = S)	[15]aneS$_5$ (X = S)	$BiCl_3$·15-crown-5 (X = O)	$BiCl_3$·[15]aneS$_5$ **2** (X = S)	
Ref.	29	14	27	This work	14	28	This work	
Distance Bi to X$_n$ plane (Å)			1.84	1.87		1.61	1.66/1.71 *	
Bi–X (Å)			2.702	3.065		2.833	3.182	
Bi–Cl (Å)			2.519	2.571		2.526	2.565	
C–X (Å)	1.428	1.815	1.413	1.805	1.836	1.425	1.795	
Minimum X–Bi–X (°)			60.7	65.6		57.5	62.3	
Cl–Bi–Cl (°)			92.9	92.3		90.0	91.0	
X–C–C (°)	110.8		115.5	114.5		109.4	102.0/115.2 *	
C–X–C (°)	113.6	101.3	111.9	102.2	101.6	112.3	102.6	
Torsion angles (°)	−75.4	−173.1	50.0	65.1	−171.9	−66.5	64.9	68.9 *
(C–C)	74.5	−172.7	39.2	67.2	174.4	−59.2	65.0	56.8
		−174.1	43.1	−56.8	−63.9	59.0	−67.8	−53.9
		−173.6	45.0	−56.1	166.6	63.5	−62.0	−60.2
					167.0	−60.5	−51.7	58.7
(C–X)	140.2	73.7	87.0	−157.4	−121.9	−83.7	77.5	−168.4
	102.7	72.5	−162.5	64.3	91.0	178.9	−172.6	87.2
	−173.6	72.2	95.7	−166.1	82.8	−85.9	161.0	−63.8
	85.2	71.0	−152.6	70.7	113.8	−176.7	−75.6	−72.9
		71.5	95.8	−94.7	−88.5	−169.8	127.0	−173.9
		76.1	−152.6	174.7	84.3	78.1	−170.5	106.7
		68.2	89.7	−50.6	−156.4	−162.5	−86.8	−162.0
		72.2	−155.5	136.4	−78.4	161.2	−60.5	77.7
					−80.9	−171.5	89.0	−178.2
					−76.1	167.0	−179.7	88.8

* Values for the two independent molecules.

each with retention of a trigonal-pyramidal $BiCl_3$ moiety within the confines of a half-sandwich structure, demonstrates that Bi^{III} can accommodate co-ordination of four to six oxygen atoms of a crown ether in an endodentate conformation. Presumably for **1** and **2** maximum Lewis acid (Bi^{III})-base (S-donor) interactions involving [12]aneS_4 and the larger and more flexible [15]aneS_5 respectively are realised by co-ordination of all available S atoms. It seems likely that the original exodentate conformers are involved in initial Bi^{III}–S bond formation followed by internal ligand rearrangements into the *endo* conformers as further S-co-ordination to the metal takes place. Attachment of sulfur atoms on one side only of a pyramidal $BiCl_3$ unit from more than one thiamacrocyclic ligand presumably causes unsatisfactory non-bonded S···S repulsions. Certainly for $BiCl_3$·[12]aneS_4 to adopt a structure similar to that of oligomeric $AlMe_3$·[12]aneS_4,[4] where the S atoms of the tetrathia ligand are exodentate and where trigonal-planar $AlMe_3$ units are stabilised by axial Al–S interactions involving two sulfur atoms from separate macrocyclic rings, would appear incompatible with a ψ-trigonal-pyramidal $BiCl_3$ unit.

Acknowledgements

We thank the SERC and the Cookson Group plc, Central Research Yarnton, Oxford for financial support.

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Received 22nd August 1991; *Paper* 1/04408G