

Crown Ether Complexes of Bi^{III}. Synthesis and Crystal and Molecular Structures of BiCl₃·12-Crown-4 and 2BiCl₃·18-Crown-6

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Crown ether complexes of bismuth(III) chloride of the types BiCl₃·12-crown-4 (**1**), 2BiCl₃·18-crown-6 (**2**), and BiCl₃·15-crown-5 (**3**) have been prepared; compound (**1**), and probably compound (**3**), is a neutral adduct with the pyramidal BiCl₃ linked to all four (five) oxygen atoms of the crown in a half-sandwich structure while compound (**2**) has the ionic formulation 2[BiCl₂·18-crown-6]⁺ [Bi₂Cl₈]²⁻, in which the bismuth cation is eight-co-ordinate involving all six oxygen atoms of the crown and two chlorine atoms in bicapped trigonal prismatic geometry.

The stratagem of incorporating a specific metal into the central cavity of a cyclic polyether, initiated by Pedersen¹ using alkali and alkaline earth cations, has been utilised over recent years to encapsulate a wide variety of metals, both as neutral and charged species. In addition to structural diversity² *e.g.* first sphere, second sphere, and sandwich complexation, the multi-chelating nature of these crown ethers allows a direct insight into the co-ordination vagaries and metal-oxygen bond characteristics of the metal in question. Bismuth(III), with a tendency to form cationic (and anionic) complexes and an ability to adopt high co-ordination geometries, presents intriguing possibilities as the metal acceptor in this context. The potential stereochemical activity of the formal lone pair of electrons associated with Bi^{III} is an added point of interest. The only previous structural study of a Group 5B halide-crown ether complex relates to SbCl₃·15-crown-5 in which a pyramidal SbCl₃ unit is bonded to the five oxygen atoms of the cyclic crown ether.³ A brief mention of a complex involving BiCl₃ and 18-crown-6 in a similar structure (unpublished work) is also included in the same report.

In this Communication we report the isolation of BiCl₃·12-

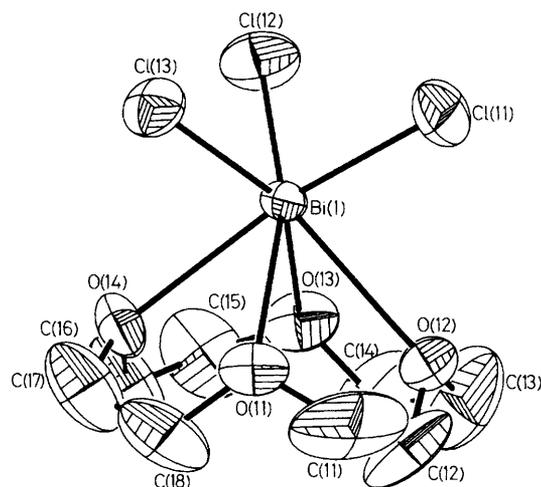


Figure 1. The BiCl₃·12-crown-4 complex. Principal distances and angles are: mean Bi–Cl 2.52(1), Bi–O 2.652(8)–2.742(9) Å; mean Cl–Bi–Cl 92.9(10), mean O–Bi–O(*trans*) 93.8(3)°.

crown-4 (1), $2\text{BiCl}_3 \cdot 18\text{-crown-6}$ (2), and $\text{BiCl}_3 \cdot 15\text{-crown-5}$ (3), and the X-ray crystal structure identification of (1) and (2).[†] Direct addition of an acetonitrile solution of the appropriate crown-ether (1 mol) to a chilled (0°C), stirred solution of BiCl_3 (1 mol) in acetonitrile provides a white microcrystalline slurry of the corresponding adduct[‡] following slow concentration of the solution. For (1), long prismatic crystals of diffraction quality were isolable directly from the resulting slurry. For (2), recrystallisation from acetonitrile/dichloromethane provided rectangular platelets.

In $\text{BiCl}_3 \cdot 12\text{-crown-4}$ (1) the bismuth atom is co-ordinated to the four oxygens of the crown giving a half-sandwich structure (Figure 1). The conformation of the ring approximates to C_4 symmetry with the four oxygens precisely coplanar; the maximum deviation from the mean plane through O(11)–O(12)–O(13)–O(14) is ± 0.001 Å. The Bi–O bond distances 2.652(8)–2.742(9) Å show no substantial variation though they are significantly longer than the 'expected' covalent distance (sum of covalent radii approximately 2.25 Å). The *trans* O–Bi–O angles and the Cl–Bi–Cl angles are all close to 90° leaving no substantial hole for lone pair occupancy. Thus the geometry would seem to argue for the absence of a stereochemically active bismuth lone pair. However, the BiCl_3 unit has very similar dimensions to those of the parent halide molecule which is normally considered to be ψ -tetrahedral

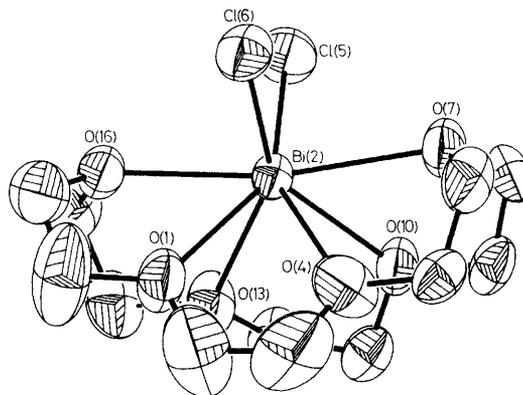


Figure 2. The $[\text{BiCl}_2 \cdot 18\text{-crown-6}]^+$ ion. Principal distances and angles are: mean Bi–Cl 2.501(6), Bi–O 2.49(1)–2.66(2) Å; Cl–Bi–Cl 91.0(2), O(1)–Bi(2)–O(10) 117.6(5), O(4)–Bi(2)–O(13) 101.4(6), O(7)–Bi(2)–O(16) 169.2(5)°.

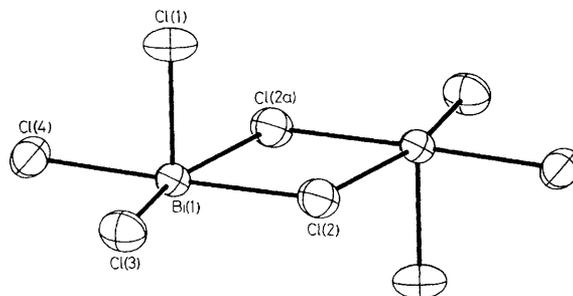


Figure 3. The $[\text{Bi}_2\text{Cl}_8]^{2-}$ ion. Distances are: Bi(1)–Cl(1) 2.500(6), Bi(1)–Cl(2) 2.787(6), Bi(1)–Cl(3) 2.506(6), Bi(1)–Cl(4) 2.701(6), Bi(1)–Cl(2a) 2.966(6) Å. Mean Cl(1)–Bi(1)–Cl angle 89.9°.

[†] Crystal data: (1); $\text{BiCl}_3 \cdot \text{C}_8\text{H}_{16}\text{O}_4$, $M = 491.5$, Monoclinic, $P2_1/c$, $a = 12.043(4)$, $b = 7.834(3)$, $c = 15.036(5)$ Å, $\beta = 90.31(3)^\circ$, $U = 1418.8(8)$ Å³, $Z = 4$, $D_c = 2.30$ g cm⁻³, Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 129.6$ cm⁻¹, $T = 290$ K, $R = 0.050$ for 2615 unique observed [$I/I_0 \geq 2.0$] reflections, $R_w = 0.062$. (2); $2[\text{C}_{12}\text{H}_{24}\text{O}_6\text{BiCl}_2]^+ [\text{Bi}_2\text{Cl}_8]^{2-}$, $M = 1790.0$, Triclinic, $P\bar{1}$, $a = 8.278(4)$, $b = 10.966(6)$, $c = 14.818(6)$ Å, $\alpha = 109.25(4)^\circ$, $\beta = 98.12(4)^\circ$, $\gamma = 103.68(4)^\circ$, $U = 1198(1)$ Å³, $Z = 1$, $D_c = 2.48$ g cm⁻³, Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 153.2$ cm⁻¹, $T = 290$ K, $R = 0.064$ for 3174 unique observed [$I/I_0 \geq 2.0$] reflections, $R_w = 0.084$. Data were collected with a Nicolet $P2_1$ four circle diffractometer in ω - 2θ mode. Maximum 2θ was 50° with scan range $\pm 1.1^\circ$ (2θ around the $K_{\alpha 1}$ – $K_{\alpha 2}$ angles, scan speed 4–29° min⁻¹, depending on the intensity of a 2s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections, and showed no changes during data collection for (1). For (2), a 10% decrease was compensated for by rescaling. Unit cell dimensions and standard deviations were obtained by least-squares fit to 15 high angle reflections. Reflections were processed using profile analysis. Those with [$I/I_0 \geq 2.0$] were considered observed and used in refinement; they were corrected for Lorentz, polarisation and absorption effects, the last by the Gaussian method. Maximum and minimum transmission factors were 0.24/0.09 (1) and 0.15/0.10 (2). Crystal dimensions were 0.26 × 0.51 × 0.15 mm (1) and 0.25 × 0.30 × 0.27 mm (2). Systematic absences: $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$ indicate space group $P2_1/c$ for (1); $P\bar{1}$ was assumed for (2). Heavy atoms were located by the Patterson interpretation section of SHELXTL and the light atoms then found on successive Fourier syntheses. Anisotropic temperature factors were used for all non-H atoms. Hydrogen atoms were given fixed isotropic temperature factors, $U = 0.07$ Å². They were inserted at calculated positions and not refined; final refinement was on F by least squares methods refining 161 (1) and 235 (2) parameters. Largest positive and negative peaks on a final difference Fourier synthesis were of height +3 and –4 el. Å⁻³ (all near Bi). Weighting schemes of the form $W = 1/[\sigma^2(F) + gF^2]$ with $g = 0.0057$ (1) and 0.0018 (2) were used and shown to be satisfactory by a weight analysis. Computing with SHELXTL PLUS⁸ on a DEC Microvax-II. Scattering factors in the analytical form and anomalous dispersion factors taken from reference 9. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] Satisfactory microanalytical data have been obtained for (1), (2), and (3).

with an active lone pair.⁴ It seems reasonable to conclude that if such a lone pair is present in (1), its spatial requirements are considerably less than would have been expected. It may be that this results from the compression exerted by the small and somewhat inflexible 12-crown-4-ring transmitted by the interaction of Bi with the lone pairs of the constituent oxygen atoms. We presume that $\text{BiCl}_3 \cdot 15\text{-crown-5}$ (3) has a similar half-sandwich structure.[§]

The 2:1 adduct (2) contains two $[\text{BiCl}_2 \cdot 18\text{-crown-6}]^+$ cations and a $[\text{Bi}_2\text{Cl}_8]^{2-}$ anion. In each cation the BiCl_2^+ unit is co-ordinated to all six of the crown oxygen atoms and the resulting eight-co-ordinate geometry approximates to a bicapped trigonal prism (Figure 2). To our knowledge, this is the first report of the structure of a discrete BiCl_2^+ complexed ion. Compared with (1) the Bi–O distances [2.49(1)–2.66(2) Å] are perceptibly shorter but, surprisingly, in view of the mono-charged BiCl_2^+ unit present, the Bi–Cl distances [mean 2.50(1) Å] are essentially the same. The third potential capping position of the prism points outwards through the centre of the crown ether ring and the large O–Bi–O angles across this position (mean 108°) strongly suggest a stereochemically active lone pair pointing in this direction. The 'wrap-around' encapsulation⁵ of the BiCl_2^+ unit results in severe distortion of the crown-6-ring (O–C–C–O torsional angles –9.3, –50.2, 55.6, –55.9, –47.6, 43.4°) away from the idealised D_{3d} point symmetry. In the absence of any long

[§] N. W. Alcock and G. R. Willey, X-ray crystal structure determination of (3) pending.

range cation-anion interactions it is unlikely that the $\text{Bi}_2\text{Cl}_8^{2-}$ counter-anion plays any part in the ring puckering.

The centrosymmetric $[\text{Bi}_2\text{Cl}_8]^{2-}$ anion (Figure 3) shows the same geometry as previously observed in $\text{Bi}_{12}\text{Cl}_{14}$,⁶ with two square-based pyramids sharing a basal edge. The lone pairs are clearly fully active giving a ψ -octahedral geometry around each bismuth centre. Surprisingly two of the terminal Bi-Cl distances [2.500(6), 2.506(6) Å] are identical to those in the cation, being substantially shorter than that linking the third terminal chlorine atom [2.701(6) Å]. As expected the Bi-Cl bonds in the rather unsymmetrical bridge [2.787(6), 2.966(6) Å] are significantly longer.⁷

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