Intramolecular C–H···π interactions influence the conformation of *N*,*N*′-dibenzyl-4,13-diaza-18-crown-6 molecules

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Interaction of $La(NO_3)_3.6H_2O$, $Eu(NO_3)_3.6H_2O$, $UO_2(NO_3)_2.6H_2O$ or hydrobromic acid with *N*,*N*′-dibenzyl-4,13-diaza-18-crown-6 leads to double protonation of the N-containing heterocycle, affording $[(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6]$[La(NO_3)_5(H_2O)]$ (**1**), $[(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6]$[Eu(NO_3)_5(H_2O)]$ (**2**), $[(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6]$[(\mu\text{-}OH)_2\{UO_2(NO_3)_2\}_2]$ (**3**) and $(H_9O_4{}^+)_2[(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6]Br_4 (**5**). The X-ray crystal structures of each compound were obtained, revealing unusual C–H···π interactions between the phenyl substituents and two macrocyclic methylene protons that govern the overall conformation of the macrocycle. We also report the X-ray crystal structure of the related $[(H_2O)_2(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6]$[UO_2Cl_4]$ (**4**), which, surprisingly, does not have the same conformation of the cation, rather, two molecules of water bind to the inner cavity of the crown ether.

Introduction

The crown ether family of macrocyclic compounds has attracted a huge amount of interest since their discovery in 1967,[1,2] especially in the fields of host–guest and coordination chemistry. Early studies involving these compounds were centered on the investigation of the binding of alkali and early alkaline earth metal ions within the macrocyclic cavity, and determining factors which influence this coordination, such as macrocycle diameter, counter ion type and solvent.[3–7] It was subsequently found that by introducing different heteroatoms into the ring, mainly nitrogen, that not only were the coordination properties modified, but that various substituents could be added onto the ring, providing another avenue for investigation of the coordination properties of these new species.[8–13]

In the course of studying the coordination properties of these ligands, and in particular *N*,*N*′-disubstituted diaza-18-crown-6, other exciting interactions have surfaced.[14–16] For example, in *N*,*N*′-dibenzyl, *N*,*N*′-dinaphthyl and *N*,*N*′-dianthryl-substituted diaza-18-crown-6 complexes, a range of C–H···O and C–H···N interactions are reported to significantly affect the conformation of the macrocyclic ring and the ability of the crown to bind ions.[14–20]

Recently, the coordination chemistry between crown ethers and the f-block elements, particularly the lanthanoids, has become a very popular field of endeavour.[21–25] Previous studies have shown that lanthanoid salts participate in a wide variety of coordination bonding with crown ethers, depending on the cavity size of the ligand, the presence of any substituents on the crown ether, the particular metal and the solvent used.[24,26,27] Uranyl complexes have also shown an affinity for binding with crown ether macrocycles, depending on the size of the crown ether cavity.[28–30] As part of our investigation into the coordination properties of various f-block metal salts with crown ethers and their derivatives, we have studied the binding of lanthanoid salts with *N*,*N*′-dibenzyl-4,13-diaza-18-crown-6 and find that some further very interesting C–H···π interactions arise which affect the conformation of the crown ether. We report here the synthesis and crystal structures of $[(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6]$[La(NO_3)_5(H_2O)]$ (**1**), $[(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6]$[Eu(NO_3)_5(H_2O)]$ (**2**) and $[(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6]$[(\mu\text{-}OH)_2\{UO_2(NO_3)_2\}_2]$ (**3**). Altering the anions bound to the uranyl centre to chloride results in the coordination of water molecules by the macrocycle, thus altering the conformation of the azacrown ligand, as evidenced in the crystal structure of $[(H_2O)_2(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6]$[UO_2Cl_4]$ (**4**). Varying the entire anion considerably from the large lanthanoid or actinoid complex anions to the bromide ion does not affect the conformation of the macrocyclic cation, as demonstrated by the synthesis and X-ray crystal structure of $(H_9O_4{}^+)_2[(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6]Br_4 (**5**).

Experimental

Uranyl nitrate, europium nitrate, lanthanum nitrate and 48% hydrobromic acid were purchased from Aldrich and used without further purification. *N*,*N*′-dibenzyl-4,13-diaza-18-crown-6 was synthesized by literature methods.[8–10,31] Infrared spectra were recorded from Nujol mulls on sodium chloride plates using a Nicolet Nexus FTIR spectrophotometer. ^1H NMR spectra were recorded at 300 MHz on a Varian Oxford 300 NMR spectrometer and were measured relative to D_2O (δ 4.80 ppm). Melting points were measured in unsealed glass capillaries.

Syntheses

$[(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6]$[La(NO_3)_5(H_2O)]$ (1). Lanthanum nitrate hexahydrate (0.1 g; 0.25 mmol), was added to an aqueous solution of *N*,*N*′-dibenzyl-4,13-diaza-18-crown-6 (0.10 g) in equimolar stoichiometry. Gentle heating aided dissolution. This solution was left open to the atmosphere

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for several weeks, which yielded colourless X-ray quality crystals in approximately 80% yield. Calc. for $C_{26}H_{42}N_7O_{20}La$: H, 4.64; C, 34.26; N, 10.76; found: H, 4.63; C, 34.24; N, 10.85%; IR (Nujol): 3376 s(br), 2359 w, 1638 w, 1322 w, 1202 w, 1161 w, 1100 m, 1031 m, 969 m, 942 w, 819 m, 810 w, 747 w, 733 m, 703 m cm^{-1}; ^{1}H NMR: δ 4.3 (s, 4 H, CH_2Ph), 4.6 (m, 24 H, OCH_2CH_2), 7.3 (m, 10 H, Ph).

[(H$^+$)$_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6][Eu(NO$_3$)$_5$(H$_2$O)] (2). Compound **2** was prepared in a similar manner to **1** using europium nitrate hexahydrate (0.1 g; 0.25 mmol), which yielded colourless X-ray quality crystals in approximately 70% yield. Calc. for $C_{26}H_{42}N_7O_{20}Eu$: H, 4.58; C, 33.77; N, 10.60; found: H, 4.64; C, 34.26; N, 10.76%; IR (Nujol): 3564 s(br), 3153 w, 2480 w, 2327 w, 1829 w, 1774 w, 1738 w, 1634 s, 1161 m, 1100 s(br), 1034 m, 970 m, 942 m, 902 m, 882 w, 817 s, 784 m, 740 s, 703 m cm^{-1}; ^{1}H NMR δ 4.3 (s, 4 H, CH_2Ph), 4.6 (m, 24 H, OCH_2CH_2), 7.3 (m, 10 H, Ph).

[(H$^+$)$_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6][(μ-OH)$_2${UO$_2$(NO$_3$)$_2$}$_2$] (3). Compound **3** was prepared in a similar manner to **1** using uranyl nitrate hexahydrate (0.1 g; 0.23 mmol), which yielded bright yellow X-ray quality crystals in approximately 60% yield. Repeated attempts to obtain a reproducible microanalysis were unsuccessful. IR (Nujol): 3153 w, 2327 w, 1829 w, 1774 w, 1738 w, 1634 s, 1100 s(br), 1034 m, 971 w, 898 s, 784 w, 703 m cm^{-1}; ^{1}H NMR δ 4.3 (s, 4 H, CH_2Ph), 4.6 (m, 24 H, OCH_2CH_2), 7.3 (m, 10 H, Ph).

[(H$_2$O)$_2$(H$^+$)$_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6][UO$_2$Cl$_4$] (4). Compound **4** was prepared in a similar manner to **1** using uranyl nitrate hexahydrate (0.1 g; 0.23 mmol) and several drops of 2 M HCl to aid dissolution, which yielded cubic, dark yellow X-ray quality crystals Yields were not maximised. Calc. for $C_{26}H_{44}N_2O_8Cl_4U_1$: H, 4.97; C, 34.99; N, 3.14; found: H, 4.85; C, 34.58; N, 4.51%; IR (Nujol): 3451 s, 1733 w, 1652 s, 1378 m, 1205 s, 1100 s, 1029 m, 910 s, 708 m, 635 m, 480 m cm^{-1}.

(H$_9$O$_4$$^+$)$_2$[(H$^+$)$_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6]Br$_4$ (5). Dilute HBr was added to an aqueous solution containing 0.1 g of *N*,*N*′-dibenzyl-4,13-diaza-18-crown-6. After stirring for several hours, the sample was left open to the atmosphere, which, after several weeks, yielded X-ray quality crystals in approximately 60% yield. Calc. for $C_{13}H_{29}N_1O_6Br_2$: H, 6.42; C, 34.30; N, 3.08; found: H, 6.14; C, 34.37; N, 2.48%; IR (Nujol): 3397 (br), 1204 w, 1105 m, 939 w, 810 w, 783 w, 747 s, 707 m cm^{-1}. ^{1}H NMR δ 4.3 (s, 4 H, CH_2Ph), 4.6 (m, 24 H, OCH_2CH_2), 7.3 (m, 10 H, Ph).

X-Ray crystallographic studies

For compounds **1**, **2**, **3** and **5**, X-ray quality crystals were sealed and mounted in thin-walled capillaries, with hemispheres of data collected at room temperature on a Bruker SMART CCD diffractometer using the omega scan mode. Data sets were corrected for absorption using the program SADABS.[32] For compound **4**, a single crystal was mounted on a glass fibre and immersed in a nitrogen stream cooled to −150 °C. Data were collected on a Nonius $^{\mathrm{KAPPA}}$CCD diffractometer and, after integration and scaling, resulted in a unique data set corrected for Lorentz and polarization 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. For all structures, the positions of the heavy atoms were found using the Patterson method for heavy atoms and refined on F^2 using SHELXL97-2[33] with X-SEED as the graphic interface.[34] All non-hydrogen atoms were located and were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions (riding model) and were not refined. Crystal data, and a summary of data collection are listed below, while selected bond distances and angles appear in Tables 1 and 2.

CCDC reference numbers 185604–185608. See http://www.rsc.org/suppdata/nj/b2/b203646k/ for crystallographic data in CIF or other electronic format.

Crystal refinement data

[(H$^+$)$_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6][La(NO$_3$)$_5$(H$_2$O)] (1). $C_{26}H_{42}N_7O_{20}La$, $M = 911.58$, triclinic, $P\bar{1}$, $a = 9.146(3)$, $b = 13.686(5)$, $c = 16.544(6)$ Å, $\alpha = 68.401(6)$, $\beta = 74.777(6)$, $\gamma = 87.234(6)°$, $V = 1855.1(11)$ Å^3, $Z = 2$, calculated density = 1.632 mg m^{-3}, $\mu_{\mathrm{Mo}} = 1.241$ mm^{-1}, $F(000) = 928$, crystal size 0.22 mm × 0.20 mm × 0.15 mm, reflections collected = 8578, unique reflections = 5263 ($R_{\mathrm{int}} = 0.0467$), $R1$ [$I > 2\sigma(I)$] = 0.0340, $wR2$ (all data) = 0.0860.

[(H$^+$)$_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6][Eu(NO$_3$)$_5$(H$_2$O)] (2). $C_{26}H_{42}N_7O_{20}Eu$, $M = 924.63$, triclinic, $P\bar{1}$, $a = 9.1065(5)$, $b = 13.5946(8)$, $c = 16.5192(10)$ Å, $\alpha = 68.5780(1)$, $\beta = 75.0350(10)$, $\gamma = 87.5710(10)°$, $V = 1836.14(18)$ Å^3, $Z = 2$, calculated density = 1.672 mg m^{-3}, $\mu_{\mathrm{Mo}} = 1.799$

Table 1 (i) C···centroid and H···centroid bond distances (Å), and (ii) C–H···centroid bond angles (°), for compounds **1**–**3** and **5**

[(H$^+$)$_2$*N*,*N*′-dibenzyl-4,13-diaza18-crown-6][La(NO$_3$)$_5$(H$_2$O)] (**1**)			
C(11)···centroid	3.830[a]	H11B···centroid	2.883[a]
C(24)···centroid	3.931[a]	H24A···centroid	2.987[a]
C11–H11b–centroid	165.6[a]	C24–H24A–centroid	164.7
[(H$^+$)$_2$*N*,*N*′-dibenzyl-4,13-diaza18-crown-6][Eu(NO$_3$)$_5$(H$_2$O)] (**2**)			
C(11)···centroid	3.846[a]	H11B···centroid	2.899[a]
C(24)···centroid	3.919[a]	H24A···centroid	2.974[a]
C11–H11B–centroid	165.6	C24–H24A–centroid	165.0
[(H$^+$)$_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6][(μ-OH)$_2${UO$_2$(NO$_3$)$_2$}$_2$)] (**3**)			
C(10)···centroid	3.693[a]	H10A···centroid	2.731[a]
C10–H10A–centroid	170.8		
(H$_9$O$_4$$^+$)$_2$[(H$^+$)$_2$*N*,*N*′-dibenzyl-4,13-diaza18-crown-6]Br$_4$ (**5**)			
C(11)···centroid	3.884	H11B···centroid	2.950
C11–H11B–centroid	170.8		

[a] E.s.d.s not given because centroid position was not refined.

Table 2 Hydrogen-bonding distances (Å) and angles (°) for compounds **1**–**5**

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠DHA
[$(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza18-crown-6][$La(NO_3)_5(H_2O)$] (**1**)				
O(16)–H(16A)···O(15)[a]	0.996(10)	1.806(17)	2.786(5)	167(5)
O(16)–H(16B)···O(12)[b]	0.994(10)	1.929(16)	2.905(5)	167(4)
N(6)–H(6C)···O(17)	0.80(4)	2.33(4)	2.704(5)	110(3)
N(6)–H(6C)···O(20)	0.80(4)	2.36(4)	2.865(5)	122(3)
N(7)–H(7C)···O(18)	0.87(4)	2.36(4)	2.849(5)	116(3)
[$(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza18-crown-6][$Eu(NO_3)_5(H_2O)$] (**2**)				
O(16)–H(16B)···O(12)[b]	0.88(9)	2.16(9)	2.955(5)	150(8)
O(16)–H(16A)···O(15)[a]	0.70(4)	2.12(4)	2.815(5)	178(5)
O(16)–H(16B)···O(4)	0.88(9)	2.40(8)	2.833(5)	117(7)
N(6)–H(6A)···O(20)	0.82(4)	2.36(4)	2.868(5)	121(4)
N(7)–H(7A)···O(18)	0.90(5)	2.27(5)	2.848(4)	122(4)
[$(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6][$(\mu\text{-}OH)_2\{UO_2(NO_3)_2\}_2$)] (**3**)				
O(3)–H(3S)···O(9)[c]	1.002(10)	1.92(3)	2.880(10)	159(6)
N(3)–H(2)···O(1C)	0.86(7)	2.29(7)	2.813(12)	119(5)
[$(H_2O)_2(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6][UO_2Cl_4] (**4**)				
O(1S)–H(1S)···O(2)	1.02(3)	2.32(14)	2.823(8)	109(9)
N(3)–H(1N)···O(1S)	0.87(9)	1.90(10)	2.769(9)	178(9)
$(H_9O_4{}^+)_2[(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza18-crown-6]Br_4 (**5**)				
N(1)–H(1)···O(1)	0.89(5)	2.20(5)	2.707(6)	116(4)
O(2S)–H(2SC)···O(3S)	0.73(8)	1.83(9)	2.550(8)	164(9)
O(1S)–H(1SA)···Br(2)	0.999(10)	2.349(10)	3.285(6)	156(3)
O(2S)–H(2SA)···O(4S)	1.003(10)	1.49(4)	2.455(9)	158(9)
O(4S)–H(4SA)···Br(2)[d]	1.021(10)	2.35(9)	3.212(7)	143(9)
O(1S)–H(1SB)···Br(1)[e]	1.000(10)	2.46(4)	3.318(5)	143(5)
O(2S)–H(2SB)···O(1S)	1.001(10)	1.509(13)	2.510(8)	178(7)
O(3S)–H(3SB)···Br(1)	0.998(10)	2.35(5)	3.299(5)	160(9)
O(4S)–H(4SB)···Br(1)[b]	1.027(10)	2.50(14)	3.220(6)	127(9)

Symmetry transformations used to generate equivalent atoms:[a] $-x+1, -y+2, -z+1$. [b] $x-1, y, z$. [c] $-x-1, -y, -z$. [d] $-x, -y+2, -z$. [e] $-x+1, -y+1, -z$.

mm^{-1}, $F(000) = 940$, crystal size 0.22 mm × 0.20 mm × 0.18 mm, reflections collected = 8533, unique reflections = 5247 ($R_{\text{int}} = 0.0370$), $R1$ [$I > 2\sigma(I)$] = 0.0311, $wR2$ (all data) = 0.0794.

[$(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6][$(\mu\text{-}OH)_2\{UO_2(NO_3)_2\}_2$] (3). $C_{26}H_{40}N_6O_{22}U_2$, $M = 1264.70$, triclinic, $P\bar{1}$, $a = 8.1390(7)$, $b = 10.6432(10)$, $c = 12.1312(11)$ Å, $\alpha = 102.865(2)$, $\beta = 102.057(2)$, $\gamma = 91.201(2)°$, $V = 999.37(16)$ Å^3, $Z = 1$, calculated density = 2.101 mg m^{-3}, $\mu_{\text{Mo}} = 8.181$ mm^{-1}, $F(000) = 598$, crystal size 0.22 mm × 0.20 mm × 0.15 mm, reflections collected = 4565, unique reflections = 2837 ($R_{\text{int}} = 0.0520$), $R1$ [$I > 2\sigma(I)$] = 0.0399, $wR2$ (all data) = 0.0976.

[$(H_2O)_2(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6)][UO_2Cl_4] (4). $C_{26}H_{44}Cl_4N_2O_8U$, $M = 829.46$, monoclinic, $P2_1/n$, $a = 8.7820(18)$, $b = 12.828(3)$, $c = 14.755(3)$ Å, $\beta = 89.84(3)°$, $V = 1662.2(6)$ Å^3, $Z = 2$, calculated density = 1.783 mg m^{-3}, $\mu_{\text{Mo}} = 5.251$ mm^{-1}, crystal size 0.30 mm × 0.35 mm × 0.35 mm, reflections collected = 11196, unique reflections = 3958 ($R_{\text{int}} = 0.0497$), $R1$ [$I > 2\sigma(I)$] = 0.0501, $wR2$ (all data) = 0.1519.

$(H_9O_4{}^+)_2[(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6]Br_4 (5). $C_{13}H_{28}Br_2NO_6$, $M = 454.18$, triclinic, $P\bar{1}$, $a = 8.199(4)$, $b = 9.361(4)$, $c = 13.206(6)$ Å, $\alpha = 92.867(9)$, $\beta = 95.030(9)$, $\gamma = 96.817(9)°$, $V = 1000.6(8)$ Å^3, $Z = 2$, calculated density = 1.511 mg m^{-3}, $\mu_{\text{Mo}} = 4.07$ mm^{-1}, $F(000) = 464$, crystal size 0.30mm × 0.30 mm × 0.26 mm, reflections collected = 4623, unique reflections = 2832 ($R_{\text{int}} = 0.0928$), $R1$ [$I > 2\sigma(I)$] = 0.0574, $wR2$ (all data) = 0.1681.

Results and discussion

The syntheses of all the compounds involved addition of the hydrated metal salt or hydrobromic acid directly to a stirred, aqueous solution of the azacrown ether. Moderate heating was required to complete full dissolution, and it was necessary to adjust the pH to approximately 4 with dilute nitric acid before full dissolution occurred. The yields for these reactions tended to be low due to the hygroscopic nature of the products. The NMR spectra for [$(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6][$Eu(NO_3)_5(H_2O)$] (**2**) and [$(H^+)_2$*N*,*N*′-4,13-diaza-dibenzyl-diaza-18-crown-6][$Br]_2$ (**5**) were recorded in D_2O and were similar to those reported previously for the naked ligand,[8–10] however, the chemical shifts associated with the methylene groups of the crown and the bridging groups from the crown to the aromatic rings were shifted to a higher frequency. This can be attributed to de-shielding of the protons *via* interactions of the folded aromatic groups. It was possible to obtain two different products from the combination of uranyl nitrate and the azacrown ligand. The use of nitric acid to adjust the pH yielded [$(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6][$(\mu\text{-}OH)_2\{UO_2(NO_3)_2\}_2$] (**3**), and the use of HCl produced the chloride derivative [$(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6][UO_2Cl_4] (**4**). Repeated attempts to obtain meaningful analyses of the hydroxide dimer yielded results that suggested the dimer dissociates to yield the hydrated nitrate.

The infrared data shows C–O ether stretches (1202 and 1322 cm^{-1}) and broad N–H stretches (around 3376 cm^{-1}). The presence of free water was also observed (3154 cm^{-1}). The nitrate groups in **1**, **2** and **3** give rise to nitrate asymmetric stretches (1638 cm^{-1}), which are absent in **4** and **5**.

Lanthanoid complexes

1 and **2** are isomorphous and crystallise in the centrosymmetric space group $P\bar{1}$, with the asymmetric unit containing an

11-coordinate, anionic $[Ln(NO_3)_5(H_2O)]^{2-}$ species and a doubly protonated $[(H^+)_2$*N*,*N′*-dibenzyl-4,13-diaza-18-crown-6] cation (Fig. 1). Previous studies involving both substituted and non-substituted neutral azacrown ethers have indicated that the lighter lanthanoid species (La–Sm) tend to form inclusion-type compounds, with a neutral, hydrated metal salt incorporated into the macrocyclic cavity, even in the presence of large aromatic substituents; *e.g.* [(*N*,*N′*-dibenzyl-4,13-diaza-18-crown-6)$\{La(NO_3)_3\}$] and [(*N*,*N′*-dibenzyl-4,13-diaza-18-crown-6)$\{Ce(SCN)_3\}$][9,10,14,15] In contrast, protonation of the azacrown ether inhibits inclusion of the lanthanoid species, affording complex metal anion species interspersed between a network of crown molecules. A similar species has previously been reported.[35]

The metal ion is formally 11-coordinate if the five nitrates are considered bidentate, with the monodentate water molecule completing the coordination sphere of the lanthanoid metal. However, if the small bite angle nitrates are considered monodentate, the coordination sphere about the lanthanoid center is pentagonal bipyramidal, with four nitrate ligands in equatorial positions, the orientation of which yields a propeller-like appearance, and a further nitrate and a water molecule in the axial positions (Fig. 2). The La–O bond lengths are similar to the closely related $[La(NO_3)_5{\cdot}MeOH]^{2-}$ species,[26] with the Eu–O bond lengths shortened by the amount expected due to the decrease in ionic radius.[36]

The geometry of the azacrown ring is close to planar and exhibits a degree of rigidity not normally observed for non-coordinated crown ether molecules such as this.[8,17,37,38] This rigidity probably stems from the presence of C–H···π interactions between two methylene hydrogens and the aromatic substituents (Fig. 1), which effectively anchor the ring into its present conformation and inhibits flexing, which has often been observed with macrocycles of this type.[38,39] This type of interaction is quite unusual in that a methylene hydrogen is participating in this interaction, rather than the hydrogen of a water molecule or other common hydrogen-bonding donor which has been reported previously.[18,20] The C···centroid distances of 3.931 and 3.830 Å for **1**, and 3.846 and 3.919 Å for **2**, however, are consistent with previous arguments for this type of interaction,[16,18,19,35,40] and, furthermore, the C–H··· centroid angles of 165.6 and 164.7° for **1**, and 165.0 and 165.6° for **2** suggests the π···H interactions at the centre of the aromatic ring are the strongest.[18]

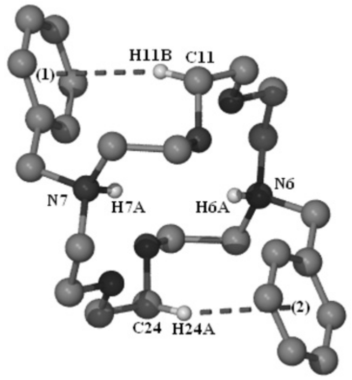

Fig. 1 Crystal structure of the $[(H^+)_2$*N*,*N′*-dibenzyl-4,13-diaza-18-crown-6] cation in **1**–**3** and **5**, clearly illustrating the C–H···π interactions.

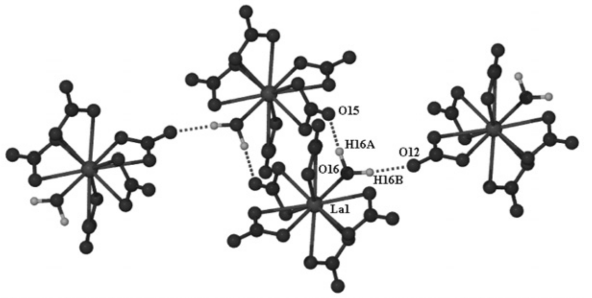

Fig. 2 Structure of the $[Ln(NO_3)_5(H_2O)]^{2-}$ anion [Ln = La, (**1**); Eu, (**2**)], illustrating the hydrogen-bonding arrangement between the anions.

Previous X-ray crystallographic studies of the neutral *N*,*N′*-dibenzyl-4,13-diaza-18-crown-6 ligand show that the benzyl groups are fully extended away from each other, resulting in an elongated horizontal axis,[17,38] while complexes involving the sodium iodide salts of this species and various other substituted (1-naphthyl or 2-naphthyl)-azacrown ethers show these molecules adopt a capsule or "basket" conformation, in which the aryl substituents are extended upward in a *cis* fashion while the macrocycle is puckered upwards, with the metal ion residing within the resulting cavity.

In all of these previous examples, there are also arguments for strong C–H···O interactions which affect the conformation of the side-arms relative to the macrocycle. Our studies, however, revealed the two benzyl groups to be coplanar and to extend back towards the centroid of the macrocycle, rather than into space as seen previously.[40] These factors would therefore indicate that the methylene C–H···π interactions are the dominant interactions influencing the conformation of these particular complexes, rather than any C–H···O or C–H···N interactions.

The packing of the two complexes consists of a hydrophilic layer of zigzagging hydrogen-bonded anions situated between hydrophobic layers of discrete azacrown molecules (Fig. 2). The interactions between the anions and cations are minimal and the intramolecular C–H···π interactions of the azacrown moieties do not extend to adjacent molecules, hence, this unusual phenomenon has no direct effect upon the crystal lattice.

Uranyl species

$[(H^+)_2$*N*,*N′*-dibenzyl-4,13-diaza-18-crown-6]$[(\mu\text{-}OH)_2\{UO_2(NO_3)_2\}_2]$ (3). Compound **3** crystallizes in the centrosymmetric space group $P\bar{1}$ and adopts a cationic/anionic system in a similar fashion to **1** and **2**, however, the asymmetric unit differs in that the uranyl nitrate anion is a binuclear hydroxide-linked dimer rather than a mononuclear anion (Fig. 3). This structure is rather unusual for aqueous uranyl nitrate-crown ether compounds, especially at pH 4, since previous studies have indicated that the uranyl anion preferentially forms either a mononuclear dihydrate salt capped with two hydrogen-bonded crown ether molecules or a uranyl pentahydrate which is hydrogen bonded to several equatorially positioned crown ethers.[23]

A Cambridge Crystallographic Database search revealed that the dimeric form of the uranyl nitrate exhibited in the present case has only been observed previously in a handful of cases, and in all structures, the asymmetric unit contained a large, slightly basic molecule in addition to the dimer

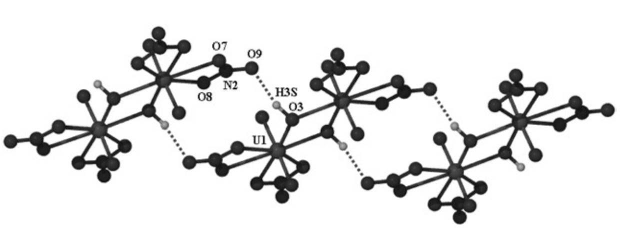

Fig. 3 Structure of the $[(\mu\text{-}OH)_2\{UO_2(NO_3)_2\}_2]^{2-}$ anion in **3**, illustrating the hydrogen-bonded polymeric strands.

(diimidazole, choline, 4,4′-bipyrimidinium and 2-dimethylaminoethanol, respectively).[23,41,42] The effect these secondary molecules have on the formation of the dimer is not fully understood.

The geometry surrounding each metal ion can best be described as distorted hexagonal bipyramidal.[43] The four nitrate anions are coplanar and lie parallel with the equatorial axis of the molecule, as do the bridging hydroxides. The U–$O_{nitrate}$ bond lengths [ranging from 2.529(6) to 2.567(7) Å], are elongated in comparison to the equivalent bonds in $UO_2(NO_3)_2(H_2O)_2$, (average U–$O_{nitrate}$ 2.51 Å).[28,42]

The geometry of the azacrown moiety is identical to that for complexes **1** and **2** (Fig. 1), with the aryl substituents folded back over the rigid, planar ring, and two of the methylene carbons participating in C–H···π interactions. It is interesting to note that in three different complexes containing f-block metal nitrates, this rather unusual geometry is adopted by the doubly protonated *N*,*N*′-dibenzyl-4,13-diaza-18-crown-6 molecule without any significant molecular interactions, and we are studying this generality to a greater extent with other simpler anions.

The crystal packing of this species is also similar to that of **1** and **2**, and consists of a hydrophilic layer of zigzag hydrogen-bonded anions (Fig. 3) situated between hydrophobic layers of discrete azacrown molecules. The position of the protons of the nitrogen heteroatoms prevents three-dimensional hydrogen bonding within the crystal lattice, hence, each hydrophilic layer is only one dimer in width and, when viewed along the equatorial axis, takes the appearance of an infinite staircase. The only two hydrogen bond donors present in the molecule are orientated towards the center of the macrocycle, and preclude any intermolecular interactions.

$[(H_2O)_2(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6]$[UO_2Cl_4]$ (4). Complex **4** crystallises in the space group $P2_1/n$, with the uranium ion residing on an inversion center. The $[UO_2Cl_4]^{2-}$ anion (Fig. 4) possesses octahedral geometry, and all the subtending angles closely approach 90°. The coordination of the chloride ions in preference to the nitrate anions is quite unusual when considering the extreme oxophilicity of the uranyl moiety,[44–50] and differs significantly from the hydroxide-bridged dimer in **3**. This type of uranyl anion has been previously reported in a number of compounds involving various crown ethers,[51–57] and these complexes often contain group I or II ions coordinated to the crown, with the uranyl anion residing in the lattice.

The conformation of the azacrown ether differs significantly from the previous three examples (Fig. 4). The four oxygen heteroatoms lie in the same general plane, however, the two nitrogens extend out in a *trans* fashion from this plane, distorting the ends of the macrocycle to such an extent that they almost fold back over the azacrown ring. The two benzyl substituents extend horizontally away from the macrocyclic ring, and are coplanar in a similar fashion to the uncoordinated ligand.[38] Two water ions are located either side of the macrocyclic cavity and reside approximately 1.6 Å above the macrocyclic plane in a twin pseudo-perched orientation. The distortion of the azacrown ligand enables the protons of the two nitrogen heteroatoms to participate in hydrogen bonding with these water molecules. The N–H···O_{water} hydrogen-bonding distance [H···O = 1.90(10), N···O = 2.769(9) Å] indicates the coordinated molecule is water and that the proton is fully attached to the nitrogen, rather than being equally distributed between the water and nitrogen heteroatoms, as is observed in the presence of oxonium ions.[58] The two waters also hydrogen bond with two oxygen heteroatoms of the macrocycle and probably contribute to the rigidity of the macrocycle.

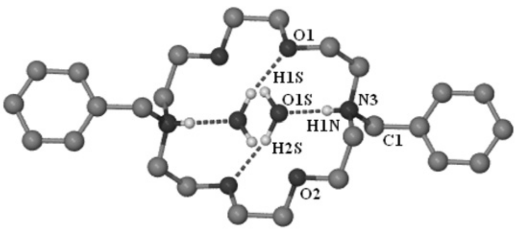

Fig. 4 Crystal structure of the $[(H_2O)_2(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6] cation in **4**, showing the water molecules residing either side of the doubly protonated macrocycle.

In a similar manner to the lanthanoid derivatives, the protonation of the nitrogen heteroatoms occurs, thus preventing the incorporation of metal ions within the macrocyclic cavity. However, the unusual C–H···π interactions observed in the previous examples are absent. The coordination of the two water molecules probably disrupts this, and the resulting intermolecular hydrogen bonding predominates over other interactions.

The packing of the molecule consists of rows of alternating azacrown ether molecules and uranyl centres. The benzyl substituents of each azacrown row overlap into the uranyl rows and appear to pack solely on steric considerations, since no additional interactions are present. The lack of any hydrogen-bonding donor molecules external to the azacrown ligand prevents intermolecular hydrogen bonding from occurring.

$(H_9O_4{}^+)_2[(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6]Br_4 (5). The complex $(H_9O_4{}^+)_2[(H^+)_2$*N*,*N*′-dibenzyl-4,13-diaza-18-crown-6]Br_4 (**5**) crystallises in the space group $P\bar{1}$ and contains three lattice water molecules and an oxonium ion in the asymmetric unit. The crown ether ligand adopts an identical conformation to compounds **1**, **2** and **3** (Fig. 1), with the two phenyl ligands folded back over the macrocyclic moiety and participating in C–H···π interactions. The oxonium ion in the lattice is further hydrogen bonded to three of the lattice water molecules, generating an $H_9O_4{}^+$ oxonium ion. The pyramidal structure of this relatively rare oxonium ion with a central H_3O^+ bound to three peripheral water molecules is similar to other $H_9O_4{}^+$ oxonium ions.[58] The packing morphology of the crystal is also quite similar, and consists of a hydrophilic layer of bromide ions and oxonium ions linked together *via* hydrogen bonding into a network (Fig. 5), with the crown ether ligands interspersed between these layers.

Conclusions

N,*N*′-Dibenzyl-4,13-diaza18-crown-6 adopts an unusual conformation when combined with several f-block nitrates or HBr. All five examples crystallize as a cation/anion system. The unusual conformation arises due to the benzyl groups participating in C–H···π bonding with two of the methylene

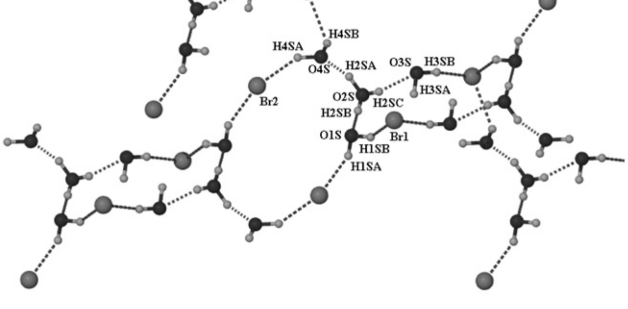

Fig. 5 Structure of the $[(H_9O_4)_2Br_4]^{2-}$ hydrogen-bonded network in **5**.

carbons in the macrocycle and appears to be dependent upon the use of acidic conditions or protic solvents, since this unusual conformation is absent in other analogous complexes synthesized from aprotic solvents (*e.g.* acetonitrile). This conformation differs dramatically from most previous crystal structures involving this ligand, in which either the phenyl substituents are splayed up from the ring and encompass any metal ions within the resulting basket[17] or the metal ion is incorporated within the macrocyclic cavity.[16,35,40] However, the $[UO_2Cl_4]^{2-}$ species demonstrates that by the incorporation of water molecules into macrocyclic ring, intramolecular hydrogen bonding within the azacrown ligand is introduced, a feature which is absent in the previous examples, and it appears that these interactions disrupt the C–H$\cdots\pi$ bonding.

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