Preparations and Structural Correlations for the Complexes of M^{III} Halides (M = As, Sb, Bi) with Crown Ethers: Structures of AsCl₃.12-Crown-4, AsCl₃.15-Crown-5, SbCl₃.12-Crown-4 and BiCl₃.15-Crown-5* and an Evaluation of Relative Binding Strengths for Crown Ligands

By Nathaniel W. Alcock,† Mythili Ravindran and Gerald R. Willey

Department of Chemistry, University of Warwick, Coventry CV4 7AL, England

Abstract

The preparations and structures of four new complexes are reported in the family of MCl₃.crown complexes (M = As, Sb, Bi; crown = 12-crown-4, 15-crown-5, 18-crown-6). The structures of the eight isolable members of the family are compared and trends established. The M—O bonding is much weaker than the M—Cl bonding, becoming stronger in the order Bi > Sb > As and 12-crown-4 > 15-crown-5 > 18-crown-6. The Cl—M—Cl angles are reduced compared to those in the free halides, but the M—Cl bonds are only slightly lengthened. The crown torsion angles show characteristic patterns involving *gauche* C—C bonds and alternating *gauche* and *anti* C—O bonds.

Introduction

Macrocyclic crown ethers can effectively bind metal ions and neutral metal species (M) either within their cavities using direct (M···O) bonding interactions or through second-sphere receptor-type interactions involving intermediate hydrogen bonding of the type [O$_{crown}$···H₂O···M] to hold the metal in place (*e.g.* Colquhoun, Stoddart & Williams, 1986; Bajaj & Poonia, 1988, and references therein) Our present interest in these multidentate O-donor ligands lies in their ability to ligate p-block metals, specifically the tervalent halides of Group 15 (MX_3, M = As, Sb, Bi). We have systematically examined the range and type of adduct formation using 12-crown-4, 15-crown-5 and 18-crown-6 as representative ligands with an optimal range of 4–6 donor atoms. The possibility that stereochemical activity of the lone pair of electrons associated with M^{III} can influence the resulting metal geometry and coordination number provided an added interest. Consideration of the nature and stereochemical role of lone pairs in these main-group elements has previously been

* 12-Crown-4 = 1,4,7,10-tetraoxacyclododecane; 15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane; 18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane.

† Author to whom correspondence should be addressed.

Table 1. *Complexes studied*

| | Ligand (L) | | |
	12-Crown-4	15-Crown-5	18-Crown-6
AsCl₃	1:1, complex (1)	1:1, complex (2)	No complex
SbCl₃	1:1, complex (3)	1:1, complex (4)ᵃ	1:1.MeCN, complex (5)ᵇ
BiCl₃	1:1, complex (6)ᶜ	1:1, complex (7)	1:1, complex (8)ᵈ
			1:1.H₂O, complex (9)ᵈ
			2[BiCl₂.L]⁺[Bi₂Cl₈]²⁻, complex (10)ᶜ

References: (a) Hough *et al.* (1987), (b) Alcock *et al.* (1990), (c) Alcock *et al.* (1989), (d) Drew *et al.* (1990).

addressed by Drew & Nicholson (1986) and Hough, Nicholson & Vasudevan (1989).

Of the nine compounds expected (Table 1), SbCl₃.15-crown-5 was the first to be isolated and characterized by X-ray crystallography (Hough, Nicholson & Vasudevan, 1987); it has all five O atoms bonded to a pyramidal SbCl₃ unit in a half-sandwich structure. BiCl₃.12-crown-4 has been shown to have a similar half-sandwich arrangement with the central bismuth atom coordinated symmetrically to the four (coplanar) O atoms of the crown (Alcock, Ravindran & Willey, 1989). Surprisingly, three compounds have been isolated from the BiCl₃.18-crown-6 system, (1) 2BiCl₃.18-crown-6 which is ionic and contains two [BiCl₂.18-crown-6]⁺ cations and the dinuclear anion [Bi₂Cl₈]²⁻ (Alcock *et al.*, 1989), (2) BiCl₃.18-crown-6.H₂O where, unusually, the Bi atom is positioned over one end of the O₆ cavity and bonded to only three of the crown O atoms together with the solvent (H₂O) molecule (Drew, Nicholson, Sylte & Vasudevan, 1990) and (3) BiCl₃.18-crown-6 in which the pyramidal BiCl₃ unit is symmetrically bonded to all six O atoms of the crown (Drew *et al.*, 1990). The adduct SbCl₃.18-crown-6.MeCN has a pyramidal SbCl₃ unit bonded to all six O atoms of the crown but with a clear displacement from a central location; here the solvent (MeCN) molecule plays no part in the metal coordination geometry but is simply trapped in the lattice (Alcock, Ravindran, Roe & Willey, 1990). SbCl₃.12-crown-4 has also been reported in a recent paper, but single crystals were not obtained and its structural characterization was based on the syn-

Table 2. *Unit-cell and crystallographic experimental conditions for* $MCl_3.crown$ *complexes*

	(1)	(2)	(3)	(7)
Formula	$C_8H_{16}O_4.AsCl_3$	$C_{10}H_{20}O_5.AsCl_3$	$C_8H_{16}O_4.SbCl_3$	$C_{10}H_{20}O_5.BiCl_3$
M_r	357.5	401.6	404.4	535.7
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$Pnma$	$P2_12_12_1$	Pa	$P2_12_12_1$
Reflection conditions	$hk0, h = 2n;$ $0kl, k + l = 2n$	$h00, h = 2n; 0k0,$ $k = 2n; 00l, l = 2n$	$h0l, h = 2n$	$h00, h = 2n; 0k0,$ $k = 2n; 00l, l = 2n$
a (Å)	14.936 (8)	7.731 (3)	14.988 (9)	7.692 (2)
b (Å)	11.876 (5)	12.815 (4)	7.938 (3)	13.285 (3)
c (Å)	7.864 (4)	16.011 (6)	12.022 (9)	15.939 (4)
β (°)			90.49 (5)	
U (Å³)	1395	1586	1430	1628
Z	4	4	4	4
D_x (Mg m⁻³)	1.70	1.68	1.88	2.19
Reflection range for cell (° 2θ)	20–22	28–30	19–21	23–26
Maximum angle (° 2θ)	50	50	45	55
Index ranges	0–10; 0–15; 0–18	0–9; −15–15; 0–19	0–16; 0–8; −12–12	−10–10; 0–16; −17–17
μ(Mo $K\alpha$) (mm⁻¹)	3.00	2.66	2.50	11.30
Crystal size (mm)	0.80 × 0.37 × 0.78	0.11 × 0.29 × 0.67	0.15 × 0.48 × 0.24	0.23 × 0.11 × 0.25
Transmission-factor range	0.21–0.43	0.45–0.70	0.69–0.84	0.22–0.44
Total No. of reflections	1454	2359	1943	7742
Unique reflections	1300	2289	1869	3743
Reflections with $I/\sigma(I) > 2.0$	1138	1960	1327	3190
R_{int}	—	0.039	0.048	0.069
Parameters refined	76	173	208	173
Weight parameters (g)	0.0030	0.00072	0.0019	0.00078
Shift/σ (last cycle)	0.12	.01	0.07	0.65
ΔF maximum peak (e Å⁻³)	0.9/−0.8	0.5/−0.5	1.9/−1.1	3.5/−3.3
Final R	0.071	0.031	0.058	0.043
Final wR	0.087	0.034	0.063	0.043
S (g.o.f.)	2.07	1.04	1.42	1.22

chrotron X-ray absorption analysis of a polycrystal-line sample (Beagley, Endregard & Nicholson, 1991).

We now report the isolation and X-ray crystal structural characterization of four of the remaining complexes of the series, including the previously elusive SbCl₃.12-crown-4, and discuss the structural correlations between the whole group. The anomalous complexes of BiCl₃ with 18-crown-6 [(9), (10)] are compared separately with the main series.

Experimental

All manipulations were carried out under a dinitrogen atmosphere with the use of standard vacuum line and Schlenk techniques. Solvents were stored over CaH₂ and freshly distilled under dinitrogen as required. MCl_3 (M = As, Sb, Bi) were purchased from Aldrich and used as received. 12-Crown-4 and 15-crown-5 (Lancaster Synthesis Ltd) were stored over preheated (523 K) molecular sieves.

The previously unreported compounds (1), (2), (3) and (7) were all obtained as white solids following direct equimolar addition of the appropriate crown ether and metal trihalide in acetonitrile solution. Removal of the solvent under vacuum, followed by recrystallization from acetonitrile/CH₂Cl₂ produced colourless crystals suitable for X-ray analysis. A typical preparation was as follows.

AsCl₃.12-*crown*-4 (1)

12-Crown-4 (1.09 g, 6.2 mmol) in acetonitrile (20 cm³) was added dropwise to a chilled (273 K) solution of AsCl₃ (1.12 g, 6.2 mmol) in acetonitrile

(20 cm³) and the resulting solution was stirred at room temperature for 24 h. Removal of solvent gave a white semi-crystalline solid which was washed with benzene (3 × 10 cm³) and *n*-hexane (3 × 10 cm³). Recrystallization from CH₃CN–CH₂Cl₂ provided colourless needle crystals of the product directly suitable for X-ray diffraction studies. Yield 1.3 g, 61%. (Found: C, 27.0; H, 4.5; Cl, 29.0%; C₈-H₁₆O₄.AsCl₃ requires C, 26.9; H, 4.5; Cl 29.8%); ν_{max}(AsCl) 367, 327 cm⁻¹ (Nujol); δ(CDCl₃) 3.74 [16H, *s*, —CH₂—(crown)].

AsCl₃.15-*crown*-5 (2)

AsCl₃ (1.08 g, 5.95 mmol), 15-crown-5 (1.33 g, 6.04 mmol). Yield 1.6 g, 67%. (Found: C, 30.1; H, 5.0; Cl, 26.3%; C₁₀H₂₀O₅.AsCl₃ requires C, 29.9; H, 5.0; Cl 26.5%); ν_{max}(AsCl) 380, 335 cm⁻¹ (Nujol); δ(CDCl₃) 3.73 [20H, *s*, —CH₂—(crown)].

SbCl₃.12-*crown*-4 (3)

SbCl₃ (2.1 g, 9.21 mmol), 12-crown-4 (1.63 g, 9.30 mmol). Yield 2.6 g, 69%. (Found: C, 23.9; H, 4.1; Cl, 26.4%; C₈H₁₆O₄.SbCl₃ requires C, 23.8; H, 4.0; Cl, 26.3%); ν_{max}(SbCl) 322, 290, 268 cm⁻¹ (Nujol); δ(CDCl₃) 3.75 [16H, *s*, —CH₂—(crown)].

BiCl₃.15-*crown*-5 (7)

BiCl₃ (2.38 g, 7.55 mmol), 15-crown-5 (1.66 g, 7.60 mmol). Yield 3.4 g, 84%. (Found: C, 22.5; H, 3.8; Cl, 20.1%; C₁₀H₂₀O₅.BiCl₃ requires C, 22.4; H, 3.8; Cl, 19.9%); ν_{max}(BiCl) 280, 245 cm⁻¹ (Nujol); δ(CD₃CN) 3.83 [20H, *s*, —CH₂—(crown)].

Table 3. *Atom coordinates* ($\times 10^4$) *and isotropic thermal parameters* ($\text{Å}^2 \times 10^3$)

	x	y	z	U
Complex (1)				
As(1)	8702.7 (6)	2500.0	2166.8 (13)	42 (1)*
Cl(1)	9443 (2)	3880 (2)	946 (3)	80 (1)*
Cl(2)	7591 (2)	2500	289 (4)	70 (1)*
O(1)	7568 (5)	1294 (6)	4288 (9)	84 (3)*
O(2)	9406 (5)	1268 (7)	5081 (10)	96 (3)*
C(1a)	7022 (13)	1842 (16)	5432 (23)	83 (6)†
C(1b)	6807 (11)	2050 (13)	4580 (26)	75 (5)†
C(2a)	8135 (14)	442 (17)	5021 (30)	93 (6)†
C(2b)	7801 (12)	762 (20)	5778 (24)	86 (6)†
C(3a)	8868 (12)	781 (21)	6204 (25)	83 (6)†
C(3b)	8747 (11)	452 (16)	5395 (33)	80 (6)†
C(4a)	10078 (14)	2148 (15)	5682 (31)	98 (7)†
C(4b)	9703 (17)	1829 (19)	6512 (24)	112 (8)†
Complex (2)				
As(1)	2344.2 (6)	4974.0 (4)	6252.7 (3)	37 (1)*
Cl(1)	980.8 (20)	3803.4 (9)	7022.3 (10)	55 (1)*
Cl(2)	289.6 (16)	5012.7 (11)	5286.5 (7)	54 (1)*
Cl(3)	1375.2 (19)	6357.4 (9)	6921.0 (10)	53 (1)*
O(1)	4230 (5)	6338 (2)	5025 (2)	48 (1)*
O(2)	4015 (5)	4124 (2)	4672 (2)	50 (1)*
O(3)	4869 (5)	3150 (3)	6229 (2)	54 (1)*
O(4)	4815 (5)	4620 (3)	7623 (2)	55 (1)*
O(5)	5575 (5)	6388 (2)	6665 (2)	48 (1)*
C(1)	5163 (8)	5855 (4)	4379 (3)	57 (2)*
C(2)	4179 (8)	4922 (4)	4069 (3)	56 (2)*
C(3)	5513 (8)	3507 (4)	4756 (3)	58 (2)*
C(4)	5189 (8)	2723 (3)	5435 (3)	58 (2)*
C(5)	6343 (8)	3533 (4)	6619 (4)	63 (2)*
C(6)	5984 (9)	3771 (4)	7508 (4)	66 (2)*
C(7)	5557 (8)	5537 (4)	7952 (3)	54 (2)*
C(8)	6653 (7)	6110 (4)	7339 (3)	55 (2)*
C(9)	6445 (8)	6927 (4)	6008 (3)	51 (2)*
C(10)	5096 (8)	7215 (3)	5376 (3)	56 (23)*
Complex (3)				
Sb(1)	1152	−72 (3)	2473	32 (1)*
Sb(2)	8845.8 (11)	4911.5 (31)	7521.9 (17)	41 (1)*
Cl(11)	−85 (9)	−2221 (13)	2470 (14)	71 (3)*
Cl(12)	1966 (8)	−1608 (12)	3879 (10)	66 (3)*
Cl(13)	1906 (9)	−1422 (16)	975 (10)	66 (3)*
Cl(21)	9995 (8)	2957 (13)	7635 (11)	60 (3)*
Cl(22)	8072 (12)	3443 (18)	6095 (15)	113 (5)*
Cl(23)	8085 (12)	3538 (16)	9054 (14)	95 (4)*
O(11)	54 (14)	1953 (21)	3655 (14)	35 (4)*
O(12)	1833 (28)	2564 (45)	3854 (25)	108 (6)*
O(13)	1895 (23)	2987 (34)	1515 (27)	99 (6)*
O(14)	20 (17)	1975 (22)	1334 (21)	47 (5)*
C(11)	454 (23)	2667 (41)	4692 (26)	64 (7)
C(12)	1266 (23)	3637 (39)	4334 (28)	64 (7)
C(13)	2514 (21)	3408 (36)	3192 (26)	52 (6)
C(14)	2418 (27)	3742 (43)	2257 (30)	76 (8)
C(15)	1213 (35)	3740 (61)	755 (39)	119 (10)
C(16)	385 (20)	3514 (33)	865 (23)	48 (6)
C(17)	−605 (39)	2660 (66)	2016 (44)	131 (10)
C(18)	−541 (27)	3154 (42)	3059 (32)	82 (8)
O(21)	9934 (23)	7146 (48)	8742 (32)	115 (6)*
O(22)	10106 (26)	6946 (54)	6202 (39)	162 (6)*
O(23)	8184 (16)	7758 (24)	6326 (22)	59 (5)*
O(24)	8130 (18)	7683 (24)	8726 (25)	73 (5)*
C(21)	10797 (25)	7227 (43)	8066 (30)	64 (7)
C(22)	10753 (33)	7431 (52)	7013 (36)	96 (9)
C(23)	9768 (36)	8140 (57)	5671 (41)	128 (10)
C(24)	8891 (54)	8294 (76)	5673 (55)	207 (11)
C(25)	7868 (35)	8988 (59)	6820 (37)	113 (9)
C(26)	7936 (26)	9235 (42)	8071 (29)	73 (8)
C(27)	8618 (28)	8199 (43)	9569 (31)	76 (8)
C(28)	9602 (63)	8009 (82)	9544 (60)	231 (11)
Complex (7)				
Bi	7568.5 (4)	75.6 (2)	6099.1 (2)	32 (1)*
Cl(1)	5149 (4)	10 (3)	5028 (2)	61 (1)*
Cl(2)	5732 (4)	1310 (2)	6929 (2)	49 (1)*
Cl(3)	6283 (4)	−1351 (2)	6931 (2)	55 (1)*
O(1)	8902 (11)	1941 (6)	5646 (6)	62 (3)*
O(2)	9966 (11)	997 (7)	7186 (6)	66 (3)*
O(3)	10618 (10)	−998 (6)	6716 (7)	65 (3)*
O(4)	9001 (11)	−1556 (7)	5191 (7)	67 (4)*
O(5)	9569 (13)	348 (8)	4625 (6)	75 (4)*
C(1)	9612 (23)	2466 (9)	6350 (10)	77 (6)*
C(2)	10914 (19)	1856 (10)	6808 (12)	88 (7)*
C(3)	11081 (17)	359 (12)	7622 (10)	82 (6)*
C(4)	11905 (15)	−409 (10)	7092 (10)	70 (5)*
C(5)	11371 (18)	−1782 (10)	6238 (11)	75 (6)*

Table 3 (*cont.*)

	x	y	z	U
C(6)	9873 (19)	−2245 (10)	5732 (12)	86 (7)*
C(7)	10005 (21)	−1364 (13)	4416 (10)	89 (7)*
C(8)	9280 (20)	−445 (12)	4067 (9)	77 (6)*
C(9)	9450 (20)	1312 (11)	4305 (9)	76 (6)*
C(10)	10033 (21)	2042 (11)	4921 (9)	82 (6)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

† All C atoms have 0.5 occupancy.

Crystal data and refinement conditions are given in Table 2, and specific details are noted below. Data were collected with a Nicolet $P2_1$ four-circle diffractometer in ω–2θ mode, with variable scan speed, 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. Three standard reflections were monitored every 200 reflections and (where noted below) the data were rescaled to correct for decay. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections. Reflections were processed using profile analysis and those with $I/\sigma(I) \geq 2.0$ were considered observed and used in refinement. They were corrected for Lorentz, polarization and absorption effects (by the Gaussian method).

Generally, 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 normally used for all non-H atoms, and H atoms were given fixed isotropic temperature factors, $U = 0.08 \, \text{Å}^2$, inserted at calculated positions and not refined. Final refinement was on F by least-squares methods, with a weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$. This was shown to be satisfactory by a weight analysis. Computing was with *SHELXTL-Plus* (Sheldrick, 1986) on a DEC MicroVAX II. Scattering factors in the analytical form and anomalous dispersion factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final atomic coordinates are given in Table 3, and selected bond lengths and angles in Table 4.*

For (1), the absences are consistent with space groups $Pnma$ or $Pn2_1a$ (non-standard setting of $Pna2_1$). A solution was obtained in $Pnma$, with the complex lying across a crystallographic mirror plane [position $4(c)$]. Refinement converged at $R = 0.061$, but the final structure contained anomalous bond lengths in the crown ether (notable C—C across the mirror plane of 1.16–1.30 Å), and the anisotropy of

Table 4. *Selected bond lengths (Å) and angles (°)*

Complex (1)

As(1)—Cl(1)	2.198 (3)	As(1)—Cl(2)	2.222 (3)
As(1)—O(1)	2.776 (6)	As(1)—O(2)	2.915 (6)
Cl(1)—As(1)—Cl(2)	94.9 (1)	Cl(1)—As(1)—Cl(1a')	96.5 (1)
Cl(2)—As(1)—Cl(1a')	94.9 (1)	O(1)—As(1)—O(2)	90.4 (4)
O(1)—As(1)—O(1a')	62.1 (4)	O(1)—As(1)—O(2a')	59.2 (4)
O(2)—As(1)—O(2a')	60.2 (4)		

Complex (2)

As(1)—Cl(1)	2.209 (2)	As(1)—Cl(2)	2.218 (2)
As(1)—Cl(3)	2.202 (2)	As(1)—O(1)	3.008 (4)
As(1)—O(2)	3.043 (4)	As(1)—O(3)	3.046 (4)
As(1)—O(4)	2.944 (4)	As(1)—O(5)	3.156 (4)
Cl(1)—As(1)—Cl(2)	93.6 (1)	Cl(1)—As(1)—Cl(3)	96.5 (1)
Cl(2)—As(1)—Cl(3)	94.4 (1)	O(1)—As(1)—O(2)	57.2 (1)
O(1)—As(1)—O(3)	97.3 (1)	O(2)—As(1)—O(3)	56.1 (1)
O(1)—As(1)—O(4)	105.2 (1)	O(2)—As(1)—O(4)	106.8 (1)
O(3)—As(1)—O(4)	58.3 (1)	O(1)—As(1)—O(5)	54.5 (1)
O(2)—As(1)—O(5)	92.5 (1)	O(3)—As(1)—O(5)	86.3 (1)
O(4)—As(1)—O(5)	54.5 (1)		

Complex (3)

Sb(1)—Cl(11)	2.519 (12)	Sb(1)—Cl(12)	2.407 (11)
Sb(1)—Cl(13)	2.389 (13)	Sb(1)—O(11)	2.710 (18)
Sb(1)—O(12)	2.854 (35)	Sb(1)—O(13)	2.914 (29)
Sb(1)—O(14)	2.712 (23)		
Sb(2)—Cl(21)	2.322 (12)		
Sb(2)—Cl(22)	2.369 (18)	Sb(2)—Cl(23)	2.432 (17)
Sb(2)—O(21)	2.814 (37)	Sb(2)—O(22)	2.958 (43)
Sb(2)—O(23)	2.852 (22)	Sb(2)—O(24)	2.848 (24)
Cl(11)—Sb(1)—Cl(12)	91.5 (4)	Cl(11)—Sb(1)—Cl(13)	92.7 (5)
Cl(12)—Sb(1)—Cl(13)	93.5 (4)	O(11)—Sb(1)—o(12)	58.4 (9)
O(11)—Sb(1)—O(13)	87.1 (7)	O(12)—Sb(1)—O(13)	58.9 (9)
O(11)—Sb(1)—O(14)	61.9 (6)	O(12)—Sb(1)—O(14)	94.2 (9)
O(13)—Sb(1)—O(14)	62.7 (8)		
Cl(21)—Sb(2)—Cl(22)	94.2 (5)	Cl(21)—Sb(2)—Cl(23)	90.5 (5)
Cl(22)—Sb(2)—Cl(23)	95.6 (6)	O(21)—Sb(2)—O(22)	64.2 (12)
O(21)—Sb(2)—O(23)	87.8 (9)	O(22)—Sb(2)—O(23)	61.2 (9)
O(21)—Sb(2)—O(24)	57.8 (9)	O(22)—Sb(2)—O(24)	95.5 (10)
O(23)—Sb(2)—O(24)	60.9 (8)		

Complex (7)

Bi—Cl(1)	2.527 (3)	Bi—Cl(2)	2.537 (3)
Bi—Cl(3)	2.515 (3)	Bi—O(1)	2.778 (8)
Bi—O(2)	2.811 (9)	Bi—O(3)	2.916 (8)
Bi—O(4)	2.830 (9)	Bi—O(5)	2.832 (9)
Cl(1)—Bi—Cl(2)	88.0 (1)	Cl(1)—Bi—Cl(3)	92.3 (1)
Cl(2)—Bi—Cl(3)	89.6 (1)	O(1)—Bi—O(2)	61.9 (3)
O(1)—Bi—O(3)	103.1 (2)	O(2)—Bi—O(3)	58.5 (2)
O(1)—Bi—O(4)	114.0 (3)	O(2)—Bi—O(4)	113.2 (3)
O(3)—Bi—O(4)	59.0 (3)	O(1)—Bi—o(5)	57.9 (3)
O(2)—Bi—O(5)	95.7 (3)	O(3)—Bi—O(5)	84.6 (3)
O(4)—Bi—O(5)	57.5 (3)		

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Table 5. *Comparative dimensions of MCl_3.crown complexes (mean values in Å and °)*

	$AsCl_3$	$AsCl_3$.-12-crown-4	$AsCl_3$.-15-crown-5
M—Cl	2.168	2.206	2.210
Cl—M—Cl	97.6	95.4	94.9
M—O		2.78–2.92	2.94–3.16
O-atom mean plane			
Maximum deviation of O		0.0	0.34
Deviation of M		2.00	1.85

	$SbCl_3$	$SbCl_3$.-12-crown-4	$SbCl_3$.-15-crown-5	$SbCl_3$.-18-crown-6
M—Cl	2.359	2.406	2.416	2.38
Cl—M—Cl	94.1	92.8	90.8	90.2
M—O		2.71–2.96	2.79–3.00	2.99–3.40
O-atom mean plane				
Maximum deviation of O		0.48/0.07	0.37	0.32
Deviation of M		2.00/1.95	1.65	1.60

	$BiCl_3$	$BiCl_3$.-12-crown-4	$BiCl_3$.-15-crown-5	$BiCl_3$.-18-crown-6
M—Cl	2.499	2.52	2.53	2.50
Cl—M—Cl	90.8	92.9	89.8	88.1
M—O		2.65–2.74	2.78–2.92	2.84–3.16
O-atom mean plane				
Maximum deviation of O		0.00	0.43	0.50
Deviation of M		1.84	1.61	1.45

the thermal parameters was extreme. Attempted refinement of an ordered molecule in $Pn2_1a$ did not converge satisfactorily [a typical experience with such problems, *e.g.* Marsh (1990)]. However, a satisfactory disordered centrosymmetric model was obtained, in which *each* C atom is disordered between two positions; these atoms were refined isotropically and H atoms were not included (which accounts for the rather higher R value in this refinement). Convergence was achieved by applying constraints (using *DFIX*) to all C—C and all C—O bonds [1.50 (2) and 1.41 (2) Å, respectively]. A unique molecule with acceptable bond and torsion angles could be traced in the mirror-imposed double image in the crystal structure, and this is shown for (1) in Fig. 1(*a*).

Crystals of (2) are moisture sensitive and were mounted in a Lindemann glass capillary. The struc-

ture was solved by direct methods (*TREF*), revealing the $AsCl_3$ unit, and light atoms were found from Fourier syntheses. The absolute structure of the individual crystal chosen was checked by refinement of a $\delta f''$ multiplier.

During a first data collection for (3), the check intensity decayed substantially; the collection was therefore repeated rapidly with $2\theta_{max}$ of 45°, which limited the decomposition to 5% overall. The systematic extinction conditions were apparently $h0l$, $h = 2n$; $0k0$, $k = 2n$, indicating space group $P2_1/a$. A Patterson synthesis in this space group located the Sb atom, and three Cl atoms were added from a Fourier synthesis. Refinement gave $R = 0.20$, but a further Fourier showed no indication of the ligand, while the Cl atoms had thermal parameters $U = 0.10$. These problems suggested possible pseudo-symmetry. The sub-groups $P2_1$ and Pa were both investigated, starting from the $SbCl_3$ unit already found, with the pseudo-symmetry-generated Sb atom. $P2_1$ produced no improvement, but in Pa refinement reduced the R factor and further Fourier syntheses revealed the remaining atoms. Refinement with isotropic light atoms converged at $R = 0.065$, but with anisotropic thermal parameters several atoms became non-positive-definite. This, and the high thermal parameters of some atoms, suggests the presence of disorder. Attempts to model this using partial occupancy positions were not successful, and in the final refinement only Sb, Cl and O atoms were refined anisotropically. The absolute structure of the individual crystal chosen was checked by refinement of a $\delta f''$ multiplier, which refined to 1.5 (8), giving a weak indication that the hand was chosen correctly. The x and z coordinates of Sb(1) were fixed to define

the origin. The two independent molecules are essentially identical, though the crown dimensions differ.

For compound (7), the check reflection intensity increased by 15% during data collection perhaps with increasing crystal mosaicity (during two separate data collections on different crystals). Because of uncertainty about the space group, a full triclinic data set was collected; however, the systematic absences indicate space group $P2_12_12_1$, which was shown to be correct by the satisfactory refinement. The Bi atom was readily located, but full structure solution was relatively difficult because of the pseudo-symmetry caused by its y coordinate being close to zero; reflections with k odd were systematically weak (mean intensity 0.2 of those with k even). The absolute structure of the chosen individual crystal was examined by refinement of a $\delta f''$ multiplier, but the refined value [0.15 (2)] indicates that the crystal was an inversion twin.

Discussion

The eight complexes [(1)–(8)] show closely similar basic structures (Fig. 1). The MCl_3 units retain the pyramidal geometry of the parent halides (M = As, Galy & Enjalbert, 1982; M = Sb, Lipka, 1979; M = Bi, Nyburg, Ozin & Szymański, 1971, 1972). The crowns form puckered rings, so that the oxygen lone pairs are all directed towards the central atom (endodentate), and the O atoms are essentially coplanar, with deviations ranging up to ±0.5 Å; they are precisely coplanar in (1) and (6). The M atoms deviate from the mean oxygen planes by 1.4–2.0 Å, and it is apparent that they move closer to the plane as the ring size increases, i.e. the M atoms tend to move into the centre of the crown. The mean dimensions (summarized in Table 5) show a number of significant features. Most notably the M—O distances are exceptionally long, ranging from 0.6 to 0.9 Å longer than the M—Cl bonds for As, to 0.1–0.4 Å in the case of Bi. Taking into account the difference in the covalent radii for Cl and O (ca 0.4 Å), these interactions are clearly very weak. Bond-valence calculations using the parameters of Brown & Altermatt (1985) for M^{3+} and O^{2-} indicate bond orders ranging between 0.05 for As and 0.2 for Bi; although these parameters are clearly not entirely appropriate, the general weakness of these bonds is fully confirmed. The bond-valence model also fits with the evidence for weakening M—O bonds in the sequence 12-crown-4 to 18-crown-6, as the number of interacting O atoms increases. The slight lengthening of the M—Cl bonds that accompanies the formation of M—O interactions is also consistent with this model; the M—Cl bonds in the 15-crown-5 adducts are longer than those with 12-crown-4, as might be expected, but the correlation appears not to

extend to the 18-crown-6 adducts, possibly because of the limited precision of these values. The irregularity of the O-atom coordination in these complexes is also noticeable, particularly with the larger rings. It is clear that the large hole size relative to the metal size, and their steric constraints limit the ability of the crown ethers to coordinate to the Group 15 halides.

The effect of complexation on the Cl—M—Cl angle is clearer. This decreases systematically as the size of the ligand increases, no doubt due to its steric effect. The angles in all the complexes are smaller than those in the free halides apart from the case of $BiCl_3$, where the Bi···Cl interactions already present in the solid chloride presumably have the same steric effect as the Bi···O interactions. It is also noticeable that the lengthening of the M—Cl bonds on complexation is least for Bi.

It follows from these correlations that the complex between $AsCl_3$ and 18-crown-6 should show the weakest interaction. Although no such complex has been isolated in pure form, a solid is produced on removing solvent from a solution of the halide and the crown ether in acetonitrile. Its infrared spectrum shows shifts in the As—Cl stretching frequencies indicative of complex formation, but on recrystallization from acetonitrile/CH_2Cl_2, the product obtained is the bis(acetontrile) adduct of 18-crown-6 (Garrell, Smyth, Fronczek & Gandour, 1988), rather than the desired complex.

Torsion angles

The torsion angles of the ligands show characteristic patterns; Table 6 compares the values for the 15-crown-5 complexes, for which a complete set of structures is available, unaffected by disorder. The As and Sb complexes are closely similar, with gauche C—C bonds, and alternating gauche and anti C—O bonds. These have the effect of pointing the oxygen

Table 6. *Comparative ring torsion angles for MCl_3.15-crown-5 complexes* (°)

Each sequence starts from the atom numbered O(1) and proceeds in the direction of increasing atom number; angle e.s.d. approximately 0.5°.

Type	AsCl₃-15-crown-5		SbCl₃-15-crown-5		BiCl₃-15-crown-5	
O—C	O(1)	178	O(1)	-179	O(1)	-84
C—C		-65		65		-67
C—O	O(2)	-79	O(4)	80	O(2)	179
O—C	O(2)	178	O(4)	179	O(2)	-86
C—C		-62		61		-59
C—O	O(3)	-57	O(7)	75	O(3)	-177
O—C	O(3)	-169	O(7)	165	O(3)	-170
C—C		-67		72		59
C—O	O(4)	-110	O(10)	107	O(4)	78
O—C	O(4)	73	O(10)	-80	O(4)	-163
C—C		61		-58		64
C—O	O(5)	-176	O(13)	-177	O(5)	161
O—C	O(5)	-177	O(13)	175	O(5)	-172
C—C		-61		58		-61
C—O	O(1)	-81	O(1)	81	O(1)	167

lone pairs towards the central atom. One all-*anti* O atom, and an adjacent almost eclipsed C—C—O—C bond (torsion angle 107–110°) are probably needed for ring closure. Remarkably, though BiCl₃.15-crown-5 is isomorphous with the As and Sb complexes, its torsion angles show a different pattern, with two *anti* O atoms. These have the effect of placing the C—O—C plane of O(5) almost in the
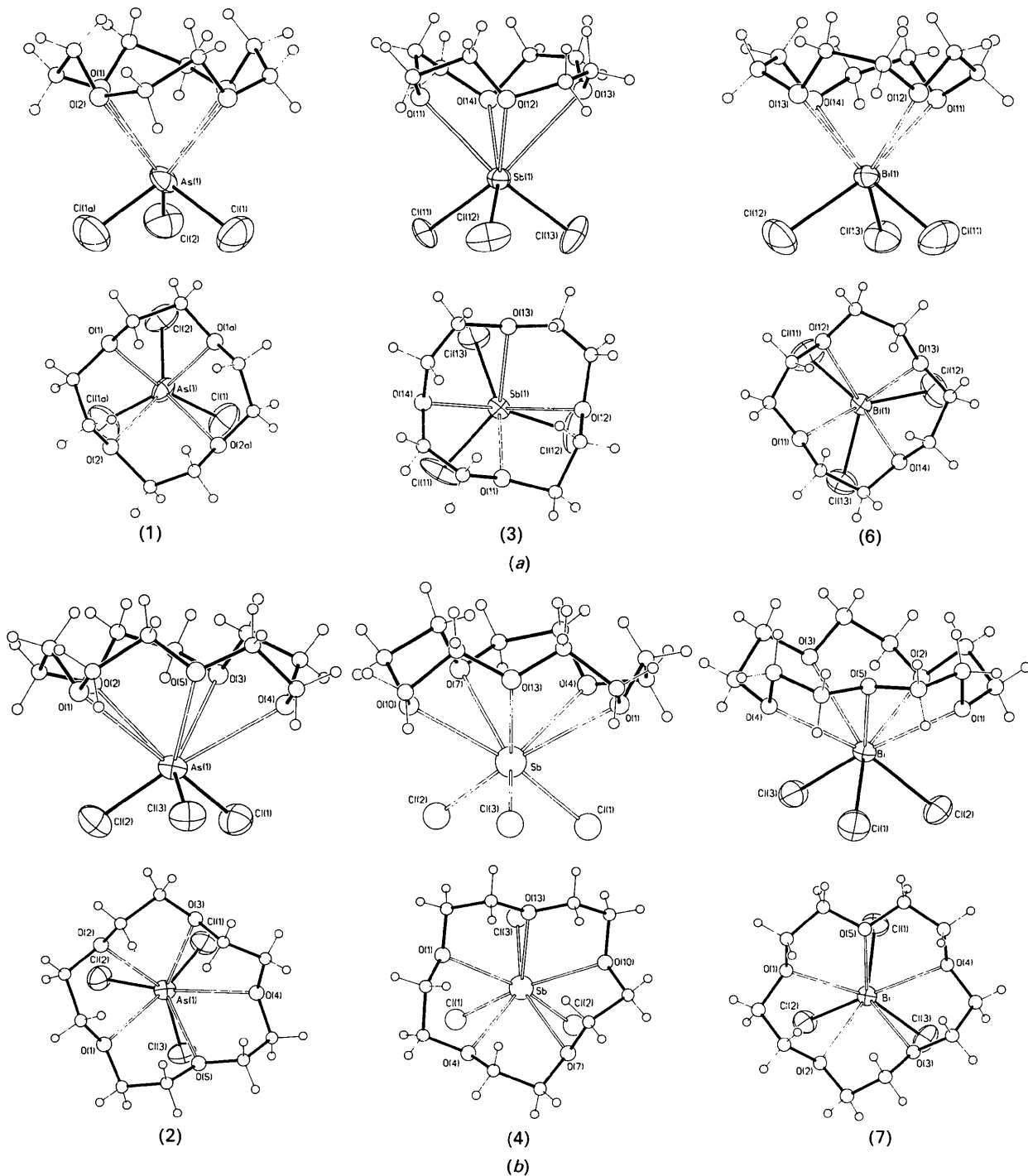

(1) (3) (6)

(a)

(2) (4) (7)

(b)

Fig. 1. Comparative top and side views of the eight MCl₃.crown complexes: (a) Complexes with 12-crown-4. (1) AsCl₃ complex, (3) SbCl₃ complex, (6) BiCl₃ complex (Alcock *et al.*, 1989). (b) Complexes with 15-crown-5. (2) AsCl₃ complex, (4) SbCl₃ complex (Hough *et al.*, 1987). (7) BiCl₃ complex.

ring plane, rather than pointing downwards towards the central Bi atom; the O atoms are also further from coplanarity than in the other complexes. These effects are presumably caused by the large size of Bi imposing different requirements on the ligand atoms. The ring C—C distances show indications of the 'macrocyclic shortening' that has frequently been reported for crown ethers (Adam et al., 1990; Luger et al., 1992). However, the relatively imprecise values obtained in the presence of the heavy MCl$_3$ units makes the present structures unsuitable for any detailed discussion.

Anomalous BiCl$_3$ complexes

The interaction between 18-crown-6 and the [BiCl$_2$]$^+$ ion (Alcock et al., 1989) [(10), Fig. 2] has a significantly different character from that in the neutral complex with BiCl$_3$. Although the Bi—Cl distance is little altered [2.501 (6) Å], the Bi—O distances are considerably shorter [2.49 (1)–2.66 (1) Å]; this is clearly a result of the enhanced attraction by the cation. The coordination geometry approximates to a bicapped trigonal prism, with the crown ether wrapped much more thoroughly around the bismuth than in (8). The crystals produced by the interaction of BiCl$_3$ with 18-crown-6 (Drew et al., 1990) contain the standard half-sandwich molecule already described (8), accompanied by a hydrated complex (9) in which the BiCl$_3$ is coordinated by three O atoms of the 18-crown-6 ligand and one water molecule. The latter has an exceptionally strong

O(water)—Bi interaction (2.51 Å), but the O(crown)—Bi distances are close to the range found in the other Bi–crown complexes.

EXAFS results

It is of interest to compare the crystallographic data reported here for SbCl$_3$.12-crown-4 with the EXAFS results (Beagley et al., 1991). These results indicated that the 12-crown-4 complex was almost indistinguishable in structure from that with 15-crown-5; mean Sb—Cl and Sb—O distances of 2.41 (1) and 2.85 (2) Å, respectively, were obtained. These agree with our crystallographic results, both qualitatively and quantitatively, though the gas-phase determination does not show the observed range of Sb—O distances. This variation is almost certainly present even in the gas phase, because of the different positioning of each Sb—O bond in relation to the Sb—Cl bonds. However, the information content of the EXAFS data is not great enough to identify it (other than perhaps as a slight broadening of the Sb—O peak).

Lone-pair effects

The new crystal structures confirm the previous conclusions, that the effect of the lone pair is to leave the geometry of the MCl$_3$ unit essentially unchanged following coordination of the crown ether. The complexes are still ψ-tetrahedral, although the Cl—M—Cl angles (already small) are further
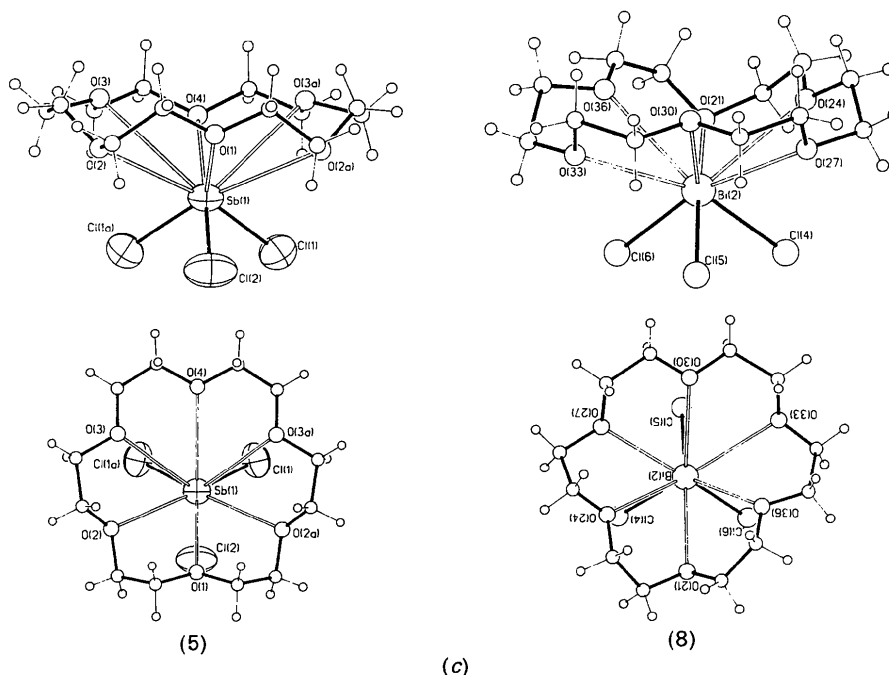

(5)   (8)

(c)

Fig. 1 (cont.) (c) Complexes with 18-crown-6. (5) SbCl$_3$ complex (Alcock et al., 1990), (8) BiCl$_3$ complex (Drew et al., 1990).

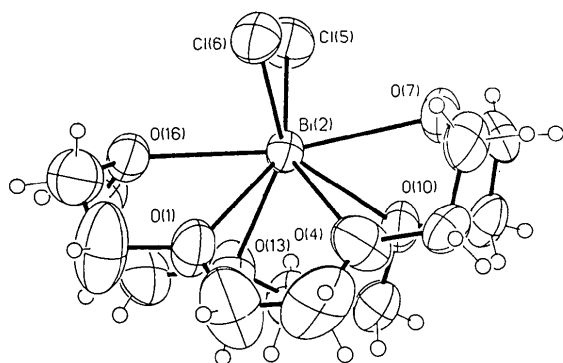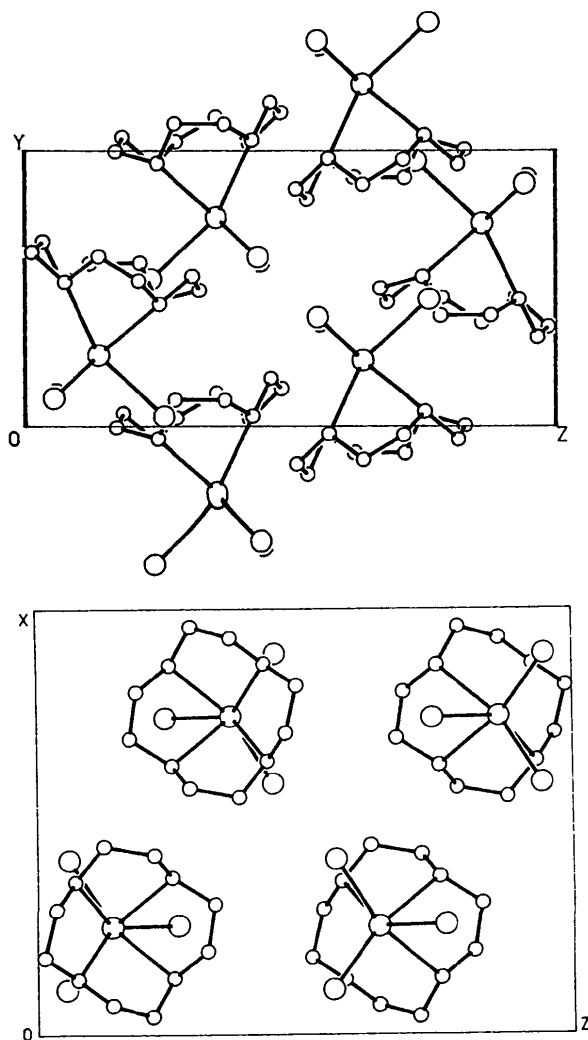Fig. 2. Side view of the [BiCl₂.18-crown-6]⁺ cation (10) (Alcock *et al.*, 1989).

Fig. 3. Packing diagrams viewed down **a** and **b** for BiCl₃.12-crown-4 (6), showing the filling of the short dimension of the cell by the complexes.

reduced on coordination. The only exception to this pattern is the [BiCl₂]⁺ complex, as discussed in Alcock *et al.* (1989); here, the lone pair must point towards the vacant capping position of the trigonal prism, still through the centre of the crown.

Packing

Despite the general similarity of the complexes, only the three 15-crown-5 complexes are crystallographically isomorphous (in space group *P*2₁2₁2₁). Several of the other complexes show similar unit cells to these, with four molecules in cells of approximate dimensions 7.8 × 12 × 15 Å. These are determined by the molecular packing, with the shortest dimension corresponding to the height (including van der Waals contact distances) from the crown ring to the Cl₃ plane; this is illustrated in the packing diagram for BiCl₃.12-crown-4 (Fig. 3). The arrangements and symmetries of the sets of four molecules within the cells vary, and they are related by screw axes, mirror planes or glide planes in different examples.

References

ADAM, K. R., DAVIS, R. L., KENNARD, C. H. L., CALOS, N. J., LINDOY, L. F. & McCOOL, B. J. (1990). *J. Chem. Soc. Chem. Commun.* pp. 1784–1785.

ALCOCK, N. W., RAVINDRAN, M., ROE, S. M. & WILLEY, G. R. (1990). *Inorg. Chim. Acta*, 167, 115–118.

ALCOCK, N. W., RAVINDRAN, M. & WILLEY, G. R. (1989). *J. Chem. Soc. Chem. Commun.* pp. 1063–1065.

BAJAJ, A. V. & POONIA, N. S. (1988). *Coord. Chem. Rev.* 87, 55–213.

BEAGLEY, B., ENDREGARD, M. & NICHOLSON, D. G. (1991). *Acta Chem. Scand.* 45, 349–353.

BROWN, I. D. & ALTERMATT, D. (1985). *Acta Cryst.* B41, 244–247.

COLQUHOUN, H. M., STODDART, J. F. & WILLIAMS, D. J. (1986). *Angew. Chem. Int. Ed. Engl.* 25, 487–507.

DREW, M. G. B. & NICHOLSON, D. G. (1986). *J. Chem. Soc. Dalton Trans.* pp. 1543–1549.

DREW, M. G. B., NICHOLSON, D. G., SYLTE, I. & VASUDEVAN, A. K. (1990). *Inorg. Chem. Acta*, 171, 11–15.

GALY, J. & ENJALBERT, R. (1982). *J. Solid State Chem.* 44, 1–23.

GARRELL, R. L., SMYTH, J. C., FRONCZEK, F. R. & GANDOUR, R. D. (1988). *J. Incl. Phenom.* 6, 73–78.

HOUGH, E., NICHOLSON, D. G. & VASUDEVAN, A. K. (1987). *J. Chem. Soc. Dalton Trans.* pp. 427–430.

HOUGH, E., NICHOLSON, D. G. & VASUDEVAN, A. K. (1989). *J. Chem. Soc. Dalton Trans.* pp. 2155–2159.

LIPKA, A. (1979). *Acta Cryst.* B35, 3020–3022.

LUGER, P., ANDRÉ, C., RUDERT, R., ZOBEL, D., KNÖCHEL, A. & KRAUSE, A. (1992). *Acta Cryst.* B48, 33–37.

NYBURG, S. C., OZIN, G. A. & SZYMAŃSKI, J. T. (1971). *Acta Cryst.* B27, 2298–2304.

NYBURG, S. C., OZIN, G. A. & SZYMAŃSKI, J. T. (1972). *Acta Cryst.* B28, 2885.

MARSH, R. E. (1990). *Acta Cryst.* C46, 1356–1357.

SHELDRICK, G. M. (1986). *SHELXTL-Plus Users Manual.* Nicolet Instrument Corporation, Madison, Wisconsin, USA.