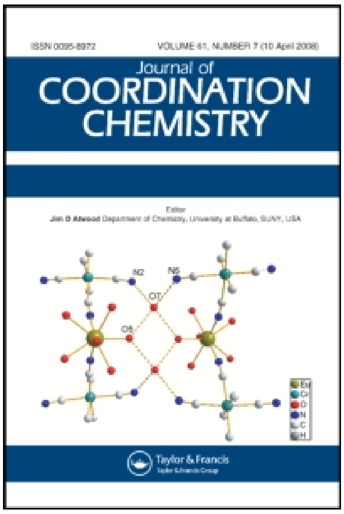

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A structural study of calcium, strontium and barium crown ether complexes

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A structural study of calcium, strontium and barium crown ether complexes

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Complexes involving the perchlorate, chloride, bromide or iodide salts of the heavy group 2 elements, calcium, strontium or barium, and either 15-crown-5 or 18-crown-6 have been synthesized and their X-ray crystal structures determined. A variety of coordination modes are presented between the crown ether and metal ions.

Keywords: Group 2 metals; Crown ethers; Main group chemistry

1. Introduction

Since the groundbreaking discovery of crown ethers in the late 1960s [1, 2] they have enjoyed remarkable interest in coordination chemistry, supramolecular chemistry, as ion transport vehicles, ion selective hosts, and ion chromophores to name a few [3–6]. Much of this interest stems from the metallophilic, macrocyclic cavity that can adopt a conformation complementary to the ionic radius of a metal to be captured. An extraordinary amount of research has focused on binding of the alkali metals within the crown ethers and this is primarily associated with the size-fit of these metals with crown ethers of varying macrocyclic cavity diameter. It has been shown that for the alkali metals, if the ratio of the ionic diameter of the metal to that of the effective diameter of the macrocycle is 0.75 to 0.90 : 1, then direct ion-crown ether binding usually occurs [7]. Thus, for 18C8 (18-crown-6; cavity diameter 2.6 to 3.2 Å) [3] 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 other factors such as chelate ring size [8], contribute to the selectivity of 18C6 for the binding of K^+ over the other metals. Likewise, for 15C5 (cavity diameter 1.7 to 2.2 Å) [3] a ratio of 0.89 to 1.15 : 1 is obtained for Na^+ thereby reflecting the preference for that metal. We have found that for the alkaline earth ions, Ca^{2+}, Sr^{2+} and Ba^{2+}, (at least for the nitrates) similar arguments can be made for this size-fit ratio of crown ether to ionic size [9].

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We have previously reported on the structural diversity shown by 12-crown-4, 15-crown-5 and 18-crown-6 (the latter two macrocycles with nitrate counterions only) with Group 2 ions [9, 10]. For 12-crown-4 the cavity of the macrocycle is much too small for complete encapsulation of the group 2 ion and predominantly single face binding of the crown ether to the metal occurs, with the remaining coordination sites being occupied by water molecules, or anions [10]. For complexes involving 15-crown-5 or 18-crown-6 and $M(NO_3)_2$ ($M = Ca$, Sr, Ba) variable binding was found ranging from single face coordination where the crown ether cavity was too small for internal complexation, through sandwich formation (i.e. two crown ethers sandwiching a metal ion) for Ba^{2+} and 15C5, to complete encapsulation of the ion, for Sr^{2+} and Ba^{2+} with 18C6 [9]. Herein we extend this study to include the bromide, iodide and perchlorate salts of calcium strontium and barium with both 15-crown-5 and 18-crown-6 to complement the nitrate analogues previously reported.

2. Experimental

2.1. *Synthesis*

The synthesis of X-ray quality crystals of all compounds involved treatment of the respective group 2 salt with one molar equivalent of either 15-crown-5 or 18-crown-6 in deionised water. This typically required gentle warming to ensure complete dissolution. The solutions were then left to stand at ambient temperature until crystals suitable for X-ray structure determination were obtained. In all cases, samples suitable for structural studies were sought, and there was no attempt to optimise yields. We also included in this study reactions involving $Sr(ClO_4)_2$ with 15C5 and MBr_2 ($M = Sr$, Ba) with 18C6 and obtained crystalline material, but the structure solution and refinement of these datasets were thwarted by extensive twinning of the crystals and therefore we do not include these studies in the present contribution.

2.2. *Crystal structure determinations*

Compounds **1**–**7** and **9**–**14** were sealed and mounted in thin walled capillaries, with hemispheres of data collected at room temperature on a Bruker SMART CCD diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å) using the omega scan mode with total reflections and unique data listed below. Data sets were corrected for absorption using the program SADABS [11]. Structural solution and refinement was carried out using the SHELX suite of programs [12, 13] with the graphical interface X-Seed [14]. All non-hydrogen atoms were located and refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions (riding model) and were not refined, except those on water molecules that were located and refined using isotropic thermal parameters. Details of the X-ray data collection and refinements appear below.

A crystal of compound **8** was mounted on a thin glass fibre using a fast setting epoxy resin and cooled on a Nonius KappaCCD diffractometer to the temperature stated using an Oxford Cryostream low temperature attachment. A total of 90 oscillation frames each of width 2° in ϕ respectively and of 20 s exposure time were recorded.

The crystal was indexed from the first ten frames using the DENZO package [15] and positional data were refined along with diffractometer constants to give the final unit cell parameters. Integration and scaling (DENZO, Scalepack [15]) resulted in a unique data set corrected for Lorentz and polarisation effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction. The structure was solved using SHELXS-97 [12] and developed *via* alternating least squares cycles and difference Fourier synthesis (SHELXL-97) [13] with the aid of the program X-Seed [14]. All non-hydrogen atoms were modelled anisotropically, while hydrogen atoms are assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride, except where stated. Details of the X-ray data collection and refinements appear below.

Crystal data for $[Ca(15C5)(H_2O)_3](ClO_4)_2$ (1). $C_{10}H_{18}CaCl_2O_{16}$, $M = 505.22$, $0.30 \times 0.20 \times 0.15\,mm^3$, orthorhombic, space group $Pca2_1$ (No. 29), $a = 17.905(4)$, $b = 9.6035(19)$, $c = 12.880(3)$ Å, $V = 2214.7(8)$ Å^3, $Z = 4$, $D_c = 1.515\,g\,cm^{-3}$, $F_{000} = 1040$, $2\theta_{max} = 49.9°$, 2045 reflections collected, 2045 unique ($R_{int} = 0.0000$). Final GoF = 1.027, $R_1 = 0.0707$, $wR_2 = 0.1783$, R indices based on 1351 reflections with $I > 2\sigma(I)$ (refinement on F^2), 309 parameters, 10 restraints. Lp and absorption corrections applied, $\mu = 0.595\,mm^{-1}$. Absolute structure parameter = −0.02(14) [16].

Variata: Hydrogen atoms on the water molecules were located and refined isotropically. There was some disorder in the carbon atoms of the crown ether, but this was successfully modelled.

Crystal data for $[Ca(15C5)(H_2O)_3]Br_2$ (2) 15-c-5. $C_{10}H_{26}Br_2CaO_8$, $M = 474.21$, $0.30 \times 0.25 \times 0.20\,mm^3$, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.5067(10)$, $b = 15.6183(18)$, $c = 14.5382(17)$ Å, $\beta = 101.589(3)°$, $V = 1892.2(4)$ Å^3, $Z = 4$, $D_c = 1.665\,g\,cm^{-3}$, $F_{000} = 960$, $2\theta_{max} = 56.1°$, 12485 reflections collected, 4467 unique ($R_{int} = 0.2002$). Final GoF = 0.910, $R_1 = 0.0824$, $wR_2 = 0.1963$, R indices based on 1402 reflections with $I > 2\sigma(I)$ (refinement on F^2), 215 parameters, 39 restraints. Lp and absorption corrections applied, $\mu = 4.583\,mm^{-1}$.

Variata: Hydrogen atoms on the water molecules were located and refined isotropically.

Crystal data for $[Ca(15C5)(H_2O)_3]I_2$ (3). $C_{10}H_{26}CaI_2O_8$, $M = 568.19$, $0.25 \times 0.20 \times 0.12\,mm^3$, orthorhombic, space group $Pca2_1$ (No. 29), $a = 17.799(3)$, $b = 9.1752(16)$, $c = 12.456(2)$ Å, $V = 2034.2(6)$ Å^3, $Z = 4$, $D_c = 1.855\,g\,cm^{-3}$, $F_{000} = 1104$, $2\theta_{max} = 56.1°$, 12441 reflections collected, 4556 unique ($R_{int} = 0.0585$). Final GoF = 1.057, $R_1 = 0.0492$, $wR_2 = 0.1205$, R indices based on 3685 reflections with $I > 2\sigma(I)$ (refinement on F^2), 214 parameters, 100 restraints. Lp and absorption corrections applied, $\mu = 3.371\,mm^{-1}$. Absolute structure parameter = 0.00(5) [16].

Variata: Hydrogen atoms on the water molecules were located and refined isotropically.

Crystal data for $[Ba(15C5)_2](ClO_4)_2 \cdot 2H_2O$ (4). $C_{20}H_{44}BaCl_2O_{20}$, $M = 812.79$, $0.30 \times 0.30 \times 0.25\,mm^3$, monoclinic, space group $P2_1/n$ (No. 14), $a = 11.052(2)$,

$b = 13.233(3)$, $c = 12.462(3)$ Å, $p = 114.57(3)^\circ$, $V = 1657.5(6)$ Å^3, $Z = 2$, $D_c = 1.629$ g cm^{-3}, $F_{000} = 828$, $2\theta_{max} = 49.9^\circ$, 2986 reflections collected, 2827 unique ($R_{int} = 0.0182$). Final GoF = 1.240, $R_1 = 0.0877$, $wR_2 = 0.2598$, R indices based on 1991 reflections with $I > 2\sigma(I)$ (refinement on F^2), 197 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.437$ mm^{-1}.

Variata: Hydrogen atoms on the water molecules were not located from the difference map and are not included in the refinement.

Crystal data for [Ba(15C5)(H$_2$O)$_3$Br]Br • H$_2$O (5). $C_{10}H_{26}BaBr_2O_9$, $M = 587.47$, $0.25 \times 0.15 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.4723(10)$, $b = 9.2445(13)$, $c = 14.512(2)$ Å, $\alpha = 83.194(3)$, $\beta = 84.778(3)$, $\gamma = 88.557(2)^\circ$, $V = 991.1(2)$ Å^3, $Z = 2$, $D_c = 1.968$ g cm^{-3}, $F_{000} = 568$, $2\theta_{max} = 46.6^\circ$, 4604 reflections collected, 2846 unique ($R_{int} = 0.0514$). Final GoF = 1.010, $R_1 = 0.0462$, $wR_2 = 0.1125$, R indices based on 2330 reflections with $I > 2\sigma(I)$ (refinement on F^2), 225 parameters, 9 restraints. Lp and absorption corrections applied, $\mu = 6.069$ mm^{-1}.

Variata: Hydrogen atoms on the water molecules were located and refined isotropically.

Crystal data for [Ba(15C5)$_2$][Ba(15C5)(H$_2$O)$_4$]I$_4$ • 3H$_2$O (6). $C_{30}H_{54}Ba_2I_4O_{22}$, $M = 1549.01$, $0.25 \times 0.18 \times 0.12$ mm^3, triclinic, space group $P\bar{1}$ (No. 2), $a = 12.6643(10)$, $b = 14.7236(12)$, $\gamma = 17.1029(14)$ Å, $\alpha = 102.707(2)$, $\beta = 107.327(2)$, $\gamma = 103.895(2)^\circ$, $V = 2805.3(4)$ Å^3, $Z = 2$, $D_c = 1.834$ g cm^{-3}, $F_{000} = 1468$, $2\theta_{max} = 46.5^\circ$, 12976 reflections collected, 7992 unique ($R_{int} = 0.0430$). Final GoF = 1.038, $R_1 = 0.0528$, $wR_2 = 0.1392$, R indices based on 6413 reflections with $I > 2\sigma(I)$ (refinement on F^2), 506 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 3.658$ mm^{-1}.

Variata: Hydrogen atoms on the water molecules were not located from the difference map and are not included in the refinement. Crown ether C was rotationally disordered. There was some disorder in the carbon atoms of the crown ethers A and B and in water molecule (O4). All disorder was satisfactorily modelled.

Crystal data for [Ca(18C6)(H$_2$O)$_3$](ClO$_4$)$_2$ (7). $C_{12}H_{30}CaCl_2O_{17}$, $M = 557.34$, $0.22 \times 0.18 \times 0.15$ mm^3, monoclinic, space group Cc (No. 9), $a = 10.8879(11)$, $b = 16.7043(18)$, $c = 13.6799(14)$ Å, $\beta = 103.159(2)^\circ$, $V = 2422.7(4)$ Å^3, $Z = 4$, $D_c = 1.528$ g cm^{-3}, $F_{000} = 1168$, $2\theta_{max} = 46.5^\circ$, 5451 reflections collected, 3002 unique ($R_{int} = 0.0614$). Final GoF = 1.101, $R_1 = 0.0896$, $wR_2 = 0.2347$, R indices based on 2648 reflections with $I > 2\sigma(I)$ (refinement on F^2), 290 parameters, 2 restraints. Lp and absorption corrections applied, $\mu = 0.554$ mm^{-1}. Absolute structure parameter = 0.00 [16].

Variata: Water molecule (O3 S) was disordered over two sites. Hydrogen atoms on this solvent molecule were not located nor included in the refinement. Hydrogen atoms on water molecule (O1S) were located and refined isotropically. Both perchlorate ions were disordered and with high thermal motion. There was some disorder in carbon atoms of the crown ether.

Crystal data for [Ca(18C6)(H$_2$O)$_3$]Br • H$_2$O (8). $C_{12}H_{36}Br_2CaO_{12}$, $M = 572.31$, colourless plate, $0.60 \times 0.20 \times 0.15$ mm^3, monoclinic, space group $P2_1/c$ (No. 14),

$a = 8.1011(6)$, $b = 17.0768(10)$, $c = 17.8840(13)$ Å, $\beta = 101.290(4)°$, $V = 2426.2(3)$ Å^3, $Z = 4$, $D_c = 1.567$ g cm^{-3}, $F_{000} = 1176$, Mo-Kα radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K, $2\theta_{max} = 50.0°$, 11689 reflections collected, 4251 unique ($R_{int} = 0.1854$). Final GoF = 1.046, $R_1 = 0.0822$, $wR_2 = 0.1974$, R indices based on 3382 reflections with $I > 2\sigma(I)$ (refinement on F^2), 248 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 3.601$ mm^{-1}.

Variata: Water molecule (O12) was disordered over three sites and was successfully modeled. Hydrogen atoms on this solvent molecule were not located nor included in the refinement. Hydrogen atoms on the other water molecules were included as the riding model.

Crystal data for $[Ca(18C6)(H_2O)_3]I_2 \cdot H_2O$ (9). $C_{12}H_{32}CaI_2O_{10}$, $M = 630.26$, $0.30 \times 0.25 \times 0.20$ mm^3, monoclinic, space group $P2_1/n$ (No. 14), $a = 10.3846(8)$, $b = 17.1641(13)$, $c = 13.2955(10)$ Å, $\beta = 98.1490(10)°$, $V = 2345.9(3)$ Å^3, $Z = 4$, $D_c = 1.785$ g cm^{-3}, $F_{000} = 1240$, $2\theta_{max} = 46.6°$, 10484 reflections collected, 3365 unique ($R_{int} = 0.0565$). Final GoF = 1.021, $R_1 = 0.0318$, $wR_2 = 0.0760$, R indices based on 3055 reflections with $I > 2\sigma(I)$ (refinement on F^2), 260 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 2.938$ mm^{-1}.

Variata: Hydrogen atoms on the water molecules were located from the difference map and refinement isotropically.

Crystal data for $[Sr(18C6)(H_2O)_3]Cl_2 \cdot 2H_2O$ (10). $C_{12}H_{34}C_{12}O_{11}Sr$, $M = 512.91$, $0.30 \times 0.25 \times 0.20$ mm^3, monoclinic, space group Cc (No. 9), $a = 18.2134(17)$, $b = 7.7686(8)$, $c = 17.8373(17)$ Å, $\beta = 117.265(2)°$, $V = 2243.4(4)$ Å^3, $Z = 4$, $D_c = 1.519$ g cm^{-3}, $F_{000} = 1064$, $2\theta_{max} = 56.0°$, 7222 reflections collected, 4215 unique ($R_{int} = 0.0415$). Final GoF = 0.996, $R_1 = 0.0435$, $wR_2 = 0.1075$, R indices based on 3737 reflections with $I > 2\sigma(I)$ (refinement on F^2), 254 parameters, 2 restraints. Lp and absorption corrections applied, $\mu = 2.687$ mm^{-1}. Absolute structure parameter = 0.030(7) [16].

Variata: Hydrogen atoms on the water molecules were located from the difference map and refinement isotropically.

Crystal data for $[Sr(18C6)(H_2O)3]Br_2 \cdot H_2O$ (11). $C_{48}H_{128}Br_8O_{40}Sr_4$, $M = 2335.26$, $0.15 \times 0.15 \times 0.10$ mm^3, monoclinic, space group Pc (No. 7), $a = 14.7867(10)$, $b = 20.5042(14)$, $c = 15.6093(10)$ Å, $\beta = 109.49°$, $V = 4461.4(5)$ Å^3, $Z = 2$, $D_c = 1.738$ g cm^{-3}, $F_{000} = 2336$, $2\theta_{max} = 46.5°$, 20511 reflections collected, 9411 unique ($R_{int} = 0.0621$). Final GoF = 0.927, $R_1 = 0.0526$, $wR_2 = 0.1525$, R indices based on 4557 reflections with $I > 2\sigma(I)$ (refinement on F^2), 543 parameters, 2 restraints. Lp and absorption corrections applied, $\mu = 6.040$ mm^{-1}. Absolute structure parameter = 0.00 [16].

Variata: Not all hydrogen atoms on water molecules were located from the difference map. Those not located were not included in the refinement. Those that were located were refined isotropically.

Crystal data for $[Ba(18C6)(ClO_4)_2]$ (12). $C_{12}H_{24}BaCl_2O_{14}$, $M = 600.55$, $0.30 \times 0.30 \times 0.20$ mm^3, monoclinic, space group $P2_1/n$ (No. 14), $a = 8.3290(17)$, $b = 11.193(2)$, $c = 11.732(2)$ Å, $\beta = 98.33(3)°$, $V = 1082.1(4)$ Å^3, $Z = 2$,

$D_c = 1.843\,g\,cm^{-3}$, $F_{000} = 596$, $2\theta_{max} = 49.9°$, 2021 reflections collected, 1886 unique ($R_{int} = 0.0547$). Final GoF = 0.990, $R_1 = 0.0572$, $wR_2 = 0.1545$, R indices based on 1308 reflections with $I > 2\sigma(I)$ (refinement on F^2), 134 parameters, 18 restraints. Lp and absorption corrections applied, $\mu = 2.147\,mm^{-1}$.

Variata: The perchlorate ion had high thermal motion.

Crystal data for [Ba(18C6)(H$_2$O)$_3$Cl]Cl · 2H$_2$O (13). $C_{12}H_{34}BaCl_2O_{11}$, $M = 562.63$, $0.20 \times 0.18 \times 0.13$ mm, monoclinic, space group $P2_1/c$ (No. 14), $a = 10.671(2)$, $b = 7.4525(15)$, $c = 28.980(6)$ Å, $\beta = 97.995(4)°$, $V = 2282.3(8)$ Å^3, $Z = 4$, $D_c = 1.637\,g\,cm^{-3}$, $F_{000} = 1136$, $2\theta_{max} = 46.6°$, 10146 reflections collected, 3289 unique ($R_{int} = 0.0569$). Final GoF = 1.135, $R_1 = 0.0349$, $wR_2 = 0.1033$, R indices based on 2890 reflections with $I > 2\sigma(I)$ (refinement on F^2), 245 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 2.020\,mm^{-1}$.

Variata: Not all hydrogen atoms on water molecules were located from the difference map. Those not located were not included in the refinement. Those that were located were refined isotropically.

Crystal data for [Ba(18C6)(H$_2$O)$_3$]I$_2$ · 0.5H$_2$O (14). $C_{48}H_{124}Ba_4I_8O_{37}$, $M = 2858.03$, $0.40 \times 0.30 \times 0.30\,mm^3$, monoclinic, space group $P2_1$ (No. 4), $a = 15.3601(11)$, $b = 21.1719(16)$, $c = 16.1005(12)$ Å, $\beta = 107.7940(10)°$, $V = 4985.4(6)$ Å^3, $Z = 2$, $D_c = 1.904\,g\,cm^{-3}$, $F_{000} = 2712$, $2\theta_{max} = 46.6°$, 23137 reflections collected, 11749 unique ($R_{int} = 0.0551$). Final GoF = 1.034, $R_1 = 0.0555$, $wR_2 = 0.1543$, R indices based on 7369 reflections with $I > 2\sigma(I)$ (refinement on F^2), 455 parameters, 1 restraint. Lp and absorption corrections applied, $\mu = 4.103\,mm^{-1}$. Absolute structure parameter = 0.00 [16].

Variata: Hydrogen atoms on water molecules were not located from the difference map and were not included in the refinement.

3. Discussion

15C5 complexes of calcium salts: [Ca(15C5)(H$_2$O)$_3$](ClO$_4$)$_2$ (1), [Ca(15C5) (H$_2$O)$_3$]Br$_2$ (2), [Ca(15C5)(H$_2$O)$_3$]I$_2$ (3). Compounds **1**, **2** and **3** crystallize in the space groups $Pca2_1$, $P2_1/c$ and $Pca2_1$ respectively, each with one whole formula unit in the asymmetric unit. Interestingly the ClO_4^- and I^- salts are isomorphous, as has been described previously for rare earth complexes. Each of these complexes crystallizes as a cation/anion pair with an eight-coordinate $[Ca(15C5)(H_2O)_3]^{2+}$ cation and with the counter ions residing in the lattice with no cation/anion interactions so these will be discussed together. The crown ether cavity is too small to accommodate the Ca^{2+} ion, so favours a facial binding with the three water molecules in a *cisoid* piano-stool type arrangement (figure 1). This arrangement has been established previously in $[Ca(15C5)(H_2O)_3](UO_2Cl_4)$ [17] but is related to the simple SCN^- [18] and NO_3^- [9] analogues where either two SCN^- ions replace water molecules in the former, or two bidentate nitrate ions substitute for three water molecules in the latter, again in a *cisoid* fashion. The main difference between the present complexes and the SCN^- and NO_3^- salts is the lack of anion binding to calcium in compounds **1** to **3**.

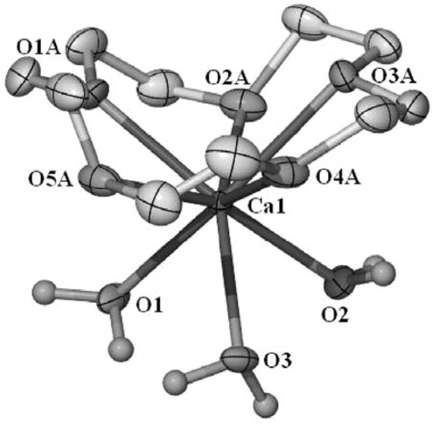

Figure 1. X-ray structure of the $[Ca(15C5)(H_2O)_3]^{2+}$ cation in $[Ca(15C5)(H_2O)_3](ClO_4)_2$ (**1**), $[Ca(15C5)(H_2O)_3]Br_2$ (**2**) and $[Ca(15C5)(H_2O)_3]I_2$ (**3**). Thermal ellipsoids are shown at the 20% level. Hydrogen atoms on the crown ether have been removed for clarity.

15C5 complexes of barium salts: $[Ba(15C5)_2](ClO_4)_2 \cdot 2H_2O$ (4), $[Ba(15C5)(H_2O)_3Br]Br \cdot H_2O$ (5), $[Ba(15C5)_2][Ba(15C5)(H_2O)_4]I_4 \cdot 3H_2O$ (6). The three complexes involving barium salts and 15C5 result in varying structural motifs. These range from the true sandwich cation in compound **4** where two crown ethers bind to one barium ion (figure 2), a barium ion with one face bound by a 15C5 molecule as well as three water ligands and bromide in compound **5** (figure 3) through to a mixed complex involving the sandwich cation $[Ba(15C5)_2]^{2+}$ as well as a facially bound 15C5 molecule and four *cisoid* water molecules within the one complex in compound **6** (figure 4). $[Ba(15C5)_2]Br_2 \cdot 2H_2O$ [19] has been previously published with a similar sandwich cation to that in compound **4** and one of the cations in **6**. Interestingly, in our studies, the only salt not containing this sandwich cation is compound **5** where the counterion is also bromide, thus establishing a new structural type for $BaBr_2$ complexed by 15C5.

18C6 complexes of calcium salts: $[Ca(18C6)(H_2O)_3](ClO_4)_2$ (7), $[Ca(18C6)(H_2O)_3]Br_2 \cdot 3H_2O$ (8), $[Ca(18C6)(H_2O)_3]I_2 \cdot H_2O$ (9) and 18C6 complexes of strontium salts: $[Sr(18C6)(H_2O)_3]Cl_2 \cdot 2H_2O$ (10), $[Sr(18C6)(H_2O)_3]$ $Br_2 \cdot H_2O$ (11). Compounds **7**, **8**, **9**, **10** and **11** crystallize in the monoclinic space groups *Cc*, $P2_1/c$, $P2_1/n$, *Cc* and *Pc* respectively, each with one whole structural formula comprising the asymmetric unit. The three calcium and two strontium complexes crystallize with a similar structural motif, *viz*. with a $[Ca(18C6)(H_2O)_3]^+$ cation (figure 5) with the anions and (in the case of **8**, **9**, **10** and **11)** water molecules residing in the lattice and being involved in a hydrogen bonded array. The only difference in formulation of all these compounds is in the number of lattice solvent water molecules. The cation found here is also similar in nature to those of $[Sr(18C6)(H_2O)_3]Cl_2 \cdot 2H_2O$ (**10**), $[Sr(18C6)(H_2O)_3]Br_2 \cdot H_2O$ (**11**) and $[Ba(18C6)(H_2O)_3]I_2 \cdot 0.5H_2O$ (**14**) except there are differences in the planarity/folding of the 18C6 macrocycle. Due to differing ionic radii of the group 2 cations, the flexibility of the 18C6 ligand allows it to fold "taco-style" to maximize the interaction of the heteroatoms with the metal ion. However, it also appears that crystal packing, or

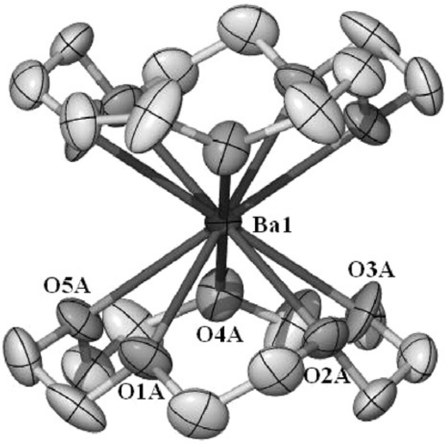

Figure 2. X-ray structure of the $[Ba(15C5)_2]^{2+}$ cation in $[Ba(15C5)_2](ClO_4)_2 \cdot 2H_2O$ (**4**). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms on the crown ether have been removed for clarity.

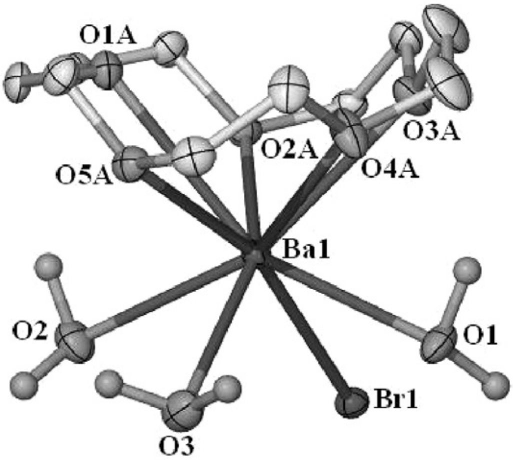

Figure 3. X-ray structure of the $[Ba(15C5)(H_2O)_3Br]^+$ cation in $[Ba(15C5)(H_2O)_3Br]Br \cdot H_2O$ (**5**). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms on the crown ether have been removed for clarity.

anion effects may dictate the folding of the crown ether. In compound **14**, the crown ether lies relatively flat with all O atoms of the crown within 0.20 Å of the least squares plane defined by all six oxygen atoms (the Ba^{2+} ion resides 0.43 Å outside this plane). In compounds **10** and **11**, where the cation is essentially the same, the folding of the crown (as defined by the angle between the least squares planes identified by O2,3,4,5 and O5,6,1,2 see figure 5; with O atoms O2 and O5 as the pivots) gives angles of 46.8(2)° and 19.1(7)° respectively. Therefore, the size of the cation here is not the overriding reason for the folding. Similarly, the analogous angles in compounds **7**, **8** (56.2(3), and 54.8(2) respectively) are significantly wider than in compound **9** where the angle is

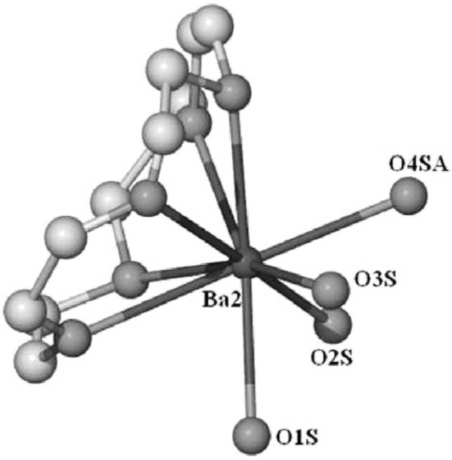

Figure 4. X-ray structure of the $[Ba(15C5)(H_2O)_4]^{2+}$ cation in $[Ba(15C5)_2][Ba(15C5)(H_2O)_4]I_4 \cdot 3H_2O$ (**6**). The $[Ba(15C5)_2]^{2+}$ cation shown in figure 2 is also present in **6**. Atoms are shown as spheres only. Hydrogen atoms have been removed for clarity.

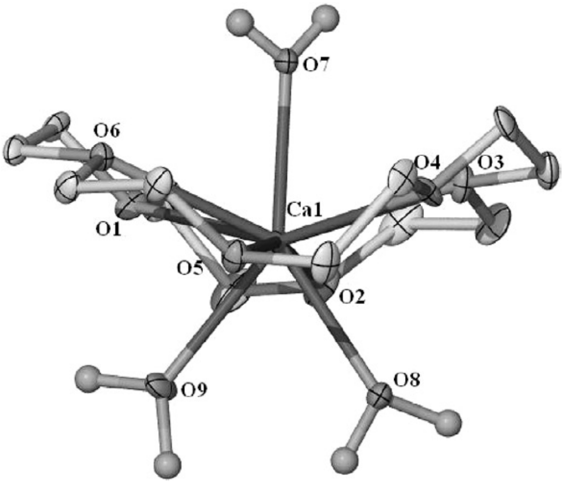

Figure 5. X-ray structure of the $[Ca(18C6)(H_2O)_3]^{2+}$ cation in $[Ca(18C6)(H_2O)_3]Br_2 \cdot 3H_2O$ (**8**). The $[M(18C6)(H_2O)_3]^{2+}$ cation has a similar structure in $[Ca(18C6)(H_2O)_3](ClO_4)_2$ (**7**), $[Ca(18C6)(H_2O)_3]I_2 \cdot H_2O$ (**9**), $[Sr(18C6)(H_2O)_3]Cl_2 \cdot 2H_2O$ (**10**), $[Sr(18C6)(H_2O)_3]Br_2 \cdot H_2O$ (**11**), $[Ba(18C6)(H_2O)_3]I_2 \cdot 0.5H_2O$ (**14**). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms on the crown ether have been removed for clarity.

47.13(9)° and similar to compound **10**. Even though Ca^{2+}, Sr^{2+} and Ba^{2+} have quite different ionic radii (1.18, 1.31 and 1.47 Å for nine-coordinate metals, respectively) [20] the coordination number about the metal ions in compounds **7** to **11** and **14** do not change, rather the macrocycle adopts differing shape/orientation to satisfy the metal's coordination requirements.

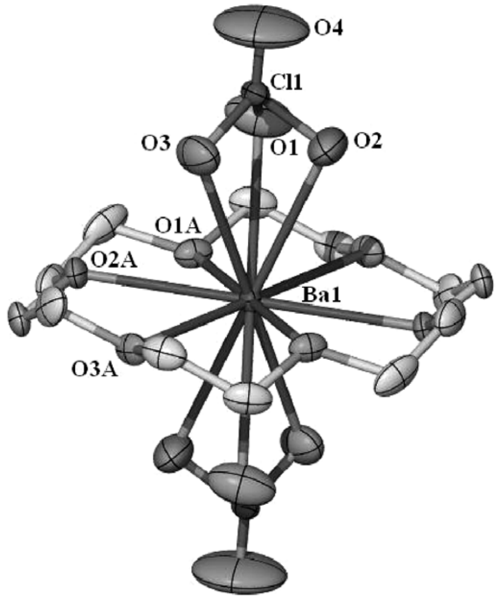

Figure 6. X-ray structure of the anhydrous [Ba(18C6)(ClO_4)$_2$] (**12**). Thermal ellipsoids are shown at the 20% level. Hydrogen atoms on the crown ether have been removed for clarity.

18C6 complexes of barium salts: [Ba(18C6)(ClO_4)$_2$] (12), [Ba(18C6)(H_2O)$_3$Cl]Cl_2 · H_2O (13), and [Ba(18C6)(H_2O)$_3$]I_2 · 0.5H_2O (14). Compounds **12** and **13** crystallize in the monoclinic space groups $P2_1/n$ and $P2_1/c$, respectively, with the barium atom in **12** residing on an inversion centre and therefore half the formula unit comprises the asymmetric unit and in **13** one whole molecular formula comprises the asymmetric unit. Compound **14** crystallizes in the monoclinic space group $P2_1$ with four similar [Ba(18C6)(H_2O)$_3$]I_2 · 0.5H_2O structural entities comprising the asymmetric unit (this compound will not be discussed any further, see above for structural discussion, and see figure 5). Compound **12** crystallizes as a molecular unit, rather than a cation/anion array with the barium atom residing in the cavity of the 18C6 macrocycle and two ClO_4^- ligands chelating the metal ion on either side of the crown ether (figure 6). While ClO_4^- is not typically a strongly coordinating anion, there are many examples in the literature and the group 2 metals are no exception to this [21] although under aqueous conditions, one might expect water molecules to bind to Ba^{2+} in preference to perchlorate. Compound **13** crystallizes with a similar structural motif to compounds **7**–**11** and **14**, where the crown ether encapsulates the metal ion with one water molecule metal-bound on one face of the crown and the remaining ligands bound on the other face. However, in the case of compound **13**, rather then two water molecules being bound on the opposing face, we now, rather surprisingly find two water molecules and a chloride atom completing the 10-coordination about Ba^{2+} (compounds **7**–**11** and **14** were all nine-coordinate, see above) (see figure 7). In compound **13**, like compound **14** (above), the O atoms of the crown ether are almost coplanar with all O atoms within 0.20 Å

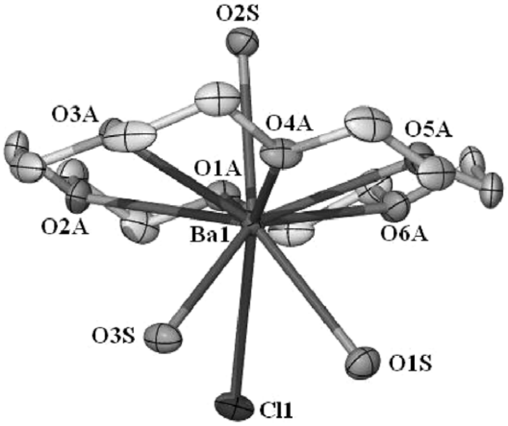

Figure 7. X-ray structure of the $[Ba(18C6)(H_2O)_3Cl]^+$ cation in $[Ba(18C6)(H_2O)_3Cl]Cl \cdot 2H_2O$ (**13**). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been removed for clarity.

of the least squares plane defined by all six oxygen atoms (the Ba^{2+} ion resides 0.75 Å outside this plane).

In all compounds except **12**, where an anhydrous species was obtained, the crystal packing is dominated by hydrogen bonding between water molecules and other water, or with halide ions. The hydrogen bonding networks are typical for these types of compounds and do not require any further discussion.

4. Conclusions

For the group 2 ions Ca^{2+}, Sr^{2+} and Ba^{2+}, 18C6 generally completely encapsulates the metal ion when the perchlorates or halides are crystallized from aqueous conditions providing $[M(18C6)(H_2O)_3]^{2+}$ cations. However, we have found that $BaCl_2$ crystallizes with a similar cationic motif, except that now a chloride ligand is metal bound and $Ba(ClO_4)_2$ crystallizes as an anhydrous species with bidentate ClO_4^- ligands bound to the Ba atom on either side of the crown ether. When crystallized in the presence of 15C5, the calcium salts crystallize with the $[Ca(15C5)(H_2O)_3]^{2+}$ cation dominating, while barium salts yield a variety of structural types.

Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 611446–611459. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223 336-033; Email: deposit@ccdc.cam.ac.uk).

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[21] For some relevant examples, see reference [10].