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Hydrogen bonded polymers and oligomers from metal salts and 18-crown-6

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Reaction of hydrated metal salts $M(ClO_4)_2$ with 18-crown-6 in water results in the isolation of $[M(H_2O)_6][ClO_4]_2\cdot$(18-crown-6) (M = Ni, **1a**; Co, **1b**; Zn, **1c**) which adopt an infinite hydrogen bonded sandwich type structure. Reaction of $Cu(ClO_4)_2$ with 18-crown-6 under similar conditions leads to a mixture of the analogous $[Cu(H_2O)_6][ClO_4]_2\cdot$(18-crown-6) **1d** and a new complex $[Cu(H_2O)_3(\text{18-crown-6})]_2[ClO_4]_4\cdot$(18-crown-6) **2**, containing both complexed and free crown ether rings as a discrete unit. This difference in behaviour arises from the preference of Cu(II) to adopt a Jahn–Teller distorted geometry. Reaction of $NiBr_2$ results in the formation of the striking complex $[Ni(H_2O)_6]_3[NiBr_2(H_2O)_4]Br_6\cdot4$(18-crown-6)$\cdot2H_2O$ **3**, closely related to complexes of type **1**. With a 3 : 1 electrolyte, hydrogen bonded dimers of $[Al(H_2O)_6][NO_3]_3\cdot$(18-crown-6) **4** are formed, unrelated to complexes **1**. Removal of equatorial aqua ligands as in the complex $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ gives $[Cu_2(O_2CCH_3)_4(H_2O)_2]\cdot$(18-crown-6)$\cdot2H_2O$ **5** which consists of a very different linear, hydrogen bonded chain. Analogous reactions with eight-coordinate complexes led to $[M(CF_3CO_2)_2(H_2O)_6][CF_3CO_2]\cdot$(18-crown-6) (M = Eu, **6a**; Y, **6b**) which somewhat resemble complexes **1**. In general, it is found that the stability of the structure as a whole, and not one dominant set of interactions, governs crystal packing, and even molecular stoichiometry within these equilibrating systems.

Introduction

A popular and effective strategy in the design of supramolecular hosts and complexes is the matching of complementary hydrogen bond donors and acceptors in order to form hydrogen bonded aggregates. Work by Rebek has resulted in a variety of chiral hydrogen bonded capsules,[1] while, Atwood *et al.* have recently reported several large, supramolecular cavitands in which hydrogen bond donor calix[4]resorcarenes are 'glued' together by solvents such as water or propanol.[2,3] Zaworotko *et al.* have produced a range of interpenetrated diamondoid solids by the matching of the hydrogen bond donor, cubane cluster $[Mn(CO)_3(\mu_3\text{-}OH)]_4$ with a variety of acceptors.[4] Indeed, even weak hydrogen bond acceptors such as benzene are incorporated into the crystal lattice. We have recently embarked upon a programme of research into the supramolecular chemistry of hydrogen bond donor/acceptor pairs which exhibit a symmetry or steric mismatch.[5,6] In this way the molecular building blocks are forced to contort in order to maximise intermolecular interactions, resulting in unusual, unsymmetrical molecular and supramolecular geometries. The concept is related to the theory of entatic state in enzymatic catalysis.[7] In particular, metal aqua ions act as excellent, readily available hydrogen bond donors with very limited acceptor properties, and hence little intermolecular self complementarity.[8,9] We have recently reported the formation of the hydrogen bonded array $[UO_2Cl_2(H_2O)_3]_{16}\cdot16$(15-crown-5) in which the steric mismatch between the bent H_2O–U–OH_2 donor moieties and the crown results in a hydrogen bonded polymer with a crystallographic asymmetric unit containing sixteen *unique* metal complex–crown pairs.[5] In contrast, the linear H_2O–U–OH_2 unit in $[UO_2(L_2)(H_2O)_2]\cdot$(crown) (L = NO_3, CH_3CO_2; crown = 15-crown-5, benzo-15-crown-5) results in a much more regular structure with only one unique metal complex–crown pair.[10–12] We now report the extension of these studies to complexes of 18-crown-6 in which a "$[M(H_2O)_n]^{m+}$" acts as the hydrogen bond donor.

Results and discussion

Co-crystallisation of hydrated metal salts $M(ClO_4)_2$ with equimolar amounts of 18-crown-6 in water was carried out for M = Co, Ni, Cu or Zn. In the case of all of the metals studied this resulted in the isolation of complexes of empirical formula $[M(H_2O)_6][ClO_4]_2\cdot$(18-crown-6) (M = Ni, **1a**; Co, **1b**; Zn, **1c**; Cu, **1d**). Complexes **1a**–**1c** are all essentially isostructural, adopting a sandwich type structure in which the crown acceptors cap two adjacent faces of the octahedral $[M(H_2O)_6]^{2+}$ ion, while two mutually *cis*, equatorial coordinated water molecules comprising the opposite edge of the octahedron interact with ClO_4^- anions, Fig. 1. Detailed structural parameters will be discussed for the Ni complex **1a** as a representative example. The mode of interaction with the crown ethers is different on the two octahedral faces, resulting in the presence of two unique half-crowns of very different conformations in the crystallographic asymetric unit (labelled 'a' and 'b'). In the case of crown ether a the axial water molecule O(2) hydrogen bonds to two non-adjacent crown oxygen atoms, O(3a) and O(2a), O···O 2.708(2) and 2.729(2) Å, respectively. The crown is orientated such that equatorial water ligand O(4) also hydrogen bonds to the central crown oxygen atom O(1a) [2.732(2) Å]. In each case the hydrogen atoms were located experimentally and found to lie close to the line joining the two oxygen atoms. Interestingly, O(4) also hydrogen bonds with the second independent crown molecule ('b') which lies above an adjacent octahedral face, O(4)···O(1b) 2.732(2) Å. The aqua ligand *cis* to O(4) also interacts with crown b, O(1)···O(3b) 2.711(2) Å, but *not* with crown A. The other axial ligand, O(3) forms rather longer contacts to crown b, 2.864(2) and 2.912(2) Å, directly across the centre of the crown ring. This complicated, unsymmetrical hydrogen bonded network has two important consequences on the molecular geometry of the $Ni(H_2O)_6^{2+}$ unit. Firstly the axial Ni–O(2) bond length is compressed to 2.0066(16) Å. The remaining five distances range from 2.0405(16)–2.0664(17) Å, while the average from a survey of the Cambridge Crystallo-

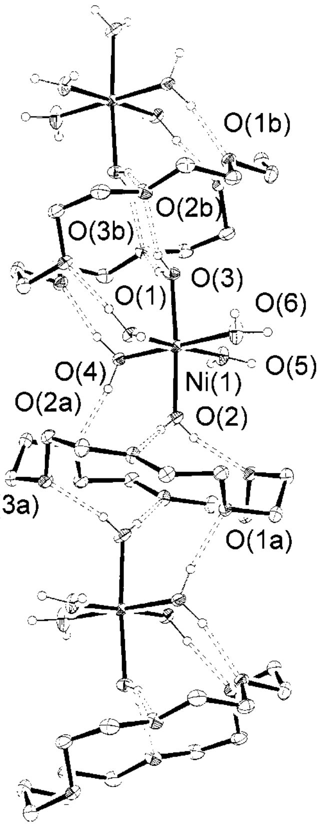

Fig. 1 Hydrogen bonded chain structure in $[Ni(H_2O)_6][ClO_4]_2 \cdot (18\text{-crown-}6)$ **1a**.

graphic Database is 2.079 Å.[13] Secondly, the axial O–Ni–O angle is significantly distorted, with O(2)–Ni–O(3) 174.43(7)°. By comparison the other mutually *trans* pairs of ligands form bond angles of 177.88(6) and 178.42(7)°. The structure of **1b** exhibits similar distortions, with slightly longer Co–O distances overall. A short, axial distance of 2.020(3) Å is observed compared with a range for the other five ligands of 2.067(3)–2.120(3) Å. The compressed O–Co–O angle is 172.24(13)° (*cf.* 176.73(15) and 177.37(13)° for the remaining angles). In the zinc complex **1c** the analogous distances and angles are 2.0222(16) *vs.* 2.0740(15)–2.1118(16) Å and 172.62(7)° *vs.* 175.65(6) and 177.12(7)°.

Repeated attempts to prepare diffraction quality crystals of the copper complex **1d** were unsuccessful, apparently as a result of severe random crystal twinning. Numerous samples all gave elemental analysis data consistent with the same stoichiometry as compounds **1a**–**1c** along with unit cell parameters: $a = 10.477(4)$, $b = 10.728(4)$, $c = 13.320(5)$ Å, $\alpha = 89.771(5)$, $\beta = 92.739(5)$, $\gamma = 120.482(5)$°, closely related to those of the other compounds of type **1** (Table 1), again suggesting a linear chain structure, although the longer *a* and *b* and shorter *c* dimensions suggest significant distortions arising from the Jahn–Teller distorted nature of the Cu(II) ion.

Interestingly, small quantities of a second Cu(II) species were also isolated from the same reaction mixtures. These crystals were readily analysed by X-ray crystallography and proved to be the 3:2, crown:metal complex $[Cu(H_2O)_3(18\text{-crown-}6)]_2[ClO_4]_4 \cdot (18\text{-crown-}6)$ **2**, containing both complexed and free crown ether rings, Fig. 2. The structure consists of a square planar Cu(II) centre coordinated to three water molecules and one crown oxygen atom, Cu–O(1) 1.924(3), Cu–O(2) 1.956(2), Cu–O(3) 1.963(3), Cu–O(1a) 2.038(3) Å. As noted for complexes of type **1** one Cu–OH_2 distance (in the direction of the Cu–crown vector) is somewhat shorter than the others. In addition, the Cu(II) centre forms longer interactions to two further crown oxygen atoms to give an overall distorted octahedral geometry; Cu–O(2a) 2.397(2), Cu–O(6a) 2.473(3) Å. Aqua ligand O(1) is threaded through the macrocyclic cavity to form two strong hydrogen bonds with crown oxygen atoms O(3a) and O(5a); 2.610(3) and 2.754(4) Å respectively. All hydrogen atoms were located experimentally and found to lie approximately along a line joining the two oxygen atoms. Aqua ligand O(2), *trans* to O(1) hydrogen bonds to an adjacent, non-complexed 18-crown-6 molecule while O(3) forms a single hydrogen bond to each crown ether. This unusual kind of hybrid first- and second-sphere complexation is apparently facilitated by the preference of the Cu(II) centre for a Jahn–Teller distorted octahedral geometry, presumably slightly de-stabilising the chain type of structure seen for **1a**–**1c**. A related tetranuclear complex, $[Cu_4Cl_2(\mu_2\text{-}Cl)_6(H_2O)_2(18\text{-crown-}6)_2]$,[14] exhibits a similar coordination of two of its four Cu(II) ions, although without the hydrogen bonding interaction to uncomplexed 18-crown-6.

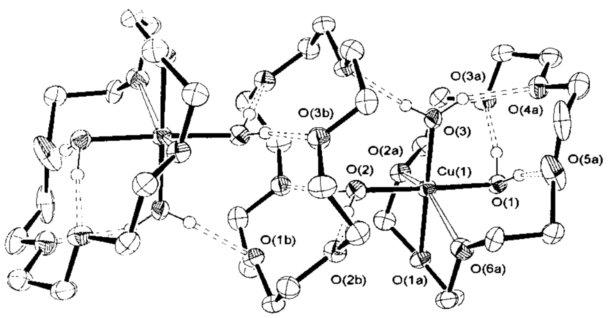

Fig. 2 Discrete $[Cu(H_2O)_3(18\text{-crown-}6)]^{2+}$ units linked by hydrogen bonding to an uncomplexed crown ether in complex **2**.

In complexes of type **1** and in previous work we have concentrated on relatively large, non-coordinating oxo anions.[15] Given the major structure stabilising role played by the ClO_4^- anions an analogous reaction was attempted with $NiBr_2 \cdot 3H_2O$, in which the smaller, more coordinating Br^- anion might be expected to play a significantly different role in the overall crystal packing scheme. Indeed, this reaction resulted in the formation of the striking complex $[Ni(H_2O)_6]_3[NiBr_2(H_2O)_4]Br_6 \cdot 4(18\text{-crown-}6) \cdot 2H_2O$ **3**. Despite the complexity of the molecular formula, complex **3** is closely related to complexes of type **1** with $Ni(H_2O)_6^{2+}$ cations sandwiched *via* hydrogen bonding interactions between pairs of 18-crown-6 ligands to give an infinite, alternating crown/metal complex chain. Unlike complexes **1** however, every *fourth* nickel complex is a neutral $[Ni(H_2O)_4Br_2]$ molecule which interacts with the rest of the chain *via* axially coordinated water molecules, Fig. 3. Thus a comparison of the unit cell dimensions of **3** with complexes **1** (Table 1) reveals close similarities in the *a* and *b* parameters. This unusual packing mode apparently arises as a direct consequence of the relatively small size of the Br^- anion and its consequently more limited ability to act as a hydrogen bonded bridge between adjacent crown–metal complex chains. In the case of the $[Ni(H_2O)_4Br_2]$ molecule the crystal packing arrangement involves the uncoordinated Br(4) hydrogen bonding between coordinated water molecules O(10) and O(11) and the lattice water O(1s), which, in turn, connects to Br(3), which forms part of an adjacent chain. This results in an interlocking of one chain into slots in the other. Intermolecular hydrogen bonded distances are given in Table 2. In the case of the $[Ni(H_2O)_4Br_2]$ molecule, the positions of the coordinated Br^- ligands, Br(1), are such that there is no room for them to be present as uncoordinated anions and in order to maintain their electrostatic interactions with the Ni^{2+} centre, direct coordination results. Hence it may reasonably be proposed that the crystallisation process drives the selection of which species are obtained from the equilibrium mixture present in solution. The $[Ni(H_2O)_4Br_2]$ molecule as a whole is incorporated into the crown ether chain primarily *via* hydrogen bonds to the axial aqua ligand O(8), stabilised by a single longer interaction to the equatorial aqua ligands O(7) [O(8)···O(5a), O(2a) 2.725(6),

Table 1 Crystallographic data for new complexes

	1a	**1b**	**1c**	**2**	**3**	**4**	**5**	**6a**	**6b**
Formula	$C_{12}H_{36}Cl_2O_{20}Ni$	$C_{12}H_{36}Cl_2O_{20}Co$	$C_{12}H_{36}Cl_2O_{20}Zn$	$C_{18}H_{42}Cl_2CuO_{20}$	$C_{48}H_{122}Br_8O_{50}Ni_4$	$C_{12}H_{36}AlN_3O_{21}$	$C_{20}H_{44}Cu_2O_{18}$	$C_{18}H_{38}EuF_9O_{19}$	$C_{18}H_{38}F_9O_{19}Y$
Formula weight/g mol^{-1}	630.02	630.24	636.68	712.96	2373.58	585.42	699.63	881.44	818.39
T/K	173(2)	173(2)	173(2)	103(2)	173(2)	173(2)	173(2)	123(2)	123(2)
λ/Å	0.7107	0.7107	0.7107	0.7107	0.7107	0.7107	0.7107	0.7107	0.7107
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/a$	$P2_1/a$
a/Å	10.0236(10)	10.0578(7)	10.0638(4)	11.8287(17)	9.6227(4)	14.0190(6)	7.983(3)	10.0790(2)	9.9795(3)
b/Å	10.1937(7)	10.2553(7)	10.2361(3)	19.219(3)	9.7835(5)	11.4604(5)	7.833(3)	22.3242(5)	22.4035(8)
c/Å	14.1856(14)	14.2283(7)	14.2184(6)	13.9886(17)	25.5561(13)	16.5452(7)	12.912(5)	14.4355(2)	14.3457(4)
α/°	88.103(2)	90.185(2)	88.119(2)		93.058(2)		75.821(2)		
β/°	87.985(2)	88.222(2)	87.882(2)	111.827(2)	96.469(2)	101.145(2)	77.275(2)	90.372(2)	90.904(2)
γ/°	60.886(2)	60.556(2)	60.870(2)		100.730(2)		90.455(2)		
U/Å^3	1265.3(2)	1277.13(14)	1278.38(8)	2952.2(7)	2341.99(19)	2608.08(19)	761.9(5)	3248.00(11)	3206.95(17)
Z	2	2	2	4	1	4	2	4	4
D_c/g cm^{-3}	1.654	1.639	1.654	1.604	1.683	1.491	1.525	1.803	1.695
μ/cm^{-1}	10.65	9.67	12.56	10.05	42.93	1.73	14.70	20.58	19.47
F(000)	660	658	664	1492	1202	1240	366	1768	1672
Crystal size/mm	0.6 × 0.4 × 0.2	0.4 × 0.4 × 0.3	0.6 × 0.4 × 0.2	0.4 × 0.4 × 0.15	0.3 × 0.05 × 0.05	0.8 × 0.4 × 0.4	0.5 × 0.3 × 0.2	0.3 × 0.2 × 0.2	0.6 × 0.2 × 0.1
θ Range/°	3.7–26.0	3.6–26.0	3.6–26.0	3.7–25.0	3.5–26.0	3.5–26.0	3.4–26.0	3.5–25.5	3.5–26
Reflections collected	7971	10 183	11 095	19 780	19 469	9887	4887	26 806	26 811
Independent reflections	4156	4552	4672	4612	8531	5089	2489	6023	6219
Parameters	316	317	345	389	519	335	218	442	444
Goodness-of-fit on F^2	1.039	1.121	1.066	1.102	1.049	1.027	1.063	1.073	1.054
Final R indices [$I > 2\sigma(I)$], $R1$	0.0343	0.0638	0.0332	0.0519	0.0605	0.0430	0.0472	0.0287	0.0570
$wR2$	0.0862	0.1658	0.0851	0.1320	0.1587	0.1181	0.1247	0.0747	0.1354
R indices (all data)[b] $R1$	0.0370	0.0665	0.0360	0.0606	0.0726	0.0524	0.0539	0.0314	0.0688
$wR2$	0.0886	0.1671	0.0871	0.1390	0.1697	0.1256	0.1319	0.0763	0.1433
Largest difference peak/e Å^{-3}	0.424	1.289[a]	0.539	0.568	1.576[a]	0.648	0.534	0.810	1.163

[a] Close to heavy atom. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$, $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

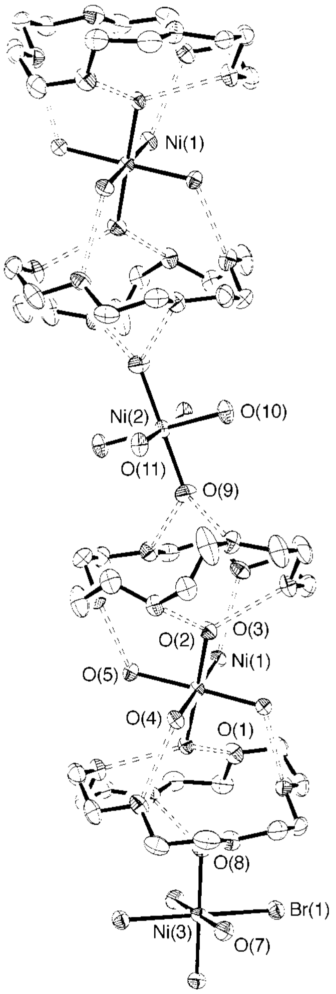

Fig. 3 The unusual $\{[Ni(H_2O)_6]_3[Ni(H_2O)_4Br_2]\cdot 4(18\text{-crown-6})\}^{8+}$ repeating unit in **3**.

2.800(6) Å; O(7) ··· O(2a) 2.932(7) Å]. The two $[Ni(H_2O)_6]^{2+}$ ions are in significantly different second-sphere coordination environments with Ni(2) in an environment related to the $[Ni(H_2O)_4Br_2]$ complex with only interactions from the crown to the axial water molecules O(9) and its symmetry equivalent. In contrast, the Ni(1) hexaaqua ion is significantly more enveloped by the crown ethers in a fashion more reminiscent of complexes **1**. The crown ether molecules cap two faces of the octahedral metal ion *via* hydrogen bonding interactions to give a total of eight hydrogen bonds with O ··· O distances ranging from 2.717(6) to 2.794(6) Å. Within the metal complexes themselves, the Ni(1) ion exhibits short distances to *both* aqua ligands in the direction of chain propagation [2.014(4) Å, average], although the O–Ni–O angle is normal. No such short distances are seen for either Ni(2) or Ni(3) [Ni(2)–O 2.043(4)–2.074(4) Å], confirming that the shortening has its origin in second-sphere packing forces. For Ni(3) longer bonds are observed for the equatorial aqua ligands 2.104(4) Å. The Ni(3)–Br distance of 2.5463(6) Å is unexceptional.[13]

Given the apparently dominant influence of anion size on crystal packing and even molecular stoichiometry exhibited in complexes **1a**–**1c** and **3**, and in previous work[15] it was of interest to see what the effect of changing the number of anions would be on the hydrogen bonding motif in these species. Crystals were therefore prepared from an equimolar mixture of $[Al(H_2O)_6][NO_3]_3$ and 18-crown-6, resulting in the formation of a further 1:1 species; $[Al(H_2O)_6][NO_3]_3\cdot$(18-crown-6) **4** incorporating a 3:1 electrolyte. Examination of the unit cell dimensions for **4** suggests that the packing motif has no relationship to complexes **1** or **3**. Indeed, while complex **4**, does incorporate hydrogen bonding between the 18-crown-6 and the octahedral aluminium(III) hexaaqua ion, this does not result in an infinite hydrogen bonded chain. Instead, the $Al(H_2O)_6{}^{3+}$ units are capped on only one face by the crown as for **1a**–**1c** and the Ni(1) hexaaqua ion in **3**, Fig. 4. Two nitrato anions hydrogen bond with equatorial aqua ligands while the third nitrato ligand is hydrogen bonded to the remaining axial position, effectively preventing the approach of a second crown. Two nitrate anions (centred on N(1) and N(2)) hydrogen bond to adjacent $Al(H_2O)_6{}^{3+}$ ions to give a dimeric $Al_2\cdot crown_2$ unit held together by four oxygen atoms O(9) and O(10) and their symmetry equivalents. The remaining nitrate anion cross-links to the aqua ligand O(6) on adjacent dimers *via* O(14) (2.6395(19) Å). Startlingly, O(14) also forms a remarkably close contact of 3.010(3) Å to the crown carbon atom C(12a) of a third hydrogen bonded dimer, suggesting a significant C–H ··· O hydrogen bond.[16]

Given the significant effect of the anions on the nature of the crystal packing in complexes **1**, **3** and **4**, 18-crown-6 was co-crystallised with a neutral metal complex, $[Cu_2(O_2CCH_3)_4(H_2O)_2]$, in which the acetate ligands are coordinated to the metal centre giving a lantern type species with an approximately linear H_2O–Cu–Cu–OH_2 moiety. The resulting product, $[Cu_2(O_2CCH_3)_4(H_2O)_2]\cdot$(18-crown-6)$\cdot 2H_2O$ **5**, does indeed consist of a linear, hydrogen bonded chain as in complexes **1a**–**1c** and **3**. However, in this case the absence of the hydrogen bond from equatorial water molecules to the crown ring necessitates the incorporation of an additional two molecules of solvent water in order to span both faces of the crown ether, Fig. 5. Notably, the conformation of the macrocycle is also significantly more planar in this case since three of the oxygen atoms are pointing outwards from each face of the crown, but do not need to distort in order to reach both axial and equatorial sites of an octahedral metal centre, in contrast to both crown ether conformations found in **1a**–**1c**, Fig. 6. Bond lengths and angles within the $Cu_2(O_2CCH_3)_4(H_2O)_2$ unit are unremarkable.[17]

As a final variable, the effects of different coordination number in the metal complexes was examined by crystallisation of 18-crown-6 in the presence of $M(CF_3CO_2)_3\cdot 6H_2O$ (M = Eu, Y). This resulted in the formation of two isostructural species; $[M(CF_3CO_2)_2(H_2O)_6][CF_3CO_2]\cdot$(18-crown-6) (M = Eu, **6a**; Y, **6b**), Fig. 7. The structures of complexes **6** somewhat resemble those of complexes **1** in that the two unique half-crown ether molecules sandwich the Eu(III) ion in a second-sphere fashion involving hydrogen bonding to four of the aqua ligands. As with complexes **1**, the two crown acceptors are not parallel to one another, but expose one side of the eight-coordinate metal centre to allow interaction with the trifluoroacetate anions either within the primary coordination sphere or *via* hydrogen bonding with two further aqua ligands. Unlike complexes **1**, the H_2O–Eu–OH_2 vectors are now no longer linear, resulting in an even more marked zig-zag structure. Also, as observed for **3**, an uncoordinated molecule of water is co-opted to complete the interactions to adjacent chains. Thus O(1s) accepts hydrogen bonds from the aqua ligands O(8) and O(10) on the less exposed side of the metal complex (distances 2.830(3) and 2.809(3) Å, respectively in **6a**), and donates to the uncoordinated oxygen atoms of two η^1-trifluoroacetate ligands attached to metal ions of two adjacent chains. Interestingly, the Eu–O(8) and Eu–O(10) bonds are significantly elongated as a result of this interaction; 2.444(2) Å (average) as opposed to 2.418(2) Å (average). The bond from Eu to aqua ligand O(11) is somewhat shorter still; 2.400(2) Å. These effects are not entirely reflected in the structure of **6b**, in which only one Y–O bond is elongated by the interaction with solvent water. In **6b** in general all the metal–oxygen distances are shorter because of the smaller radius of the Y^{3+} ion. Also noteworthy is the fact that the trifluoroacetate ligands themselves display no significant evidence of localisation into double and single C–O bonds despite their η^1-coordination mode. This may arise from the hydrogen bond-

Table 2 Hydrogen bonded distances for complexes **1a**, **2**–**5** and **6a**

Complex **1a**^{a}											
O1–014	2.979(3)	O1–O3b	2.711(2)	O2–O2a	2.729(2)	O4–O1a$^{\mathrm{I}}$	2.732(2)	O4–O1b$^{\mathrm{II}}$	2.732(2)	O5–O8	2.819(3)
O2–03a$^{\mathrm{i}}$	2.708(2)	O3–O2b	2.864(2)	O3–O2b$^{\mathrm{II}}$	2.912(2)	O5–O13$^{\mathrm{III}}$	2.843(3)	O6–O9	2.765(3)	O6–O11	2.887(3)
Complex **2**^{b}											
O1–O3a	2.610(3)	O1–O5a	2.754(4)	O2–O2b	2.703(3)						
O2–O3b$^{\mathrm{I}}$	2.690(4)	O3–O4a	2.876(4)	O3–O1b$^{\mathrm{I}}$	2.737(4)						
Complex **3**^{c}											
Br1–O7	3.255(4)	Br1–O7$^{\mathrm{I}}$	3.350(5)	Br1–O8	3.267(4)	O2–O1b	2.747(6)	O2–O3b	2.749(6)	O3–O4b	2.780(6)
Br1–O8$^{\mathrm{I}}$	3.267(4)	Br2–O4	3.313(4)	Br2–O 6	3.314(4)	O4–O1a	2.786(6)	O5–O6b	2.719(6)	O6–O3a	2.794(6)
Br3–O3	3.334(4)	Br3–O5	3.312(4)	Br3–O1s	3.277(5)	O7–O2a	2.932(7)	O8–O2a	2.800(6)	O8–O5a	2.725(6)
Br4–O10$^{\mathrm{II}}$	3.256(4)	Br4–O11$^{\mathrm{II}}$	3.203(4)	Br4–O1s$^{\mathrm{III}}$	3.344(5)	O9–O2b	2.855(6)	O9–O5b	2.716(6)	O10–O1s$^{\mathrm{V}}$	2.802(6)
Br4–O2s$^{\mathrm{IV}}$	3.349(5)	O1–O4a	2.717(6)	O1–O6a	2.755(5)	O11–O2s$^{\mathrm{VI}}$	2.666(6)	O1s–O2s	2.798(7)		
Complex **4**^{d}											
O1–O5a	2.7024(18)	O2–O1a	2.7193(18)	O2–O2a	2.929(2)	O5–O13	2.6443(19)	O5–O4a	2.6394(19)	O6–O10$^{\mathrm{III}}$	2.578(2)
O2–O3a	3.021(2)	O2–O6a	3.0092(19)	O3–O7$^{\mathrm{I}}$	2.7198(19)	O6–O14$^{\mathrm{II}}$	2.6395(19)	O14–C12a$^{\mathrm{IV}}$	3.010(3)		
O3–O15$^{\mathrm{II}}$	2.6253(19)	O4–O9$^{\mathrm{III}}$	2.724(2)	O4–O11	2.744(2)						
Complex **5**^{e}											
O7–O2b$^{\mathrm{I}}$	2.650(10)	O7–O2c$^{\mathrm{I}}$	2.891(10)	O7–O1s	3.056(5)	O10–O1c	2.876(11)	O10–O3b	2.793(7)	O10–O3c	2.795(9)
O8–02a	2.877(4)	O8–O6	2.625(5)	O9–O1a$^{\mathrm{II}}$	2.825(10)	O11–O5	2.666(4)	O11–O2	2.765(4)	O12–O1s	2.765(4)
O9–O2a$^{\mathrm{II}}$	3.011(10)	O9–O3a$^{\mathrm{II}}$	2.939	O10–O1b	2.660(7)	O12–O4	2.717(5)	O1s–O4$^{\mathrm{III}}$	2.808(6)	O1s–O2$^{\mathrm{IV}}$	2.876(6)
Complex **6a**^{f}											
O2–O1s$^{\mathrm{I}}$	2.815(3)	O4–O1s$^{\mathrm{II}}$	2.848(3)	O5–O7	2.654(3)	O9–O2a$^{\mathrm{III}}$	2.875(3)	O10–O2b$^{\mathrm{IV}}$	2.770(4)	O10–O1s	2.809(3)
O6–O11	2.644(3)	O8–O1s	2.830(3)	O9–O1a	2.850(3)	O11–O3a	2.822(3)	O12–O1b	2.850(3)	O12–O3b	2.834(3)

[a] Symmetry operations: I $-2-x, 3-y, 1-z$; II $-2-x, 3-y, -z$; III x $1+y, z$. [b] Symmetry operation: I $1-x, -y, 1-z$. [c] Symmetry operations: I $3-x, 1-y, -1-z$; II $2-x, -y, -z$; III $x-1, y, z$; IV $2-x, 1-y, -z$; V $x-1, y-1, z$; VI $3-x, 1-y, -z$. [d] Symmetry operations: I $\frac{1}{2}+x, 1\frac{1}{2}-y, \frac{1}{2}+z$; II $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; III $-x, -2-y, -z$; IV $-\frac{1}{2}+x, 1\frac{1}{2}-y, \frac{1}{2}+z$. [e] Symmetry operations: I $-x+1, -y+2, -z+2$; II $-x+1, -y+2, -z+1$; III $x-\frac{1}{2}, -y+\frac{3}{2}, z$; IV $x-1, y, z$. [f] Symmetry operations I $-\frac{1}{2}+x, \frac{1}{2}-y, z$; II $x-1, y, z$; III $2-x, 1-y, 1-z$; IV $2-x, 1-y, -z$.

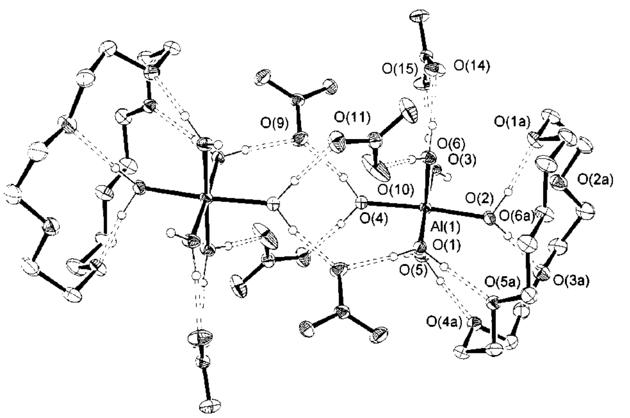

Fig. 4 The dimeric structure of $[Al(H_2O)_6][NO_3]_3\cdot(18\text{-crown-}6)$ **4**.

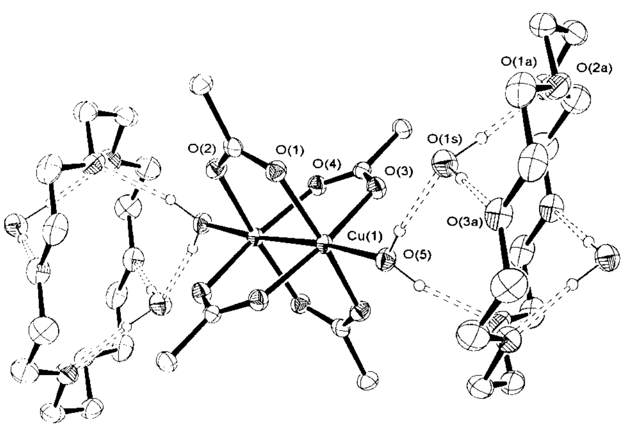

Fig. 5 Chain structure of $[Cu_2(O_2CCH_3)_4(H_2O)_2]\cdot(18\text{-crown-}6)\cdot 2H_2O$ **5** supported by two molecules of solvent water per formula unit. Selected distances: Cu–Cu 2.6286(12), Cu–O_{Ac} 1.965(3) (average), Cu–OH_2 2.144(3) Å. Hydrogen bonds: O(5)···O(2a) 2.814(4), O(5)···O(1s) 2.710(4), O(1s)···O(1a) 2.919(5), O(1s)···O(3a) 2.882(5) Å.

ing interactions displayed by both coordinated and uncoordinated anions. The hydrogen bonds from the uncoordinated anion to aqua ligands O(7) and O(11) in **6a** being particularly short; 2.6490(3) Å (average). The analogous distances in **6b** are longer as a result of the closer proximity of the aqua ligands to the metal centre.

Conclusions

This study has demonstrated that despite the large number of potential hydrogen bonding modes, a common type of interaction is seen for a range of metal hexaaqua ions with 18-crown-6. This multi-point hydrogen bonding may be disrupted however, by the influence of the counter anions or the steric requirements of the metal centre. Hence it is the stability of the structure as a whole, and not one dominant set of interactions, which govern crystal packing and even molecular stoichiometry within such equilibrating systems.

Experimental

Instrumental

Microanalyses were performed in the Department of Chemistry at James Cook University. Products generally displayed some degree of moisture sensitivity when exposed to the atmosphere, gradually dissolving in absorbed atmospheric moisture. For this reason isolated yields were not measured in order to protect crystals for the X-ray experiment but are estimated to be *ca.* 30–40% based on hydrated metal salt.

Preparations

$[Co(H_2O)_6][ClO_4]_2\cdot(18\text{-crown-}6)$ 1b. A sample of $Co(ClO_4)_2\cdot$

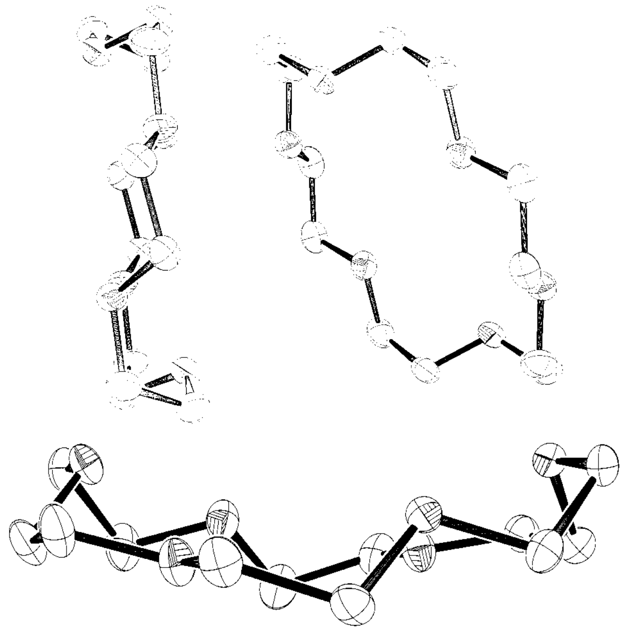

Fig. 6 The three 18-crown-6 conformations found in **1a** (a and b) and **4**.

6H$_2$O (0.14 g, 0.38 mmol) and 18-crown-6 (0.10 g, 0.38 mmol) were dissolved in H$_2$O (5 cm^3) and allowed to evaporate at room temperature. Large pink crystals of **1b** were isolated (Found: C, 23.19; H, 6.04. C$_{12}$H$_{36}$O$_{20}$Cl$_2$Co requires C, 22.87; H, 5.76%). Infrared (Nujol, ν/cm^{-1}): 3541s (br), 1644s, 1303m, 1150m, 1084m, 949m, 839w.

[Ni(H$_2$O)$_6$][ClO$_4$]$_2$·(18-crown-6) 1a. Compound **1a** was prepared similarly to **1b**, except Ni(ClO$_4$)$_2$·6H$_2$O (0.14 g, 0.38 mmol) was used in place of Co(ClO$_4$)$_2$·6H$_2$O. Lime green crystals of the **1b** were obtained (Found: C, 23.12; H, 6.16. C$_{12}$H$_{36}$O$_{20}$Cl$_2$Ni requires C, 22.88; H, 5.76%). Infrared (Nujol, ν/cm^{-1}): 3563s (br), 1650s, 1303m, 1151w, 1084m, 964m, 843w.

[Zn(H$_2$O)$_6$][ClO$_4$]$_2$·(18-crown-6) 1c. Compound **1c** was prepared similarly to **1b**, except Zn(ClO$_4$)$_2$·6H$_2$O (0.14 g, 0.38 mmol) was used in place of Co(ClO$_4$)$_2$·6H$_2$O. Colourless crystals of the **1c** were obtained (Found: C, 22.54; H, 5.95. C$_{12}$H$_{36}$O$_{20}$Cl$_2$Zn requires C, 22.64; H, 5.70%). Infrared (Nujol, ν/cm^{-1}): 3541s (br), 1633s, 1302m, 1151m, 1084m, 950m, 839w.

[Cu(H$_2$O)$_6$][ClO$_4$]$_2$·(18-crown-6) 1d and [Cu(H$_2$O)$_3$(18-crown-6)]$_2$[ClO$_4$]$_4$·(18-crown-6) 2. Compounds **1d** and **2** were prepared similarly to **1b**, except Cu(ClO$_4$)$_2$·6H$_2$O (0.14 g, 0.38 mmol) was used in place of Co(ClO$_4$)$_2$·6H$_2$O. Two types of light blue crystals were obtained and were separated manually. Compound **1d** was by far the most prevalent but the crystals proved to be highly multiple despite repeated attempts at crystallisation (see discussion). Insufficient amounts of pure **2** (free of **1d**) could be isolated for elemental analysis (Found for **1d**: C, 22.83; H, 5.83. C$_{12}$H$_{36}$O$_{20}$Cl$_2$Cu requires C, 22.76; H, 5.73%). Infrared (Nujol, ν/cm^{-1}): 3563s (br), 1633s, 1303m, 1257w, 1105s (br), 952m, 835w.

[Ni(H$_2$O)$_6$]$_3$[NiBr$_2$(H$_2$O)$_4$]Br$_6$·4(18-crown-6)·2H$_2$O 3. Compound **3** was prepared similarly to **1b**, except NiBr$_2$ (0.10 g, 0.38 mmol) was used in place of Co(ClO$_4$)$_2$·6H$_2$O. Lime green crystals of the **3** were obtained (Found: C, 22.28; H, 6.28. C$_{48}$H$_{144}$O$_{48}$Br$_8$Ni$_4$ requires C, 24.39; H, 6.14%). Infrared (Nujol, ν/cm^{-1}): 3563s (br), 1650s, 1302m, 1097m (br), 939m, 838w.

[Al(H$_2$O)$_6$][NO$_3$]$_3$·(18-crown-6) 4. Compound **4** was prepared similarly to **1b**, except Al(NO$_3$)$_3$·9H$_2$O (0.14 g, 0.38 mmol) was used in place of Co(ClO$_4$)$_2$·6H$_2$O. Colourless crystals of **4** were obtained (Found: C, 26.02; H, 7.27; N, 7.33. C$_{12}$H$_{36}$N$_3$O$_{21}$Al requires C, 24.62; H, 6.20; N, 7.18%). Infrared (Nujol, ν/cm^{-1}): 3540s (br), 1650s, 1302m, 1100m (br), 955m, 835w.

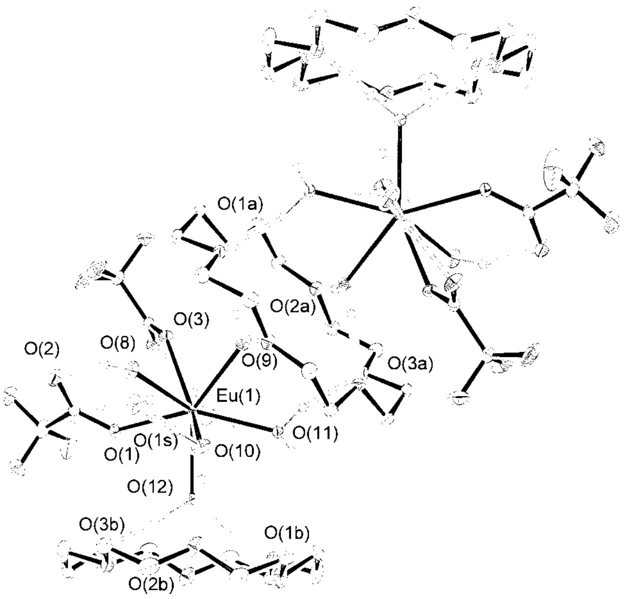

Fig. 7 Zig-zag hydrogen bonded chain in [Eu(CF$_3$CO$_2$)$_2$(H$_2$O)$_6$]-[CF$_3$CO$_2$]·(18-crown-6) **6a**.

[Cu$_2$(O$_2$CCH$_3$)$_4$(H$_2$O)$_2$]·(18-crown-6)·2H$_2$O5. Compound **5** was prepared similarly to **1b**, except Cu(CH$_3$CO$_2$)$_2$·H$_2$O (0.08 g, 0.38 mmol) was used in place of Co(ClO$_4$)$_2$·6H$_2$O. Large blue-green crystals of the **5** were obtained (Found: C, 34.33; H, 6.34. C$_{20}$H$_{44}$O$_{18}$Cu$_2$ requires C, 34.37; H, 6.83%). Infrared (Nujol, ν/cm^{-1}): 3520s, 1631s, 1351m, 1295m, 1256m, 1101s, 1040m, 957s, 836m, 805m, 684m, 623w.

[Eu(CF$_3$CO$_2$)$_2$(H$_2$O)$_6$][CF$_3$CO$_2$]·(18-crown-6) 6a. Compound **6a** was prepared similarly to **1b**, except Eu(CF$_3$CO$_2$)$_3$·3H$_2$O (0.21 g, 0.38 mmol) was used in place of Co(ClO$_4$)$_2$·6H$_2$O. Colourless crystals of **6a** were obtained (Found: C, 24.87; H, 4.37. C$_{18}$H$_{36}$F$_9$O$_{18}$Eu requires C, 25.04; H, 4.20%). Infrared (Nujol, ν/cm^{-1}): 3584s (br), 1682s, 1305m, 1150m, 1084m, 963m, 835w.

[Y(CF$_3$CO$_2$)$_2$(H$_2$O)$_6$][CF$_3$CO$_2$]·(18-crown-6) 6b. Compound **6b** was prepared similarly to **1b**, except Y(CF$_3$CO$_2$)$_3$·3H$_2$O (0.18 g, 0.38 mmol) was used in place of Co(ClO$_4$)$_2$·6H$_2$O. Colourless crystals of **6b** were obtained (Found: C, 26.84; H, 4.63. C$_{18}$H$_{36}$F$_9$O$_{18}$Y requires C, 27.01; H, 4.53%). Infrared (Nujol, ν/cm^{-1}): 3583s (br), 1681s, 1305m, 1150m, 1084m, 962m, 836w.

Crystallography

Crystal data and data collection parameters are summarised in Table 1. Crystals were mounted using silicon grease on the end of a glass fibre and cooled on the diffractometer using an Oxford Cryostream low temperature attachment. All crystallographic measurements were carried out with a Nonius KappaCCD diffractometer equipped with graphite monochromated Mo-Kα radiation using φ rotations with 2° frames and a detector to crystal distance of 25 mm. Integration was carried out by the program DENZO-SMN.[18] Data sets were corrected for Lorentz and polarization effects and for the effects of absorption using the program Scalepack. Structures were solved using the direct methods option of SHELXS 97 and developed using conventional alternating cycles of least squares refinement and Fourier-difference synthesis (SHELXL 97).[19] In general all non-hydrogen atoms were refined anisotropically, while CH hydrogen atoms were fixed in idealised positions and allowed to ride on the atom to which they were attached. Hydrogen atoms on water molecules were located experimentally on the final Fourier-difference maps and treated similarly. Hydrogen atom thermal parameters were fixed at 1.2 times those of the parent atom.

Compounds **6a** and **6b** exhibited disorder of one of the two unique crown ethers in both cases. This was modelled successfully in terms of two sets of positions, common occupancy refined to 50%. In the case of **6b** hydrogen atoms were not included for disordered atoms.

All calculations were carried out either on a Silicon Graphics Indy workstation or an IBM-PC compatible personal computer.

CCDC reference number 186/1137.

See http://www.rsc.org/suppdata/dt/1998/3417/ for crystallographic files in .cif format.

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