

Crown ether chemistry of the alkaline earth nitrates

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Received 8th September 1998, Accepted 24th November 1998

Crystallization of the alkaline earth nitrates $M(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ($M = \text{Mg}$, $x = 6$; $M = \text{Ca}$, $x = 4$; $M = \text{Sr}$ or Ba , $x = 0$) from an aqueous solution of either 15-crown-5 or 18-crown-6 resulted in complex formation in all cases. Thus, $[\text{Mg}(\text{H}_2\text{O})_2(15\text{-crown-5})_3][\text{NO}_3]_6$ and $[\text{Mg}(\text{H}_2\text{O})_5(\text{NO}_3)]\text{NO}_3 \cdot 18\text{-crown-6} \cdot \text{H}_2\text{O}$, $[\text{Ca}(\text{NO}_3)_2(15\text{-crown-5})]$, $[\text{Sr}(\text{H}_2\text{O})(\text{NO}_3)_2(15\text{-crown-5})]$, $[\text{Sr}(\text{NO}_3)_2(18\text{-crown-6})]$, $[\text{Ba}(15\text{-crown-5})_2][\text{Ba}(\text{NO}_3)_3(15\text{-crown-5})]_2$ and $[\text{Ba}(\text{H}_2\text{O})(\text{NO}_3)_2(18\text{-crown-6})]$ have all been characterized using X-ray crystallography. Wide variations in the co-ordination sphere of the metals are observed as the ionic radius increases, and the mode of bonding to the crown ether varies considerably as the diameter of the crown is modified.

Introduction

Crown ethers have received much attention since the pioneering work of Pedersen^{1,2} in 1967. The focus of this attention has predominantly been on the binding capacity of the crown to alkali metals, but also to a lesser extent the alkaline earth metals.³ The major factors influencing binding capacity of a metal ion by crown ethers are the solvent and solvation free energies, degree of preorganization, ligand flexibility and host-guest complementarity. A major aspect of the complementarity of crown and metal ion guests is the "size fit" of the metal with respect to the size of the crown ether cavity which can therefore be related to the ratio of the ionic diameter of the metal ion to the effective diameter of the macrocycle. Studies have shown that, for the alkali metals, ratios of 0.75 to 0.90:1 are favourable for direct ion-crown ether binding.⁴ Thus, for 18-crown-6 (cavity diameter 2.6 to 3.2 Å)⁵ ratios of 0.61 to 0.75, 0.83 to 1.02 and 1.03 to 1.27:1 are obtained for Na^+ , K^+ and Cs^+ respectively and, along with factors such as chelate ring size,⁶ contribute to the selectivity of 18-crown-6 for binding of K^+ over the other alkali metals. Likewise, for 15-crown-5 (cavity diameter 1.7 to 2.2 Å)⁵ a ratio of 0.89 to 1.15:1 is obtained for Na^+ and reflects the size match for that ion. For the alkaline earth metals limited studies have shown capacity for binding of the ions by crown ethers, and we extend this work to those of the Group 2 nitrates. The nitrates are of interest, particularly in aqueous media, because both the nitrate and water ligands can compete with the crown ether for binding sites on the metal. While the chelate and macrocyclic effects of the crown ether would be expected to overcome the competition offered by the water molecule, the possibility of bidentate binding by nitrate is well known and is of interest from a structural point of view.

As part of our study of crown ether complexation of metal species and hydrogen bonding interactions of hydrated metal salts in the presence of crown ethers,⁷⁻¹¹ we have now investigated the formation of complexes obtained by the interaction between a Group 2 nitrate and either 15-crown-5 or 18-crown-6 under aqueous conditions. Thus we report herein the syntheses and crystal structures of $[\text{Mg}(\text{H}_2\text{O})_2(15\text{-crown-5})_3][\text{NO}_3]_6$ **1**, $[\text{Mg}(\text{H}_2\text{O})_5(\text{NO}_3)]\text{NO}_3 \cdot 18\text{-crown-6} \cdot \text{H}_2\text{O}$ **2**, $[\text{Ca}(\text{NO}_3)_2(15\text{-crown-5})]$ **3**, $[\text{Sr}(\text{H}_2\text{O})(\text{NO}_3)_2(15\text{-crown-5})]$ **4**, $[\text{Sr}(\text{NO}_3)_2(18\text{-crown-6})]$ **5**, $[\text{Ba}(15\text{-crown-5})_2][\text{Ba}(\text{NO}_3)_3(15\text{-crown-5})]_2$ **6** and $[\text{Ba}(\text{H}_2\text{O})(\text{NO}_3)_2(18\text{-crown-6})]$ **7**. There has been a previous

report of $[\text{Ca}(\text{NO}_3)_2(18\text{-crown-6})]$ where the complex has similar structure to the strontium analogue reported in this paper.¹²

Experimental

All alkaline earth metal nitrates, 15-crown-5 and 18-crown-6 were obtained from Aldrich Chemical Co. Distilled water was used as solvent. Infrared spectra were recorded as Nujol mulls in sodium chloride plates on a Perkin-Elmer 1600 series FTIR spectrophotometer. Microanalytical data for all compounds were obtained on a Carlo Erba EA 1108 C,H,N analyzer at James Cook University and several cases were hampered by either water loss or extreme hygroscopic nature. Yields were good in all cases (*ca.* >80%) and no attempts were made to maximize yields. Reaction conditions throughout were optimized to yield X-ray quality crystals.

Preparations

All compounds were prepared following the same general procedure. The salts $M(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.45 mmol) and the appropriate crown ether (0.45 mmol) were dissolved in water (3 cm³) and allowed to stand at room temperature. In all cases colourless crystals of the product grew over 1–2 weeks. Complexes **1** and **2** proved extremely difficult to separate from free crown ether, a problem compounded by their extreme deliquescence. In both cases analytical data indicated contamination by *ca.* 7% free crown ether.

$[\text{Mg}(\text{H}_2\text{O})_2(15\text{-crown-5})_3][\text{NO}_3]_6$ **1** (Found: C, 31.51; H, 6.56; N, 6.06. Calc. for $\text{C}_{10}\text{H}_{22}\text{MgN}_2\text{O}_{12}$: C, 29.69; H, 5.98; N, 6.92%). IR (Nujol, ν): 3564s (br), 1681s (br), 1130s, 945m, 870w and 828m cm⁻¹.

$[\text{Mg}(\text{H}_2\text{O})_5(\text{NO}_3)]\text{NO}_3 \cdot 18\text{-crown-6} \cdot \text{H}_2\text{O}$ **2** (Found: C, 29.45; H, 7.98; N, 4.72. Calc. for $\text{C}_{12}\text{H}_{36}\text{MgN}_2\text{O}_{18}$: C, 27.68; H, 6.97; N, 5.38%). IR (Nujol, ν): 3564s (br), 1642s (br), 1135s, 1100m, 962m, 865w and 820w cm⁻¹.

$[\text{Ca}(\text{NO}_3)_2(15\text{-crown-5})]$ **3** (Found: C, 31.49; H, 5.67; N, 7.05. Calc. for $\text{C}_{10}\text{H}_{20}\text{CaN}_2\text{O}_{11}$: C, 31.25; H, 5.24; N, 7.29%). IR (Nujol, ν): 1091s (br), 1000m, 946m, 867m and 822m cm⁻¹.

$[\text{Sr}(\text{H}_2\text{O})(\text{NO}_3)_2\text{H}(15\text{-crown-5})]$ **4** (Found: C, 27.27; H, 5.27; N, 5.95. Calc. for $\text{C}_{10}\text{H}_{22}\text{N}_2\text{O}_{12}\text{Sr}$: C, 26.70; H, 4.93; N, 6.23%). IR (Nujol, ν): 3541s (br), 1650s (br), 1085s, 1010m, 948m, 867m and 825m cm⁻¹.

[Sr(NO₃)₂(18-crown-6)] **5** (Found: C, 30.45; H, 5.28; N, 5.92. Calc. for C₁₂H₂₄N₂O₁₂Sr: C, 30.28; H, 5.08; N, 5.89%); IR (Nujol, ν): 1094s, 1035m, 964m, 867m, 838m and 825m cm⁻¹.

[Ba(15-crown-5)]₂[Ba(NO₃)₃(15-crown-5)]₂ **6** (Found: C, 28.89; H, 5.16; N, 5.05. Calc. for C₄₀H₈₀Ba₃N₆O₃₈: C, 28.85; H, 4.84; N, 5.05%); IR (Nujol, ν): 1244m, 1081s, 1034m, 945m, 859m and 824m cm⁻¹.

[Ba(H₂O)(NO₃)₂(18-crown-6)] **7** (Found: C, 27.44; H, 5.11; N, 5.23. Calc. for C₁₂H₂₆BaN₂O₁₃: C, 26.51; H, 4.82; N, 5.15%); IR (Nujol, ν) 3563s (br), 1644s (br), 1153m, 1078m, 1010w, 962m, 890m and 831w cm⁻¹.

Crystallography

Single crystals of complexes **1** to **7** were sealed in thin walled glass capillaries. For **3**, **4** and **7** final lattice parameters as determined from the least-squares refinement of the angular settings of 25 high angle reflections ($2\theta > 30^\circ$) accurately centered on an Enraf-Nonius CAD4 diffractometer are given in Table 1. A summary of data collection parameters is also given. Gaussian absorption corrections were performed on these three compounds and calculations were carried out using the XTAL 3.4 system of computer programs.¹³ For compounds **1**, **2**, **5** and **6** data were collected on a Nonius K α CCD diffractometer and calculations carried out using the SHELX-97 suite of computer programs¹⁴ with the aid of RES2INS.¹⁵

Positions of heavy atoms in all compounds were determined from a three-dimensional Patterson function. All other non-hydrogen atoms were located from a Fourier-difference synthesis except water hydrogen atoms which were located from the difference map. All non-hydrogen atoms were refined anisotropically. Remaining hydrogen atoms were placed at calculated positions and their parameters were not refined.

CCDC reference number 186/1263.

See <http://www.rsc.org/suppdata/dt/1999/407/> for crystallographic files in .cif format.

Results and discussion

Preparation of complexes

Complexes were prepared by mixing equimolar mixtures of the alkaline earth metal nitrate and the respective crown ether in an aqueous medium. The ease of formation contrasts with the report that isolation of these and the alkali metal salt complexes as crystalline solids is difficult due to the very high lattice energies resulting in a reassembling of the metal nitrate.³ Indeed, we have also been able to isolate the alkali metal nitrate-crown ether complexes as crystalline solids from aqueous media.¹¹ For compounds **1** to **5** and **7** a 1:1 M(NO₃)₂:crown ether was obtained; for **6** the resulting stoichiometry was 3:4. The reason for the latter stoichiometry is not known, but may be due to the incorrect fit of Ba in 15-crown-5 thus not favouring the 1:1 stoichiometry due to "sandwich" complexation of Ba by two 15-crown-5 molecules in the cation and concurrent triple bidentate nitrate coordination in the anion (see structural section).

Structural results

Selected bond distances and angles for complexes **1**–**7** are shown in Tables 2–8.

[Mg(H₂O)₂(15-crown-5)]₃[NO₃]₆ **1**. This complex crystallizes as [Mg(H₂O)₂(15-crown-5)]⁺ cations and NO₃⁻ anions which exhibit a hydrogen bonded array through O–H...O (NO₃⁻) interactions (see Fig. 1). The cation is similar to that observed in [Mg(H₂O)₂(15-crown-5)]Cl₂·H₂O¹⁶ and [Mg(H₂O)₂(15-crown-5)][CuCl₄]·H₂O¹⁷ where the Mg(H₂O)₂⁺ moiety is threaded through the macrocycle and displays close to regular pentagonal bipyramidal stereochemistry [Mg–O_(crown) distances

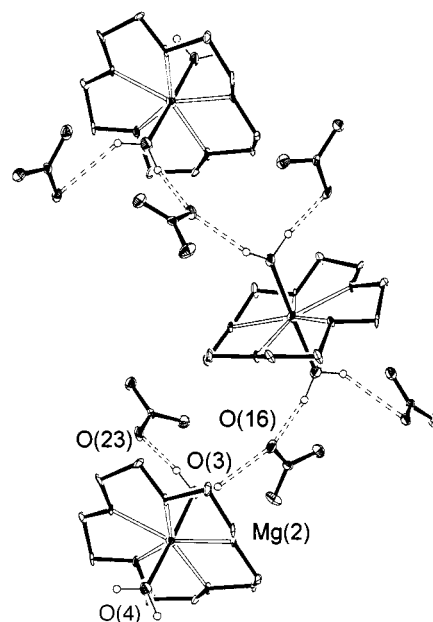


Fig. 1 Structure of pentagonal bipyramidal Mg²⁺ complex [Mg(H₂O)₂(15-crown-5)]₃[NO₃]₆ **1**, showing the hydrogen bonded array.

range from 2.012(7) to 2.357(8) Å and Mg–O_(water) distances are 2.002(4) and 2.026(5) Å]. The Mg resides within the plane defined by the heteroatoms of the crown and demonstrates the close-fit relationship of the cavity of this crown ether for Mg²⁺. It is significant that crown ether complexation of the Mg²⁺ ion is favoured over Mg...O(NO₂) binding. Furthermore, the crown ether complexation occurs in preference to hydration, which for magnesium is energetically favourable because of its high charge/radius ratio (*cf.* complex **2**, see below). The ionic diameter of Mg (1.30 Å) is slightly small for selective encapsulation by the crown ether. The ratio of the ionic diameter¹⁸ to the effective diameter of the 15-crown-5 cavity is between 0.59 and 0.76:1, and lies on the low side of the viable range of 0.75 to 0.90:1 established for alkali metal binding.⁴ The axial water molecules form an extended hydrogen-bonded array by interacting with the NO₃⁻ anions [see Table 2(ii)].

[Mg(H₂O)₅(NO₃)]NO₃·18-crown-6·H₂O **2**. This complex does not crystallize as discrete anions and cations. There are significant hydrogen-bonded contacts between the [Mg(H₂O)₅(NO₃)⁺ cations and NO₃⁻ anions and the neutral 18-crown-6 and water molecule of solvation giving an extended hydrogen-bonded network (see Fig. 2).

The six-co-ordinate [Mg(H₂O)₅(NO₃)⁺ cation has very close to regular octahedral geometry with five water ligands and a monodentate NO₃⁻ ligand. It is isostructural with a series of transition metal complexes (Mn, Co, Ni, Zn, Cd) which have recently been studied.⁸ The Mg–O_(water) and Mg–O_(nitrate) distances of 2.057(2) Å (average) and 2.154(2) Å respectively are similar to those in the isostructural [Zn(H₂O)₅(NO₃)](18-crown-6)·H₂O (2.092 and 2.233 Å respectively).⁸ The aqua ligands of the [Mg(H₂O)₅(NO₃)⁺ cation are hydrogen bonded in a second-sphere fashion by the 18-crown-6 molecule which in turn is also hydrogen-bonded to the unbound water molecule [see Table 3(ii)]. The unbound nitrate anion and water molecule are also bound in this hydrogen-bonded network. While Mg²⁺ complexation by 18-crown-6 has been observed, for example in [Mg(18-crown-6)][HCl₂]₂,¹⁸ the hydration energies of Mg²⁺ in aqueous systems are apparently more favorable and thus metal complexation does not occur as with the analogous 15-crown-5 complex **1**, where the cavity of the crown ether is more closely related to the ionic radius of Mg²⁺ (the ratio of the

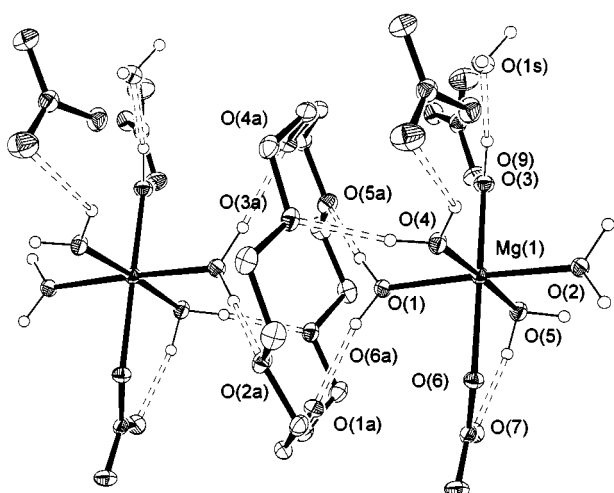
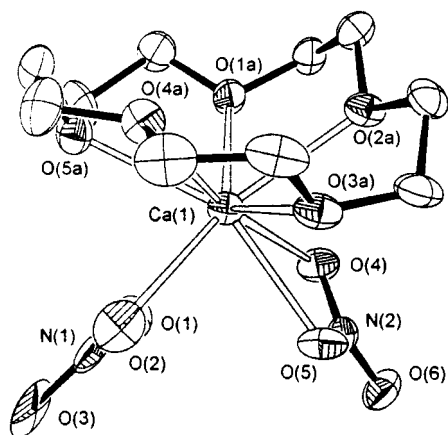
Table 1 Crystal data and summary of data collection for complexes 1–7

	1	2	3	4	5	6	7
Formula	C ₃₀ H ₅₂ Mg ₃ N ₆ O ₃₉	C ₁₂ H ₃₆ MgN ₂ O ₁₈	C ₁₀ H ₂₀ CaN ₂ O ₁₁	C ₁₀ H ₂₂ N ₂ O ₁₂ Sr	C ₁₂ H ₂₄ N ₂ O ₁₂ Sr	C ₄₀ H ₈₀ Ba ₃ N ₆ O ₃₈	C ₁₂ H ₂₆ BaN ₂ O ₁₃
<i>M</i>	1192.71	520.74	384.4	449.9	475.96	1665.12	543.7
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	14.4935(6)	7.1335(4)	16.029(2)	8.245(1)	7.5064(4)	10.4078(3)	9.204(6)
<i>b</i> /Å	14.1996(3)	16.0605(11)	13.473(2)	9.967(3)	15.5520(11)	16.1040(4)	15.802(7)
<i>c</i> /Å	25.7650(10)	20.8953(10)	15.221(1)	11.542	8.1597(4)	19.5482(7)	14.062(9)
α /°				81.87(9)		91.542(1)	
β /°	96.525(2)	99.306(2)		84.04(9)	106.313(2)	104.877(1)	96.39(9)
γ /°				73.68(9)		104.036(1)	
<i>V</i> /Å ³	5268.2(3)	2362.3(2)	3286.9(7)	899(1)	914.23(9)	3058.1(2)	2032(2)
<i>Z</i>	4	4	8	2	2	2	4
<i>D</i> _c /g cm ⁻³	1.505	1.464	1.553	1.662	488	1668	1088
<i>F</i> (000)	2488	1112	1616	460	1.729	1.808	1.776
μ /mm ⁻¹	0.17	0.16	0.44	3.06	3.02	2.02	2.02
Crystal size/mm	0.80 × 0.60 × 0.10	0.20 × 0.10 × 0.05	0.58 × 0.32 × 0.20	0.76 × 0.44 × 0.42	0.40 × 0.40 × 0.40	0.30 × 0.30 × 0.20	0.32 × 0.32 × 0.80
Diffractometer	Nonius ^K CCD	Nonius ^K CCD	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Nonius ^K CCD	Nonius ^K CCD	Enraf-Nonius CAD4
Radiation	Mo-K α	Mo-K α	Mo-K α	Mo-K α	Mo-K α	Mo-K α	Mo-K α
2 θ range/°	6.40–50.00	7.58–52.00	2–50	2–50	7.38–52.00	6.70–52.00	2–50
Reflections collected	43962	20656	3256	3392	7811	25782	3947
Unique data	9210	4582	2874	3150	1770	11048	3556
Observed reflections	—	—	1460	2091	—	—	2697
Parameters	842	299	218	227	125	842	254
Cut-off	—	—	3 σ	3 σ	—	—	3 σ
<i>T</i> /K	100	123	296	296	123	123	296
<i>R</i> 1 ^a	0.1117	0.046	0.046	0.064	0.070	0.032	0.047
<i>R'</i> (or <i>wR</i> 2) ^a	0.2472	0.105	0.054	0.069	0.190	0.086	0.060
Largest peak/e Å ⁻³	0.594	0.180	0.745	2.217 ^b	2.03 ^b	0.957	2.232 ^b

^a For ^KCCD structures (SHELXL 97), *wR*2, *R*1; for CAD4 structures *R'*. ^b Close to metal atom.

Table 2 Selected bond lengths (Å) (i) and hydrogen-bonding distances (Å) and angles (°) (ii) for $[\text{Mg}(\text{H}_2\text{O})_2(15\text{-crown-5})]_3[\text{NO}_3]_6 \mathbf{1}$

(i)				
Mg(1)–O(1)	2.003(5)	Mg(1)–O(2)	2.026(5)	
Mg(1)–O(1a)	2.282(4)	Mg(1)–O(2a)	2.180(4)	
Mg(1)–O(3a)	2.140(5)	Mg(1)–O(4a)	2.197(5)	
Mg(1)–O(5a)	2.153(5)			
D–H···A	D–H	H···A	D···A	D–H–A
(ii)				
O(6)–H(61a)···O(5)	1.01	1.77	2.739(7)	159.8
O(6a)–H(62a)···O(2)	0.98	1.92	2.867(8)	161.1
O(7a)–H(71a)···O(15)	0.96	1.82	2.757(7)	165.5
O(7a)–H(72a)···O(6)	1.04	1.71	2.743(7)	175.3
O(6b)–H(61b)···O(10)	0.97	1.84	2.793(6)	166.8
O(7b)–H(71b)···O(7)	0.99	1.75	2.736(6)	168.3
O(6c)–H(61c)···O(16)	0.95	1.82	2.756(6)	168.2
O(6d)–H(61d)···O(13)	1.06	1.84	2.832(8)	153.7
O(6d)–H(61d)···O(13)	1.06	2.20	3.078(7)	139.4

**Fig. 2** Hydrogen-bonding network in $[\text{Mg}(\text{H}_2\text{O})_5(\text{NO}_3)]\text{NO}_3 \cdot 18\text{-crown-6} \cdot \text{H}_2\text{O} \mathbf{2}$.**Fig. 3** Molecular structure of nine-co-ordinate $[\text{Ca}(\text{NO}_3)_2(15\text{-crown-5})] \mathbf{3}$.

Mg^{2+} ionic diameter¹⁹ to the effective diameter of the 18-crown-6 cavity is 0.41 to 0.50:1 and lies outside the 0.75 to 0.90:1 alkali metal binding range.⁴

[Ca(NO₃)₂(15-crown-5)] 3. This complex crystallizes as distinct $[\text{Ca}(\text{NO}_3)_2(15\text{-crown-5})]$ molecules with no significant

Table 3 Selected bond lengths (Å) (i) and hydrogen-bonded distances (Å) and angles (°) (ii) for $[\text{Mg}(\text{H}_2\text{O})_5(\text{NO}_3)]\text{NO}_3 \cdot 18\text{-crown-6} \cdot \text{H}_2\text{O} \mathbf{2}$

(i)				
Mg(1)–O(1)	2.054(2)	Mg(1)–O(4)	2.067(2)	
Mg(1)–O(2)	2.048(2)	Mg(1)–O(5)	2.092(2)	
Mg(1)–O(3)	2.024(2)	Mg(1)–O(6)	2.154(2)	
D–H···A	D–H	H···A	D···A	D–H–A
(ii)				
O(1)–H(12)···O(1a)	0.90	1.93	2.821(2)	168.0
O(1)–H(11)···O(5a)	0.98	1.88	2.846(2)	172.4
O(4)–H(41)···O(3a)	0.90	1.95	2.824(2)	165.9
O(3)–H(31)···O(1s)	0.92	1.78	2.690(2)	168.0
O(5)–H(52)···O(6a)	0.93	1.91	2.838(2)	173.7
O(2)–H(22)···O(4a)	0.98	1.91	2.884(2)	170.7
O(2)–H(21)···O(2a)	0.97	1.90	2.860(2)	172.1
O(4)–H(42)···O(10)	0.86	1.98	2.814(2)	164.6
O(1s)–H(1s1)···O(10)	0.91	1.98	2.809(2)	150.6
O(1s)–H(1s2)···O(8)	0.90	1.98	2.874(2)	172.0

Table 4 Selected bond lengths (Å) for $[\text{Ca}(\text{NO}_3)_2(15\text{-crown-5})] \mathbf{3}$

Ca(1)–O(1)	2.484(4)	Ca(1)–O(2a)	2.499(4)
Ca(1)–O(2)	2.458(4)	Ca(1)–O(3a)	2.524(4)
Ca(1)–O(4)	2.567(4)	Ca(1)–O(4a)	2.524(4)
Ca(1)–O(5)	2.446(4)	Ca(1)–O(5a)	2.581(4)
Ca(1)–O(1a)	2.474(3)		

intermolecular interactions. The Ca atom is nine-co-ordinate, being ligated by five crown ether oxygen atoms and two bidentate nitrate ligands (see Fig. 3). The calcium centre is too large to be encapsulated by the crown ether (diameter 1.98 Å) and adopts a perching geometry. The ratio of the ionic diameter to the effective diameter of the 15-crown-5 cavity is between 0.75 to 1.16:1 and lies on the upper limit of the range of 0.75 to 0.90:1 established for alkali metal binding.⁴ The Ca–O_(crown) distances range from 2.474(3) to 2.581(4) Å and are similar to those in $[\text{Ca}(\text{SCN})_2(\text{H}_2\text{O})(15\text{-crown-5})]$ (average 2.540 Å).²⁰ One of the bidentate nitrate ligands is bound in a rather symmetrical fashion with Ca–O_(nitrate) distances of 2.458(4) and 2.484(4) Å, while the other nitrate group is far more unsymmetrical with distances of 2.446(4) and 2.567(4) Å.

[Sr(H₂O)(NO₃)₂(15-crown-5)] 4. This complex does not crystallize as discrete molecules but exists as a non-molecular polymer as a consequence of *intermolecular* hydrogen-bonding contacts between the water molecule and nitrate oxygen atoms. The water molecule O(7) hydrogen bonds to nitrate oxygen atoms O(1) and O(6), O···O distances 2.82(10) and 2.84(10) Å, but is also within hydrogen bonding distance of the nitrate oxygen atoms O(1) and O(5) where the O···O distances are 2.95(1) and 2.93(1) respectively.

Complex **4** is similar to $[\text{Ca}(\text{NO}_3)_2(15\text{-crown-5})] \mathbf{3}$ in which the metal atom adopts a perching geometry. However, the most striking difference between **3** and **4** is the incorporation of a water molecule into the co-ordination sphere of **4** (see Fig. 4), due to the much larger ionic radius of strontium compared with calcium (1.13 Å for Sr and 0.99 Å for Ca)¹⁹ resulting in a ten-co-ordinate Sr (*cf.* nine-co-ordinate Ca in compound **3**). The Sr–O_(crown) distances range from 2.705(9) to 2.788(7) Å and are similar to those in $[\text{Sr}(\text{OSiPh}_3)_2(15\text{-crown-5})] \cdot \text{thf}$ (thf = tetrahydrofuran) (average 2.78 Å).²¹ Both of the bidentate nitrate ligands are bound in a rather symmetrical fashion with two short Sr–O_(nitrate) distances of 2.642(8) and 2.61(1) Å and two longer ones of 2.748(9) and 2.87(1) Å. This type of binding, where the Sr is bound out of the face of the cavity and further ligands bind to the opposing side of the metal centre

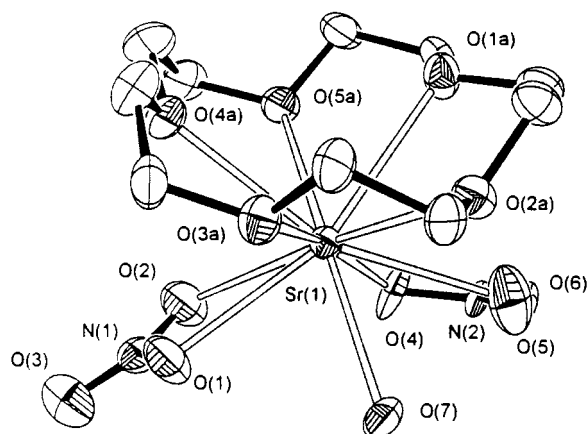


Fig. 4 Molecular structure of ten-co-ordinate $[\text{Sr}(\text{H}_2\text{O})(\text{NO}_3)_2(15\text{-crown-5})]$ **4**.

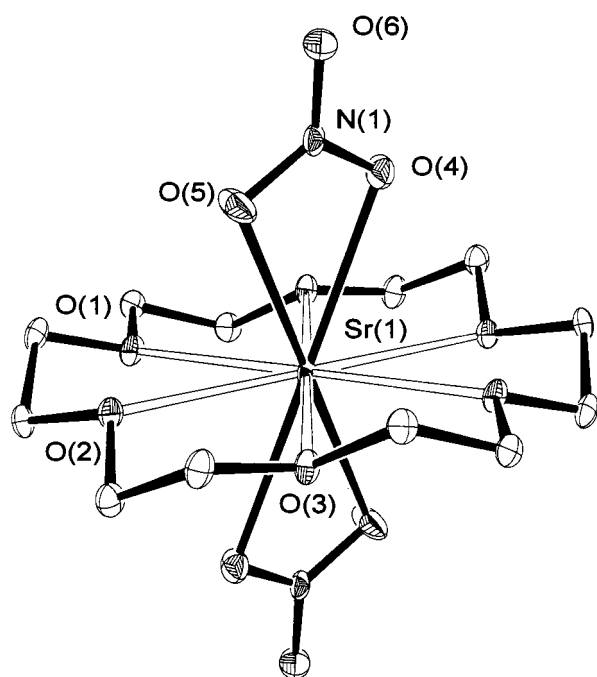


Fig. 5 Molecular structure of ten-co-ordinate $[\text{Sr}(\text{NO}_3)_2(18\text{-crown-6})]$ **5**.

has been seen in several complexes, including $[\text{Sr}(\text{OSiPh}_3)_2(15\text{-crown-5})]\cdot\text{thf}$ mentioned above.²¹

The ratio of the ionic diameter to the effective cavity diameter for strontium (ionic diameter 2.26 Å)¹⁹ and 15-crown-5 (cavity diameter 1.7 to 2.2 Å)⁵ is 1.02 to 1.33:1, and reflects the lack of size match between the two entities, thus dictating that the Sr resides exterior to the macrocycle.

$[\text{Sr}(\text{NO}_3)_2(18\text{-crown-6})]$ **5.** This complex crystallizes as discrete molecules with no significantly short intermolecular contacts (see Fig. 5). The strontium atom resides on an inversion centre. The compound is also isostructural with its calcium analogue,¹² where the metal atom is threaded through the crown ether with two O,O'-bidentate nitrates on opposing sides of the macrocycle plane. The Sr–O_(crown) distances range from 2.667(5) to 2.755(3) Å and are similar to those in compound **4** above (average 2.75 Å) even though the mode of crown binding is significantly different and, as expected, slightly longer than in the calcium analogue (Ca–O_(crown) average 2.615 Å).¹² Unlike compounds **3** and **4**, the bidentate nitrate ligands are rather symmetrical with Sr–O_(nitrate) distances of 2.645(4) and

Table 5 Selected bond lengths (Å) for $[\text{Sr}(\text{H}_2\text{O})(\text{NO}_3)_2(15\text{-crown-5})]$ **4** (H atom positions not determined)

Sr(1)–O(1)	2.642(8)	Sr(1)–O(1a)	2.788(7)
Sr(1)–O(2)	2.748(9)	Sr(1)–O(2a)	2.705(9)
Sr(1)–O(4)	2.61(1)	Sr(1)–O(3a)	2.708(9)
Sr(1)–O(5)	2.87(1)	Sr(1)–O(4a)	2.769(9)
Sr(1)–O(7)	2.543(9)	Sr(1)–O(5a)	2.757(8)

Table 6 Selected bond lengths (Å) for $[\text{Sr}(\text{NO}_3)_2(18\text{-crown-6})]$ **5**

Sr(1)–O(1)	2.667(5)	Sr(1)–O(4)	2.680(3)
Sr(1)–O(2)	2.752(3)	Sr(1)–O(5)	2.645(4)
Sr(1)–O(3)	2.755(3)		

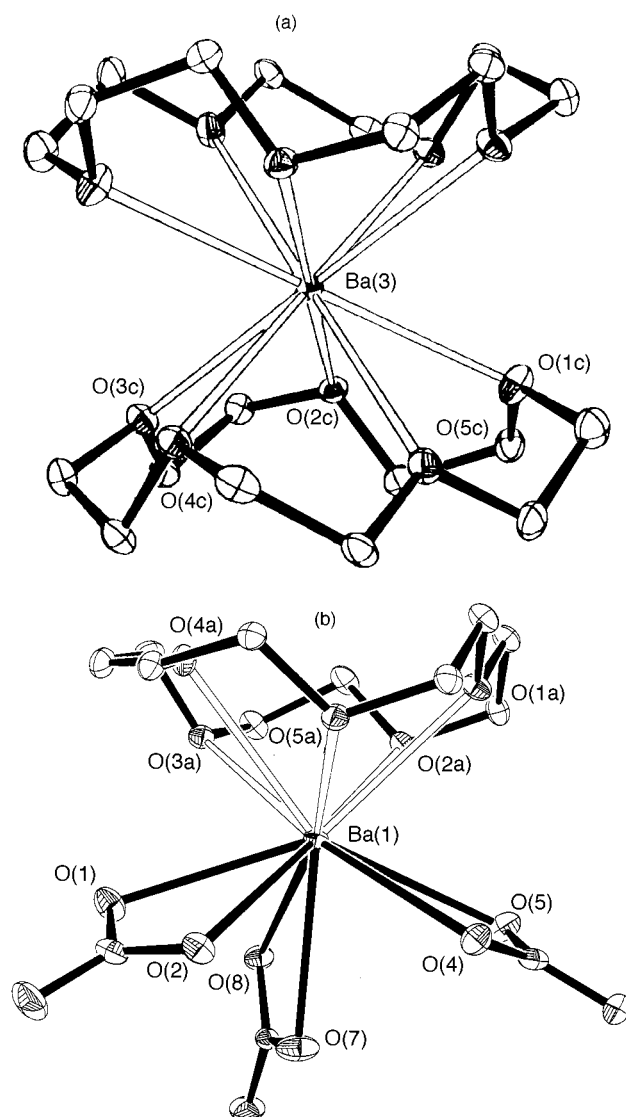


Fig. 6 Structures of (a) the ten-co-ordinate cation and (b) the eleven-co-ordinate anion in $[\text{Ba}(15\text{-crown-5})_2][\text{Ba}(\text{NO}_3)_2(15\text{-crown-5})]$ **6**.

2.680(3) Å, which is also the case for the calcium analogue where the Ca–O_(nitrate) distances are much shorter 2.500 and 2.520 Å.¹² This type of Sr²⁺ binding where the metal ion resides within the crown has also been identified in $[\text{Sr}(\text{Bu}_2\text{PO})_2(18\text{-crown-6})]\cdot\text{H}_2\text{O}$ ²² and $[\text{Sr}(\text{BH}_4)_2(18\text{-crown-6})]$.²³

The ratio of the ionic diameter to the effective cavity diameter for strontium (ionic diameter 2.26 Å)¹⁷ and 18-crown-6 (cavity diameter 2.6 to 3.2 Å)⁵ is 0.71 to 0.87:1, and thus falls within the range of 0.75 to 0.90:1, favourable for direct ion–crown ether binding for alkali metals.⁴

Table 7 Selected bond distances (Å) and angles (°) for [Ba(15-crown-5)₂][Ba(NO₃)₃(15-crown-5)]₂ **6**

Barium environments in the anions: *r* is the barium–ligand distance; other entries in the matrices are the angles subtended by the relevant atoms at the head of the rows and column; non-italicized entries are for the environment about Ba(1) and *italicized* entries for that about Ba(2)

Atom	<i>r</i>	O(2a)/B	O(3a)/B	O(4a)/B	O(5a)/B	O(1)/10	O(2)/11	O(4)/13	O(5)/14	O(7)/16	O(8)/17
O(1a)	2.903(2)	58.34(6)	98.80(6)	81.66(6)	58.88(6)	150.54(7)	126.64(6)	73.76(7)	70.51(7)	138.81(7)	134.22(6)
<i>O(1b)</i>	<i>2.914(2)</i>	<i>58.09(6)</i>	<i>98.24(6)</i>	<i>81.56(6)</i>	<i>58.86(6)</i>	<i>76.19(7)</i>	<i>69.72(6)</i>	<i>131.16(6)</i>	<i>140.65(7)</i>	<i>153.50(7)</i>	<i>127.40(6)</i>
O(2a)	2.879(2)		59.56(6)	94.48(6)	113.01(6)	129.34(6)	174.25(6)	109.81(7)	70.91(7)	111.71(7)	78.48(6)
<i>O(2b)</i>	<i>2.893(2)</i>		<i>59.51(6)</i>	<i>94.53(7)</i>	<i>112.75(6)</i>	<i>112.77(7)</i>	<i>72.65(7)</i>	<i>76.39(6)</i>	<i>113.27(7)</i>	<i>127.30(6)</i>	<i>171.38(6)</i>
O(3a)	2.910(2)			57.22(6)	111.28(6)	72.21(7)	115.24(6)	169.37(7)	125.68(7)	109.28(6)	67.94(6)
<i>O(3b)</i>	<i>2.861(2)</i>			<i>57.00(6)</i>	<i>110.70(6)</i>	<i>172.27(7)</i>	<i>128.16(7)</i>	<i>69.68(6)</i>	<i>109.24(6)</i>	<i>71.44(7)</i>	<i>111.94(7)</i>
O(4a)	2.963(3)				55.72(6)	69.81(7)	83.91(7)	127.37(6)	152.17(7)	138.97(7)	118.82(6)
<i>O(4b)</i>	<i>2.966(2)</i>				<i>55.47(6)</i>	<i>126.31(6)</i>	<i>151.18(6)</i>	<i>121.48(6)</i>	<i>137.09(7)</i>	<i>72.32(7)</i>	<i>80.53(7)</i>
O(5a)	2.868(2)					97.42(6)	70.60(6)	71.77(6)	107.27(6)	130.30(7)	166.72(7)
<i>O(5b)</i>	<i>2.856(2)</i>					<i>71.24(6)</i>	<i>104.95(6)</i>	<i>169.97(7)</i>	<i>129.73(7)</i>	<i>101.04(7)</i>	<i>70.28(6)</i>
O(1)	2.852(2)						44.95(7)	117.98(7)	137.75(7)	69.16(8)	69.52(7)
<i>O(10)</i>	<i>2.835(2)</i>						<i>45.06(7)</i>	<i>109.80(6)</i>	<i>73.30(6)</i>	<i>115.88(7)</i>	<i>75.79(7)</i>
O(2)	2.822(2)							75.38(7)	112.78(7)	66.83(7)	97.43(6)
<i>O(11)</i>	<i>2.833(2)</i>							<i>81.35(6)</i>	<i>71.19(7)</i>	<i>135.99(7)</i>	<i>114.89(7)</i>
O(4)	2.841(2)								45.07(7)	73.70(7)	111.58(6)
<i>O(13)</i>	<i>2.908(2)</i>								<i>44.35(6)</i>	<i>69.34(7)</i>	<i>100.08(6)</i>
O(5)	2.838(2)									68.70(8)	82.32(7)
<i>O(14)</i>	<i>2.828(2)</i>									<i>64.87(7)</i>	<i>67.28(7)</i>
O(7)	2.865(2)										43.90(6)
<i>O(16)</i>	<i>2.920(2)</i>										<i>44.48(6)</i>
O(8)	2.908(2)										
<i>O(17)</i>	<i>2.808(2)</i>										

Barium environments in the cations: *r* is the bismuth–ligand distance; other entries in the matrices are the angles subtended by the relevant atoms at the head of the rows and column; non-italicized entries are for the environment about Ba(3) (X = C), and *italicized* entries for that about Ba(4) (X = D)

Atom	<i>r</i>	O(1X ^a)	O(2X)	O(2X ^a)	O(3X)	O(3X ^a)	O(4X)	O(4X ^a)	O(5X)	O(5X ^a)
O(1X)	2.841(2)	180.0	59.03(6)	120.97(6)	108.07(7)	71.93(7)	111.87(6)	68.13(6)	58.62(7)	121.38(7)
	<i>2.887(2)</i>	<i>180.0</i>	<i>58.89(6)</i>	<i>121.11(7)</i>	<i>109.1(2)</i>	<i>70.9(2)</i>	<i>109.79(7)</i>	<i>70.21(7)</i>	<i>57.5(2)</i>	<i>122.5(2)</i>
O(2X)	2.824(2)			180.0	59.40(7)	120.60(7)	107.57(6)	72.43(6)	97.67(7)	82.33(7)
	<i>2.841(2)</i>			<i>180.0</i>	<i>61.2(3)</i>	<i>118.8(3)</i>	<i>108.47(7)</i>	<i>71.53(7)</i>	<i>98.4(2)</i>	<i>81.6(2)</i>
O(3X)	2.818(2)					180.0	59.00(6)	121.00(6)	97.97(7)	82.03(7)
	<i>2.81(1)</i>					<i>180.0</i>	<i>59.8(3)</i>	<i>120.2(3)</i>	<i>99.8(3)</i>	<i>80.2(3)</i>
O(4X)	2.825(2)							180.0	58.52(6)	121.48(6)
	<i>2.761(2)</i>							<i>180.0</i>	<i>57.8(2)</i>	<i>122.2(2)</i>
O(5X)	2.845(2)									180.0
	<i>2.728(9)</i>									<i>180.0</i>

^a Symmetry transformations used to generate equivalent atoms: for Ba(3), $-x - 1, -y, -z + 1$; for Ba(4), $-x, -y + 1, -z + 1$.

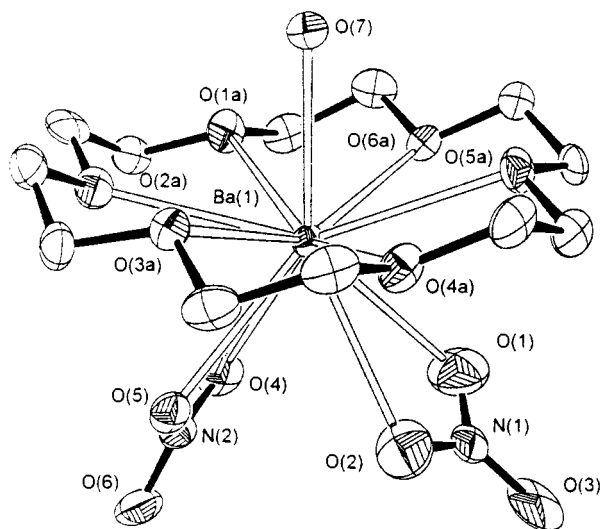


Fig. 7 Molecular structure of eleven-co-ordinate $[\text{Ba}(\text{H}_2\text{O})(\text{NO}_3)_2(18\text{-crown-6})]$ 7.

$[\text{Ba}(15\text{-crown-5})_2][\text{Ba}(\text{NO}_3)_3(15\text{-crown-5})]_2$ 6. This compound crystallizes in space group $P\bar{1}$ with two anions and two half cations comprising the asymmetric unit. The Ba atoms in the sandwich cations [Ba(3) and Ba(4)] reside on inversion centres. The overall compound comprises distinct cations and anions with no significantly short distances representing any interionic contacts. In the cations [Fig. 6(a)] the ten-coordinate Ba centre is sandwiched between two 15-crown-5 molecules in a fashion similar to that in $[\text{Ba}(15\text{-crown-5})_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ with Ba–O distances of 2.728(9) to 2.887(2) Å, {*cf.* $[\text{Ba}(15\text{-crown-5})_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ where the distances range from 2.75(2) to 2.88(2) Å}.²⁴ The anion is a remarkable example of an eleven-co-ordinate “barate” complex involving three O,O'-bidentate nitrate ligands and a crown ether molecule bound through the five oxygen atoms [see Fig. 6(b)]. In the anions the Ba–O_(crown) distances range from 2.856(2) to 2.966(2) Å which are marginally longer than those in the cations (see above). The bidentate nitrate ligands show very close to symmetrical binding to the Ba with Ba–O_(nitrate) distances from 2.822(2) to 2.908(2) Å. The reason for this $[\text{Ba}(\text{NO}_3)_3(15\text{-crown-5})]^-$ complex anion formation is unknown, but presumably favourable binding between nitrate and Ba²⁺ and 15-crown-5 and Ba²⁺ as well as efficient crystal packing tips the balance towards complex anion formation over “free nitrate” counter ions. Barate anion complexes are comparatively rare in the literature. A search of the Cambridge crystallographic database reveals the recently reported $[\text{BaCp}_3]^-$ (Cp = cyclopentadienyl),²⁵ and the much more closely related $[\text{C}_{36}\text{H}_{48}\text{N}_{18}][\text{Ba}(\text{NO}_3)_6][\text{NO}_3]_2 \cdot 6\text{H}_2\text{O}$ ²⁶ containing the $[\text{Ba}(\text{NO}_3)_6]^{4-}$ anion. The ratio of the ionic diameter for Ba²⁺ (2.70 Å)¹⁹ to the effective cavity diameter for 15-crown-5 (1.7 to 2.2 Å)⁵ of 1.23 to 1.59:1 indicates that 15-crown-5 is not large enough for effective encapsulation of Ba²⁺.⁴ Thus, for the cations, sandwich formation is more favourable and for the anions there is a balance between perching macrocyclic binding and bidentate nitrate binding.

$[\text{Ba}(\text{H}_2\text{O})(\text{NO}_3)_2(18\text{-crown-6})]$ 7. Compound 7 crystallizes as distinct molecules exhibiting short hydrogen-bonded contacts between the aqua ligand and the unco-ordinated oxygen atoms of nitrate ligands on two adjacent molecules; O(7)⋯O3 2.838(5), O(7)⋯O(6) 2.876(5) Å. The aqua ligand itself resides in the centre of a bowl-like cavity formed by the adjacent crown ether.

The eleven-co-ordinate Ba is co-ordinated to six O_(crown) ether, two bidentate O_(nitrate) and one O_(water) ligand thus increasing the co-ordination sphere compared with the analogous 18-crown-6 compounds for Ca and Sr (see above). The barium

Table 8 Selected bond lengths (Å) for $[\text{Ba}(\text{H}_2\text{O})(\text{NO}_3)_2(18\text{-crown-6})]$ 7

Ba(1)–O(1)	2.94(1)	Ba(1)–O(2a)	2.887(9)
Ba(1)–O(2)	2.98(1)	Ba(1)–O(3a)	2.908(8)
Ba(1)–O(4)	2.90(1)	Ba(1)–O(4a)	2.83(1)
Ba(1)–O(5)	2.845(9)	Ba(1)–O(5a)	2.878(9)
Ba(1)–O(7)	2.809(8)	Ba(1)–O(6a)	2.860(9)
Ba(1)–O(1a)	2.846(9)		

centre resides roughly in the plane of the crown ether cavity with the two nitrate ligands in a *cisoid* type arrangement on one side of the crown and the water ligand on the opposing side of the crown ether (see Fig. 7). In-crown binding of Ba²⁺ has been seen in other 18-crown-6 complexes, for example $[\text{Ba}(\text{CF}_3\text{COCHCOCF}_3)_2(18\text{-crown-6})]$ ²⁷ and $[\text{Ba}(\text{H}_2\text{O})_2(18\text{-crown-6})][\text{Co}(\text{SCN})_4]$.²⁸ The Ba–O(crown) distances of 2.830(10) to 2.908(8) Å are very similar to those in the anions of compound 6 above, and slightly longer than in the cation sandwiches in the same complex, while the roughly symmetrical bidentate nitrates are bound at distances of 2.845(9) to 2.980(10) Å, again similar to the anion in 6. Similar results are observed for $[\text{Ba}(\text{OC}_6\text{H}_3\text{Bu}^i\text{-3,5})(18\text{-crown-6})] \cdot 3,5\text{-Bu}^i\text{C}_6\text{H}_3\text{OH} \cdot 18\text{-crown-6}$.²⁹

The ratio of the ionic diameter for Ba²⁺ (2.70 Å)¹⁹ to the effective cavity diameter for 18-crown-6 (2.6 to 3.2 Å)⁵ of 0.84 to 1.04:1 indicates that 18-crown-6 is a more suitable size for effective encapsulation of Ba²⁺ compared with 15-crown-5.

Conclusion

This work has established that both 15-crown-5 and 18-crown-6 compete effectively with nitrate for binding sites about the metal centre. With increasing ionic radius of the metal from Mg²⁺ through to Ba²⁺ there is a corresponding increase in the co-ordination sphere about the metal from a co-ordination number of 6 to 11. This chemistry highlights the binding ability of the alkaline earth metals by both 15-crown-5 and 18-crown-6 but, due to size limitations of the cavity of the crown ethers, complete encapsulation only occurs for Mg²⁺ in 15-crown-5 and Ca²⁺, Sr²⁺ and Ba²⁺ by 18-crown-6. In other cases a balance is found between the often observed sandwich formation by two crown ethers and the “one-face” complexation by the crown and bidentate NO₃⁻ binding on the opposing face. For all four metals studied, complexation by both the crown ethers and nitrate is observed, and reflects the affinity of the alkaline earth metal cations for hard oxyanions. For alkali metals the ratio of the ionic diameter of the metal ion to the effective diameter of the macrocycle reflects the binding capacity of the particular crown for the ion. Studies have shown that for the alkali metals, ratios of 0.75 to 0.90:1 are favourable for direct ion–crown ether binding and we find in this work that these ratios are also relevant for the alkaline earth metals. Further work is continuing on crown ether chemistry of the Group 2 metals with anions that have a poorer ligating ability to establish the bonding modes in the absence of competing anionic ligands.

Acknowledgements

We thank the EPSRC and King's College London for funding of the diffractometer system. Grateful acknowledgement is also given to the Nuffield Foundation for the provision of computing equipment. We also thank Mr Brian Foster at James Cook University for performing the microanalyses.

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Paper 8/07006G