Hydrogen-bonded Networks in Crown Ether Complexes of Hydrated Metal Ions

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The hydrated metal nitrates ($M(NO_3)_3.6H_2O$, M=Co, Ni, Cu, Zn and Cd) have been crystallised from water in the presence of 18-crown-6 and their structures determined by X-ray crystallography. In the case of copper, a pseudo four-coordinate square planar complex resides in an extended six-coordinate octahedral array which is further bound in a single-stranded one-dimensional hydrogen bonded polymeric mode. For M=Co, Ni, Zn and Cd isomorphous complexes are isolated where the octahedral $[M(H_2O)_5(NO_3)]^+$ cation resides in a two-dimensional polymeric network through hydrogen bonds between the water ligands and either the crown ether oxygens or unbound nitrate ions or water molecules.

INTRODUCTION

Crown ethers have received much attention since the pioneering work of Pedersen in 1967 [1,2]. Studies involving transition metal ions and crown ethers in aqueous systems have shown that for 18-crown-6 in particular, the macrocyclic ligand shows little affinity to bind the metal ion within its cavity [3–5]. Instead, the hydrated metal ions form hydrogen bonded arrays with the heteroatoms of the crown ether to give polymeric one- and two-dimensional products. For the smaller crown ethers, 12-crown-4 and 15-crown-5, where the diameter of the crown is more suitable for complexing the first row transition metal ions, encapsulation occurs much more readily [6]. For example when $Cu(NO_3)_2.3H_2O$ is crystallised in the presence of 12-crown-4 or 15-crown-5, coordination by the crown occurs giving $[Cu(NO_3)_2(12\text{-crown-}4)]$ and $[Cu(OH_2)_2(15\text{-crown-}5)][NO_3]_2$ [6b]. In the former, the Cu centre is a distorted octahedron where the 12-crown-4 molecule coordinates to one face of the copper and the nitrates are both monodentate. In the latter, the copper is completely encapsulated by the 15-crown-5 molecule with the $H_2O—Cu—OH_2$ group threaded through the macrocycle [6b].

A crystallographic report of the complex obtained from the crystallisation of $Mn(NO_3)_2.6H_2O$ in the presence of 18-crown-6 showed a $[Mn(H_2O)_5(NO_3)]^+$ cation sandwiched between

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two 18-crown-6 molecules to which it is hydrogen bonded through the metal bound water molecules [7]. Further hydrogen bonding was evident through unbound nitrate ions and water molecules to produce a two-dimensional hydrogen bonded polymeric array. It was our intention to complete the first row transition metal nitrate series when crystallised from aqueous conditions in the presence of 18-crown-6 to study the hydrogen bonding between the hydrated metal centre and the macrocycle and herein we report the complexes obtained from the interaction between $M(NO_3)_2.xH_2O$, (M = Co, Ni, Zn, Cd; x = 6; M = Cu; x=3) where for Co, Ni, Zn, and Cd isomorphous complexes to the analogous Mn complex above are obtained and for Cu a one dimensional hydrogen bonded polymeric complex is revealed. In the case of $Fe(NO_3)_3.9H_2O$, a more complex system is obtained, and this will be the subject of a future publication.

Experimental

18-crown-6 was purchased from Fluka Chemical Company and hydrated metal(II) nitrate salts were purchased from Aldrich Chemical Co and were not purified prior to use. Deionised water was used as solvent, and microanalyses were performed at the Department of Chemistry at James Cook University.

Synthesis of Compounds

In all experiments, a 1:1 mixture of hydrated metal salt ($\sim$0.11 g, 0.38 mmol) and 18-crown-6 (0.10 g, 0.38 mmol) were dissolved in a minimum of water (*ca.* few mL) and allowed to slowly evaporate. Infrared spectra confirmed the presence of 18-crown-6 with bands near 960 and 1355 cm^{-1}. Suitable microanalyses were obtained for all compounds. Crystals suitable for the X-ray diffraction experiments were isolated from the mass of crystals obtained. Details for each particular compound are given below.

[18-crown-6][Cu(NO₃)₂(H₂O)₃], 1

Long light blue acicular crystals of the *title compound* deposited from solution. M.Pt.= 98–102°C (dec.). (Found: C, 28.05; H, 6.85; N, 6.45%. $C_{12}H_{30}N_2O_{15}Cu$ requires: C, 28.49; H, 5.98; N, 5.54; %). Infrared, (Nujol, ν, cm^{-1}): 3381s(br), 1722m, 1644s, 1350m, 1306s, 1255s, 1143m, 1096s, 1015s, 952s, 839m, 810m, 750m.

[18-crown-6][Co(NO₃)(H₂O)₅]NO₃.H₂O, 2

Long light pink acicular crystals of the *title compound* deposited from solution. M.Pt.=105–8°C (dec.). (Found: C, 24.91; H, 7.17; N, 5.86%. $C_{12}H_{36}N_2O_{18}Co$ requires: C, 25.95; H, 6.53; N, 5.04; %). Infrared, (Nujol, ν, cm^{-1}): 3444s(br), 1746w, 1668m, 1634s, 1352s, 1316s, 1139m, 1108s, 1037m, 961s, 845m, 827m, 701m.

[18-crown-6][Ni(NO₃)(H₂O)₅]NO₃.H₂O, 3

Long light green acicular crystals of the *title compound* deposited from solution. M.Pt.=118–22°C (dec.). (Found: C, 25.59; H, 7.43; N, 5.99%. $C_{12}H_{36}N_2O_{18}Ni$ requires: C, 25.96; H, 6.54; N, 5.05; %). Infrared, (Nujol, ν, cm^{-1}): 3443s(br), 1788w, 1747m, 1667s, 1650s, 1348m, 1088s, 956s, 846s.

[18-crown-6][Zn(NO₃)(H₂O)₅]NO₃.H₂O, 4

Large colorless plates of the *title compound* deposited from solution. M.Pt. = 110–5°C. (Found: C, 25.01; H, 7.40; N, 5.82%. $C_{12}H_{36}N_2O_{18}Zn$ requires: C, 25.66; H, 6.46; N, 4.99; %). Infrared, (Nujol, ν, cm^{-1}): 3520s(br), 1788m, 1632s, 1350m, 1105s, 959s, 836s.

[18-crown-6][Cd(NO₃)(H₂O)₅]NO₃.H₂O, 5

Large colorless plates of the *title compound* deposited from solution. M.Pt.=90–4°C. (Found:

C, 23.27; H, 4.60; N, 5.11%. $C_{12}H_{36}N_2O_{18}Cd$ requires: C, 22.49; H, 5.66; N, 4.37; %). Infrared, (Nujol, ν, cm^{-1}): 3520s(br), 1788m, 1644s, 1345m, 1106s, 968s, 837s.

Structure Determinations

Crystal data and summary of data collection for complexes **1–5** are shown in Table I. All compounds were very hygroscopic and were therefore sealed in thin-walled capillaries for data collection. Unique room temperature diffractometer data sets (T ~ 296 K; monochromatic Mo Kα radiation, λ = 0.71073Å; $2\theta/\theta$ scan mode) were measured, yielding N_0 independent reflections, N_0 with $I>3\sigma(I)$ being considered 'observed' and used in the large block least squares refinements after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; hydrogen atoms being placed at calculated positions and their parameters were not refined. Conventional residuals R, R_w on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004$ $\sigma^4(I_{\text{diff}})$ being used. Neutral atom complex scattering factors were employed, computation using the XTAL 3.4 program system implemented by S. R. Hall [8]. Pertinent results are quoted in the Figures and Tables; material deposited comprises all atomic coordinates and thermal parameters, complete bond distances and angles tables, full non-hydrogen atom geometries, and structure factor amplitudes.

Discussion

The complexes studied were prepared by slow evaporation of aqueous solutions of M(NO$_3$)$_2$.x-H$_2$O (M = Co, Ni, Cu, Zn and Cd) compounds in the presence of 18-crown-6 in the ratio 1:1. In each case, crystalline material suitable for X-ray crystallographic studies was obtained and the X-ray crystal structures are discussed.

Structure of [18-crown-6][Cu(NO$_3$)$_2$.3H$_2$O], 1

For M = Cu, a compound of stoichiometry Cu(NO$_3$)$_2$.3H$_2$O:18-crown-6, 1:1 was obtained as a long light blue needles and its structure is shown in Figure 1 with pertinent bond lengths and angles shown in Tables II and III. The compound crystallises as a one-dimensional polymeric strand with the copper bound water molecules binding to the macrocyclic heteroatoms through hydrogen bonds.

The geometry about the metal centre is not straightforward. There are four oxygens bound in a square planar arrangement about the copper at a mean distance of 1.972(5) Å. These oxygens arise from two water molecules and two monodentate nitrate ligands which are disposed in a *trans* configuration; the O—Cu—O angles ranging from 86.6(2) to 93.2(2)°, (with *transoid* angles being 174.6(2) and 179.8(4)°). A third water molecule is loosely bound at a longer distance (2.260(5) Å) in an apical position of the pseudo square pyramidal geometry; O(ap)O—Cu—O(eq) angles ranging from 87.6(2) to 92.4(2)°. Furthermore, two of the oxygen atoms of the Cu-bound nitrate ligands are at 2.588(5) and 2.788(6) Å from the copper, giving a pseudo seven-coordinate arrangement about Cu with potentially bidentate nitrate ligands. Countering this argument is that these Cu—O(nitrate) distances are >24% longer than the sum of the ionic radii for six-coordinate Cu^{2+} and O^{2-}(2.08Å) [9]. This also suggests the H$_2$O molecule at the apical position is only very loosely coordinated to the Cu centre (for five-coordinate Cu^{2+}, the ionic radius is 0.65 Å leading to the sum of the ionic radii for Cu^{2+} and O^{2-} being 2.00 Å) [9]. This coordination about the Cu centre is reminiscent of that found in Cu(NO$_3$)$_2$.2.5H$_2$O where there are *transoid* nitrate and H$_2$O ligands in the square plane at an average distance of 1.972(2) Å [10]. A further O atom of an adjacent nitrate ligand is 2.39(2) Å from the Cu in an apical position relative to the square plane, while two O atoms of Cu-bound

TABLE I   Crystal data and summary of data collection for complexes (1)–(5)

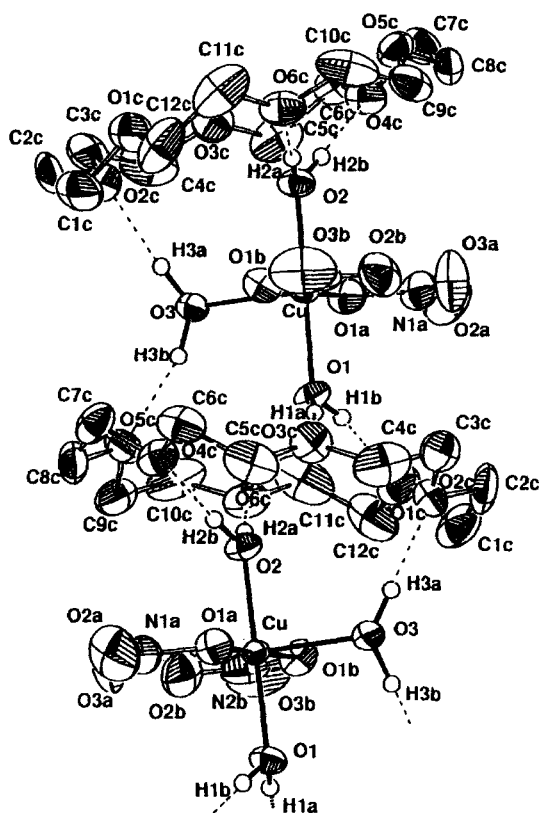| Compound	(18-C-6)(Cu(NO$_3$)$_2$·3H$_2$O)	(18-C-6)(Co(NO$_3$)$_2$·6H$_2$O)	(18-C-6)(Ni(NO$_3$)$_2$·6H$_2$O)	(18-C-6)(Zn(NO$_3$)$_2$·6H$_2$O)	(18-C-6)(Cd(NO$_3$)$_2$·6H$_2$O)
	(1)	(2)	(3)	(4)	(5)
Mol. Formula	C$_{12}$H$_{30}$N$_2$O$_{15}$Cu	C$_{12}$H$_{36}$N$_2$O$_{18}$Co	C$_{12}$H$_{36}$N$_2$O$_{18}$Ni	C$_{12}$H$_{36}$N$_2$O$_{18}$Zn	C$_{12}$H$_{36}$N$_2$O$_{18}$Cd
Mol. Wt	505.92	555.36	555.12	561.80	608.83
Space group	P2$_1$/n	P2$_1$/n	P2$_1$/n	P2$_1$/n	P2$_1$/n
cell constants					
a, Å	10.0773(7)	7.242(2)	7.215(2)	7.239(2)	7.425(1)
b, Å	13.064(2)	16.139(2)	16.119(1)	16.125(2)	16.277(2)
c, Å	16.757(2)	20.807(3)	20.778(3)	20.845(2)	20.828(2)
α, deg	90	90	90	90	90
β, deg	91.716(7)	99.04(1)	99.39(1)	99.20(1)	98.92(1)
γ, deg	90	90	90	90	90
V, Å^3	2205.1(4)	2401.7(7)	2384.0(7)	2402.1(8)	2486.8(6)
molecules/unit cell	4	4	4	4	4
D$_c$, g cm^{-3}	1.687	1.536	1.547	1.553	1.626
μ, cm^{-1}	10.8	8.0	9.0	11.1	9.6
A$^*_{min, max}$	1.260, 1.394	1.159, 1.280	1.126, 1.208	1.387, 1.527	1.361, 1.455
Dimensions, mm	0.24 × 0.32 × 0.24	0.34 × 0.32 × 0.20	0.32 × 0.22 × 0.14	0.46 × 0.40 × 0.32	0.50 × 0.40 × 0.34
F(000)	1180	1172	1176	1184	1256
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
2θ range, deg	2–50	2–50	2–50	2–55	2–50
no. reflcns collcd	3868	4225	4197	5492	4363
no. of obsd reflcns	2424	2642	2046	2642	3030
no. of params varied	272	298	298	298	298
sigma cutoff	3σ	3σ	3σ	3σ	3σ
temp of data colln, K	296	296	296	296	296
R	0.058	0.077	0.078	0.075	0.059
R$_w$	0.067	0.066	0.066	0.063	0.056

FIGURE 1 Structure of [18-crown-6] [Cu(NO₃)₂.3H₂O], 1 showing the binding of the Cu(NO₃)₂.3H₂O molecule to the 18-crown-6 molecule.

TABLE II Copper environment in [18-crown-6][Cu(NO₃)₂.3-H₂O], 1. *d* is the copper-ligand distance (Å); other entries in the matrices are the angles subtended by the relevant atoms at the head of the rows and column (degrees)

Atom	d	O(2)	O(1a)	O(1b)	O(3)
O(1)	1.961(5)	174.6(2)	91.8(3)	88.4(2)	89.7(2)
O(2)	1.972(5)		93.2(2)	86.6(2)	92.4(2)
O(1a)	1.964(5)			179.8(4)	87.6(2)
O(1b)	1.992(5)				92.3(2)
O(3)	2.260(5)				
O(2b)*	2.588(5)				
O(3a)*	2.788(6)				

* Not considered bonding.

nitrate groups are loosely coordinated at ~2.66 Å [10].

The Cu(NO₃)₂.3H₂O molecule is further bound in a second-sphere fashion in a hydro-gen-bonded polymeric array linked by 18-

TABLE III Hydrogen bonding in [18-crown-6][Cu(NO₃)₂.3-H₂O], 1

Atoms	Distance (Å)
O(1)...O(1c)	2.803(8)
O(1)...O(3c)	2.827(8)
O(2)...O(4c)'	2.721(8)
O(2)...O(6c)'	2.880(8)
O(3)...O(2c)'	2.773(8)
O(3)...O(5c)	2.860(8)

Primed atoms have been generated using the following symmetry transformation: 0.5−x, 0.5+y, 0.5−z.

crown-6 molecules (see packing diagram in Fig. 2), the Cu(NO₃)₂.3H₂O being sandwiched between successive macrocyclic rings. Figure 1 shows the hydrogen bonding pattern around the Cu(NO₃)₂.3H₂O core. O(1) is hydrogen bonded to O(1c) and O(3c) at distances of 2.803(8) and 2.827(8) Å respectively while O(2) is bound to O(4c) and O(6c) (mean=2.800(8) Å) and O(3) is hydrogen bonded to O(2c) and O(5c) (mean = 2.817(8) Å). The uncoordinated O atoms of the nitrate groups are not involved in hydrogen bonding, with no contacts less than 3.25 Å.

Structures of [18-crown-6][M(NO₃)₂.6H₂O], (M=Co, 2; M=Ni, 3; M=Zn, 4; M=Cd, 5)

The structures of complexes 2 to 5 are isomorphous, and since the cadmium complex is the most accurate, structural features pertaining to
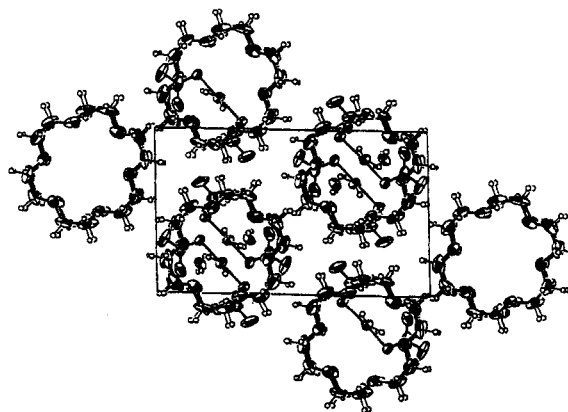

FIGURE 2 Unit cell contents [18-crown-6][Cu(NO₃)₂.3H₂O], 1, viewed down C.

this complex will be discussed in depth, while similar features appear in the other structures. They are also isomorphous to the previously published [18-crown-6][Mn(NO$_3$).5H$_2$O](NO$_3$) (H$_2$O) [7]. Selected bond lengths and angles for compounds 2 to 5 are compiled in Tables IV and V. The structure of [18-crown-6] [Cd(NO$_3$)$_2$.6- H$_2$O] is shown in Figure 3, while the unit cell contents is shown in Figure 4 and the hydrogen bonding about the [Cd(NO$_3$).5H$_2$O]$^+$ core is shown in Figure 5.

The overall structure features an octahedrally coordinated metal centre with five water molecules and a monodentate nitrate ligand completing the six-coordination. This core is then bound in a two-dimensional array through hydrogen bonds to two crown ether molecules and both the unbound nitrate ion and water molecule. The coordination sphere about the octahedral metal centre is unexceptional (see Tab. IV for bonding parameters). There are six hydrogen bonding contacts between the metal bound

water molecules (O(1b), O(1d), O(1f) and O(1g)) and oxygen atoms of the crown ether (O(1c), O(3c), O(4c), O(5c) and O(6c)) at a mean distance of 2.847(9) Å (see Tab. V for hydrogen bonding distances in compounds 2 to 4), which effectively sandwiches the [Cd(NO$_3$).5H$_2$O]$^+$ core between successive macrocyclic ligands in a second-sphere bonding mode. The [Cd(NO$_3$).5H$_2$O]$^+$ core is further bound to the non-metal bound nitrate ion (O1h) and water molecule O(1i) through hydrogen bonds. The O(1d)···O(1h), O(1f)···O(1h), O(1f)···O(1i), and O(3a)···O(1i) distances being 2.836(9), 2.836(9), 2.66(1) and 2.89(1) Å respectively establishing the two-dimensional polymeric array by bridging adjacent crown ether/metal core polymeric strands. The unbound nitrate and water molecules are also hydrogen bonded within this network (O(1h)···O(1i) being 2.76(1) Å).

The complexes obtained herein show no complexation of the metal centre within the cavity of the crown ether molecule. This phe-

TABLE IV Metal environments in [18-crown-6][M(NO$_3$).5H$_2$O](NO$_3$)(H$_2$O). *d* is the metal-ligand distance (Å); for each metal-ligand distance the entries are in the order, Co, Ni, Zn, Cd; other entries in the matrices are the angles subtended by the relevant atoms at the head of the rows and column (degrees)

Atom	*d*	O(1b)	O(1d)	O(1e)	O(1f)	O(1g)
O(1a)	2.131(6)	90.9(2)	87.9(2)	89.3(2)	177.1(2)	86.9(2)
	2.101(6)	90.0(3)	87.3(2)	91.3(2)	178.1(3)	88.1(3)
	2.233(4)	89.1(2)	86.5(2)	87.5(2)	176.0(2)	84.7(2)
	2.350(5)	89.5(2)	85.8(2)	96.5(3)	176.8(2)	87.3(2)
O(1b)	2.070(5)		90.0(2)	89.3(2)	90.4(2)	176.6(2)
	2.033(7)		91.4(3)	88.5(3)	91.7(3)	177.5(2)
	2.105(6)	89.6(2)	89.5(2)	92.4(2)	172.9(2)	
	2.233(5)		91.3(2)	86.5(2)	90.6(2)	175.0(2)
O(1d)	2.107(5)			177.0(2)	94.7(2)	87.3(2)
	2.077(6)			178.6(2)	93.6(3)	86.8(3)
	2.097(4)			173.9(2)	97.3(2)	86.6(2)
	2.337(5)			176.8(3)	91.0(2)	84.6(2)
O(1e)	2.108(5)				88.2(2)	93.3(2)
	2.071(6)				87.9(3)	93.2(3)
	2.129(4)				88.8(2)	93.7(2)
	2.349(7)				86.7(3)	97.7(2)
O(1f)	2.052(6)					92.0(2)
	2.044(6)					90.2(3)
	2.061(4)					93.9(2)
	2.278(6)					92.3(2)
O(1g)	2.085(5)					
	2.057(7)					
	2.067(5)					
	2.248(5)					

TABLE V   Hydrogen bonding in [18-crown-6][M(NO₃).5-H₂O](NO₃)(H₂O). For each hydrogen-bonding distance, the order of the entries are Co, Ni, Zn, Cd

| Atoms	Distance (Å)
O(1b)· · ·O(1c)	3.025(7)
	3.05(1)
	3.109(7)
	3.043(7)
O(1b)· · ·O(2c)	2.863(9)
	2.88(1)
	2.861(7)
	2.811(8)
O(1b)· · ·O(6c)	2.843(8)
	2.856(9)
	2.901(6)
	2.880(7)
O(1d)· · ·O(1c)	2.797(8)
	2.79(1)
	2.759(9)
	2.781(9)
O(1d)· · ·O(1h)	2.769(9)
	2.80(1)
	2.863(7)
	2.836(9)
O(1e)· · ·O(2a)	2.682(8)
	2.679(9)
	2.722(6)
	2.92(1)
O(1e)· · ·O(4c)	2.825(8)
	2.85(1)
	2.726(8)
	2.75(1)
O(1f)· · ·O(3h)	3.02(1)
	3.02(1)
	2.982(8)
	2.87(1)
O(1f)· · ·O(1i)	2.696(9)
	2.681(9)
	2.629(6)
	2.66(1)
O(1g)· · ·O(3c)	2.829(7)
	2.846(8)
	2.846(6)
	2.812(7)
O(1g)· · ·O(5c)	2.840(9)
	2.84(1)
	2.832(7)
	2.817(8)
O(1h)· · ·O(1i)	2.830(9)
	2.82(1)
	2.821(8)
	2.76(1)
O(1i)· · ·O(3a)	2.909(9)
	2.92(1)
	2.861(7)
	2.89(1)
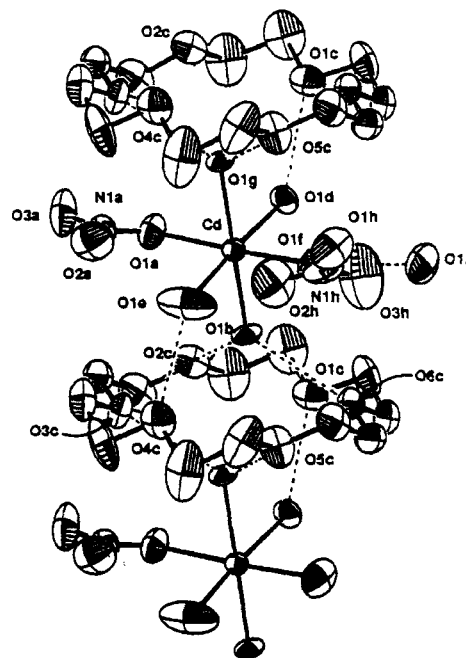
FIGURE 3   Structure of [18-crown-6][Cd(NO₃).5H₂O](NO₃)(H₂O), 5 showing the binding of the [Cd(NO₃).5H₂O] cation to the 18-crown-6 molecule. Complexes 2 to 4 are isomorphous.
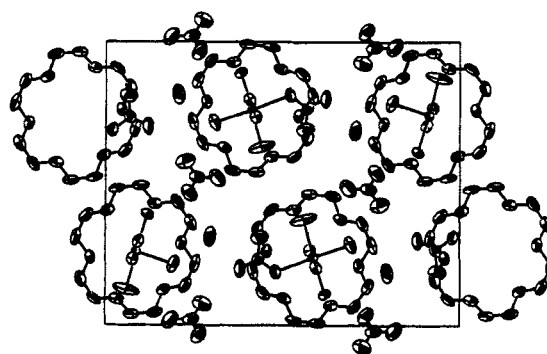

FIGURE 4   Unit cell contents of [18-crown-6][Cd(NO₃).5-H₂O](NO₃)(H₂O), 5, viewed down A.

nomenon is similar to that seen in other complexes of hydrated transition metal ions, and can furthermore be related to the ratio of the ionic diameter of the metal ion to the effective diameter of the macrocycle. In previous studies for alkali metals, it has been established that
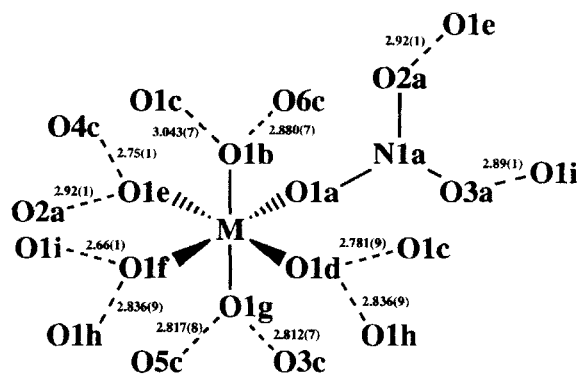
FIGURE 5   Hydrogen bonding about the [Cd(NO₃).5H₂O] cation in [18-crown-6][Cd(NO₃).5H₂O](NO₃)(H₂O), 5.

ratios of 0.75 to 0.90 are favorable for direct ion-crown ether bonding, [11] and for the five and six-coordinate transition metals studied herein, ratios of 0.44 to 0.53 for Co^{2+}, 0.43 to 0.53 for Ni^{2+}, 0.41 to 0.50 for Cu^{2+}, 0.46 to 0.57 for Zn^{2+} and 0.59 to 0.73 for Cd^{2+} (the effective diameter of the 18-crown-6 cavity is 2.6 to 3.2 Å [6a]) are found [9]. Thus, apart from the overwhelming influence to form hydrated metal ions, the 18-crown-6 cavity appears to be of non-optimal size for effective encapsulation of these metals. However, the 18-crown-6 molecule does appear to perform a stabilising influence on the crystallisation of these complexes due to the formation of polymeric hydrogen bonded networks.

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