More examples of the 15-crown-5···H$_2$O—M—OH$_2$···15-crown-5 motif, M = Al^{3+}, Cr^{3+} and Pd^{2+}

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Five structures of co-crystals grown from aqueous solutions equimolar in 15-crown-5 (or 15C5) and [M(H$_2$O)$_6$](NO$_3$)$_n$, M = Al^{3+}, Cr^{3+} and Pd^{2+}, are reported. The hydrogen-bonding patterns in all are similar: metal complexes including the fragment *trans*-H$_2$O—M—OH$_2$ alternate with 15C5 molecules, to which they are hydrogen bonded, to form stacks. A literature survey shows that this hydrogen-bonding pattern is very common. In each of the two polymorphs of the compound [Al(H$_2$O)$_6$](NO$_3$)$_3$·15C5·4H$_2$O there are two independent cations; one forms hydrogen bonds directly to the 15C5 molecules adjacent in the stack, while the other cation is hydrogen-bonded to two water molecules that act as spacers in the stack. These stacks are then crosslinked by hydrogen bonds formed by the three nitrate counterions and the three lattice water molecules. The hydrogen-bonded stacks in [Cr(H$_2$O)$_5$(NO$_3$)](NO$_3$)$_2$·1.5(15C5)·H$_2$O are discrete rather than infinite; each unit contains two Cr^{3+} complex cations and three 15C5 molecules. These units are again crosslinked by the uncoordinated nitrate ions and a lattice water molecule. In [Pd(H$_2$O)$_2$(NO$_3$)$_2$]·15C5 the infinite stacks are electrically neutral and are not crosslinked. In [Pd(H$_2$O)$_2$(NO$_3$)$_2$]·2(15C5)·2H$_2$O·2HNO$_3$ a discrete, uncharged unit containing one Pd complex and two 15C5 molecules is 'capped off' at either end by a lattice water molecule and an included nitric acid molecule. In all five structures the infinite stacks or discrete units form an array that is at least approximately hexagonal.

1. Introduction

During a previous study (Siegler, Parkin *et al.*, 2008) aimed at inserting a Ni^{2+} ion into a 15-crown-5 ring (1,4,7,10,13-pentaoxacyclopentadecane; hereafter, 15C5) we made five new compounds containing an H$_2$O–Ni–OH$_2$ fragment, nitrate ions and the 15C5 molecule. One of the five was the desired product; the other four all contain the hydrogen-bonded motif ···15C5···H$_2$O—Ni—OH$_2$···15C5···H$_2$O—Ni—OH$_2$···15C5. A search of the Cambridge Structural Database (Allen, 2002; hereafter, the CSD) showed that this motif is very common for a variety of metals (see also Steed, 2001).

Neither this CSD search nor previous work (see Siegler, Hao *et al.*, 2008, and references therein) turned up any structure of a similar crystal containing 15C5, a weakly coordinating counterion like nitrate, and Al^{3+}, Cr^{3+} or Pd^{2+}.[1]

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[1] There are three structures [CSD refcodes FIGLEM (Bott *et al.*, 1987), FUFTOP (Strel'tsova *et al.*, 1987) and LEWMAB (Bulychev *et al.*, 1993)] in which an [AlX_2]$^+$ unit, X = Cl or Me, lies at the approximate center of the 15C5 ligand. The structure TADFEJ (Ernst *et al.*, 1990) has a [Cr(H$_2$O)Cl$_3$] unit that is attached to a 15C5 molecule by two Cr—O bonds, but the Cr^{III} cannot be said to be 'in' the crown cavity.

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When reacted with 15C5, Al(NO$_3$)$_3$(aq) gave two polymorphic structures, Pd(NO$_3$)$_2$(aq) gave two compounds of different composition, and Cr(NO$_3$)$_3$(aq) gave a single product, so five structures are reported here. All include the basic hydrogen-bonding motif described above, but in two cases the hydrogen-bonded units are discrete rather than infinite. Results of a CSD search for compounds with similar motifs are also discussed.

2. Experimental

2.1. Syntheses

Evaporation over several days at room temperature of concentrated aqueous solutions equimolar in 15C5 and M(NO$_3$)$_n$ (M = Al^{3+}, Cr^{3+}, n = 3; M = Pd^{2+}, n = 2) yielded the following crystals (see Fig. 1):

(i) [Al(H$_2$O)$_6$](NO$_3$)$_3$·15C5·4H$_2$O (colorless; two polymorphs),
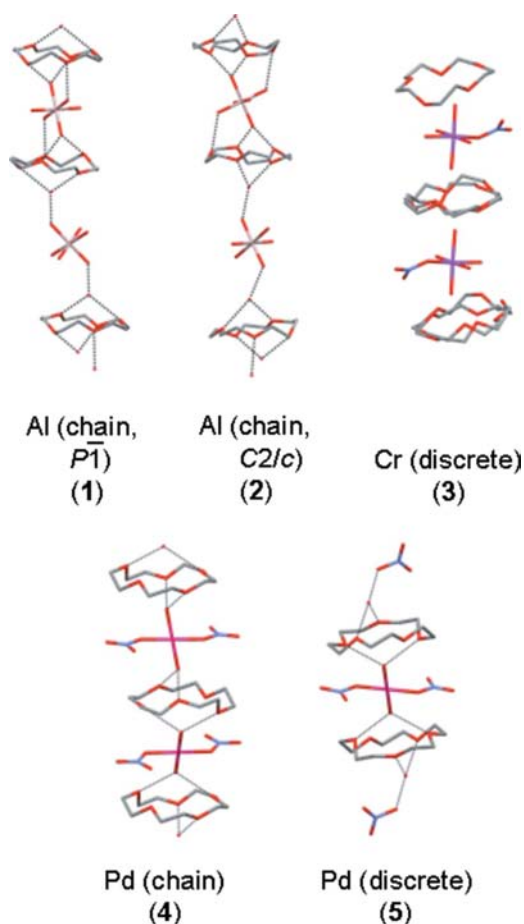
Figure 1
The connectivities of [Al(H$_2$O)$_6$](NO$_3$)$_3$·(15-crown-5)·4H$_2$O (two polymorphs), [Cr(H$_2$O)$_5$(NO$_3$)](NO$_3$)$_2$·1.5(15-crown-5)·H$_2$O, [Pd(H$_2$O)$_2$-(NO$_3$)$_2$]·(15-crown-5) and [Pd(H$_2$O)$_2$(NO$_3$)$_2$]·2(15-crown-5)·2H$_2$O··2HNO$_3$. Only the hydrogen bonds within the units are shown. No hydrogen bonds are shown for the very disordered Cr structure and not all of its disorder is shown. H atoms have been omitted for the sake of clarity in this and all subsequent drawings except for Fig. 10.

(ii) [Cr(H$_2$O)$_5$(NO$_3$)](NO$_3$)$_2$·1.5(15C5)·H$_2$O (dark teal blue),

(iii) [Pd(H$_2$O)$_2$(NO$_3$)$_2$]·15C5 and [Pd(H$_2$O)$_2$-(NO$_3$)$_2$]·2(15 C5)·2H$_2$O·2HNO$_3$ (both colorless).

The second Pd compound was grown from a solution that had been acidified with a few drops of 10% nitric acid.

The chemical formulae were determined during the structure determinations.

2.2. Structure determinations

All X-ray data were collected with a Nonius KappaCCD diffractometer equipped with a CRYOCOOL-LN2 low-temperature system (CRYO Industries of America, Manchester, NH). Mo $K\alpha$ radiation from a fine-focus sealed tube was used. Crystals were normally flash-cooled to 90 K for data collection, but the Cr crystal was cooled slowly (see below) to improve the quality of the data.

In all cases the H atoms were placed in chemically reasonable positions, as suggested by C and O positions, peaks in difference-Fourier maps and O···O distances. The H atoms of the 15C5 ligands were placed at calculated positions [instruction AFIX 23 in *SHELXL*97 (Sheldrick, 2008)] with isotropic displacement parameters having values 1.2U_{eq} of the attached C atom. The H atoms of coordinated waters were restrained such that the O—H distances and H—O—H angles had values within accepted ranges [d(O—H) = 0.82–0.84 Å,

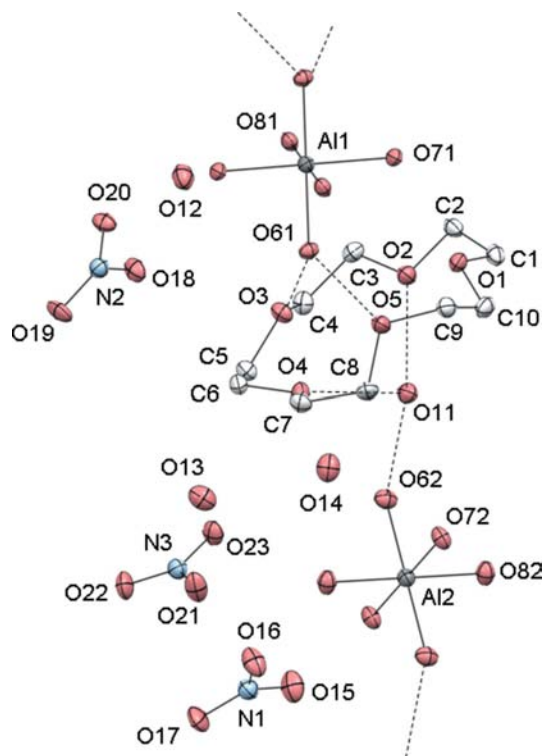**Figure 2**
Ellipsoid plot (50% probability level) for one formula unit of the triclinic polymorph of [Al(H$_2$O)$_6$](NO$_3$)$_3$·(15-crown-5)·4H$_2$O at 90 K. The atom-numbering scheme is shown. Each Al^{3+} ion is located on an inversion center. The only O—H···O bonds shown are those within the hydrogen-bonded stacks.

Table 1
Experimental details.

Experiments were carried out at 90 K with Mo $K\alpha$ radiation using a Nonius KappaCCD diffractometer. H atoms were treated by a mixture of independent and constrained refinement.

	(1)	(2)	(3)	(4)	(5)
Crystal data					
Chemical formula	$C_{10}H_{20}O_5 \cdot AlH_{12}O_6 \cdot 3NO_3 \cdot 4H_2O$	$C_{10}H_{20}O_5 \cdot AlH_{12}O_6 \cdot 3NO_3 \cdot 4H_2O$	$3C_{10}H_{20}O_5) \cdot 1.68CrH_8NO_8 \cdot 0.32CrO_6 \cdot 4.32NO_3 \cdot 2H_2O$	$C_{10}H_{20}O_5 \cdot H_4N_2O_8Pd$	$2C_{10}H_{20}O_5 \cdot H_4N_2O_8Pd \cdot 2HNO_3 \cdot 2H_2O$
M_r	613.43	613.43	1351.48	486.71	869.04
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a, b, c (Å)	9.8642 (1), 11.7922 (1), 12.8064 (2)	18.6039 (3), 9.3611 (1), 31.5795 (5)	18.0939 (2), 9.4487 (1), 19.0682 (3)	7.4649 (1), 9.5487 (1), 13.3944 (3)	7.0048 (1), 9.8871 (2), 13.8440 (3)
α, β, γ (°)	99.1087 (5), 112.2703 (5), 92.3805 (5)	90.00, 99.3468 (7), 90.00	90.00, 116.0858 (6), 90.00	73.8388 (7), 88.0601 (7), 73.6959 (7)	79.8454 (9), 87.7567 (9), 70.4587 (11)
V (Å^3)	1352.72 (3)	5426.65 (14)	2927.90 (6)	879.13 (2)	889.21 (3)
Z	2	8	2	2	1
μ (mm^{-1})	0.18	0.18	0.49	1.13	0.62
Crystal size (mm)	$0.25 \times 0.15 \times 0.07$	$0.25 \times 0.22 \times 0.17$	$0.30 \times 0.20 \times 0.15$	$0.15 \times 0.07 \times 0.03$	$0.50 \times 0.10 \times 0.10$
Data collection					
Absorption correction	Multi-scan *SCALE-PACK*	Multi-scan *SCALE-PACK*	Multi-scan *SCALE-PACK*	Multi-scan *SCALE-PACK*	Multi-scan *SADABS*
T_{min}, T_{max}	0.957, 0.988	0.957, 0.970	0.879, 0.937	0.849, 0.972	0.596, 0.940
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	33 872, 6187, 3888	40 687, 6212, 4125	49 028, 6683, 5576	21 461, 4016, 3440	24 163, 4040, 3946
R_{int}	0.066	0.061	0.035	0.035	0.052
Refinement					
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.117, 0.99	0.042, 0.114, 1.04	0.073, 0.215, 1.05	0.021, 0.052, 1.08	0.024, 0.063, 1.09
No. of reflections	6187	6212	6683	4016	4040
No. of parameters	407	440	660	251	248
No. of restraints	31	41	974	6	6
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.35, −0.36	0.79, −0.47	1.38, −0.38	0.83, −0.80	0.61, −0.78

Computer programs used: *COLLECT* (Nonius, 2000), *SCALEPACK*, *DENZO-SMN* (Otwinowski & Minor, 2006), *SHELXS*97, *SHELXL*97, *SADABS* (Sheldrick, 2008), *XP* in *SHELXTL* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008), and local procedures.

$d(\text{H}\cdots\text{H}) \simeq 1.30$ Å so that $\text{H}-\text{O}-\text{H} \simeq 104.5°$]. Isotropic displacement parameters for the water H atoms were $1.5U_{eq}$ of the attached O atom.

Experimental details are given in Table 1 and in the supplementary material.[2] Plots showing the connectivity, atom-numbering schemes and displacement ellipsoids are given in Figs. 2–7. Some additional comments are given below.

2.2.1. Al^{3+} compounds (1) and (2). The triclinic polymorph is fully ordered, but in the monoclinic form two of the three nitrate counterions have major and minor orientations. The occupancy factors for the two major and for the two minor sites were held equal [value 0.873 (3) for the major sites] because very short inter-nitrate contacts suggest correlation of the two occupancies. The atoms of the low-occupancy sites were refined isotropically. The major and minor sites for each nitrate ion are related by a rotation (*ca* 25 and 35° in the two anions) around an axis roughly perpendicular to the atomic plane.

In the triclinic form the two independent cations are both located on inversion centers; in the monoclinic form one

cation has inversion symmetry and the other has twofold rotation symmetry. Both structures have one independent 15C5 molecule, three nitrate ions and four uncoordinated water molecules, one of which is part of the hydrogen-bonded stack.

2.2.2. Cr^{3+} compound (3). The first crystal was studied after flash cooling to 90 K. Initial attempts at structure solution indicated a discrete hydrogen-bonded unit located on an inversion center and containing two $[\text{Cr}(\text{H}_2\text{O})_5(\text{ONO}_2)]^{2+}$ ions sandwiched between three 15C5 molecules (see Fig. 1). Disorder of the central 15C5 over more than the two sites required by the inversion symmetry quickly became obvious; the outer 15C5 molecule and one of the two nitrate counterions are also disordered. One of the other two nitrate ions appeared to be coordinated in a monodentate fashion to most, but not all, Cr^{3+} ions; in 15.8 (3)% of the cations the nitrate containing N1 is outside the coordination sphere and is replaced in the sphere by an additional water ligand (see Fig. 4). We tried determining the structure at room temperature in the hope that the disorder might be complete, but were disappointed. Finally we tried slow cooling (*ca* 60 K h^{-1} from room temperature to 90 K). The slow cooling did improve the quality of the data to some extent, but the structure was still found to be very disordered.

The reciprocal lattice slices $nk\ell$, $hn\ell$ and hkn, $n = 0$–3 were reconstructed with the PRECESSION routine in *COLLECT* (Nonius, 2000) from the data in the unprocessed frames collected at 90 K from the crystal that had been cooled slowly. Examination of these slices shows structured diffuse scattering that probably indicates short- or medium-range order. The $0k\ell$, $hk0$ and $hk3$ images are included with the supplementary material.

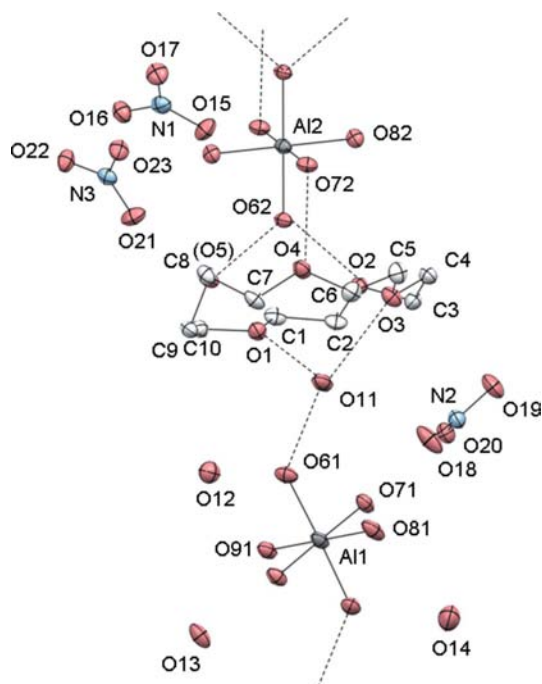The structure of the crystal that had been slow-cooled to 90 K was modeled as well as possible using many of the options in *SHELXL*97 (SAME, FLAT, DELU, SIMU, EADP). Occupancy factors for the components of the central 15C5 were all held at 0.25; occupancy factors for the components of the disordered outer 15C5 ring and the disordered nitrate counterion were held at 0.5. Occupancy factors for all the atoms involved in the coordination shell of the Cr ion were held equal.

The final difference map includes peaks as high as 1.38 e Å^{-3}, but peaks 1–4, 9–11 and 15–20 (the last with peak height 0.34 e Å^{-3}) are associated with the outer 15C5 rings and peak 6 (0.70 e Å^{-3}) with the central 15C5 ring. Peak 5 (0.74 e Å^{-3}) is approximately midway between O11 and O11W (see Fig. 4); peaks 8 and 14 (0.65 and 0.50 e Å^{-3}) are also near atoms N1 and N1′. Peaks 7 and 13 (0.69 and 0.52 e Å^{-3}) suggest an alternate orientation of the nitrate counterion that includes atom N3.

The final least-squares input file has been archived in the CIF. Although this structure could not be determined as well as we would have liked, it is included because we think a more precise determination is unlikely and because the structure does show the basic geometry and bonding of the compound obtained from $Cr(NO_3)_3(aq)$ and 15C5.

2.2.3. Pd^{2+} compounds (4) and (5). Structure solutions in the expected space group $P\overline{1}$ failed initially so the structures

Figure 3
Ellipsoid plot (50% probability level) for one formula unit of the monoclinic polymorph of $[Al(H_2O)_6](NO_3)_3 \cdot (15\text{-crown-5}) \cdot 4H_2O$ at 90 K. The atom-numbering scheme is shown. The Al1 ion is located on a twofold axis and the Al2 ion is located on an inversion center. The only O—H···O bonds shown are those within the hydrogen-bonded stacks. The disorder of the nitrate ions containing N1 and N3 is not shown.
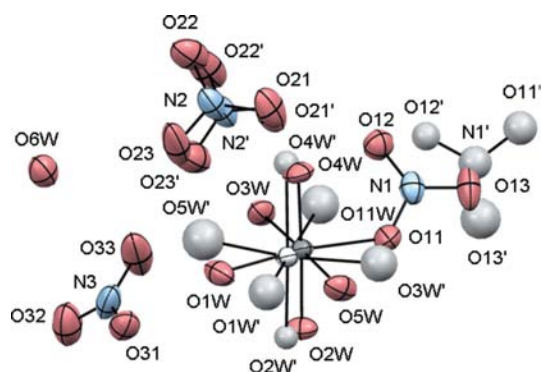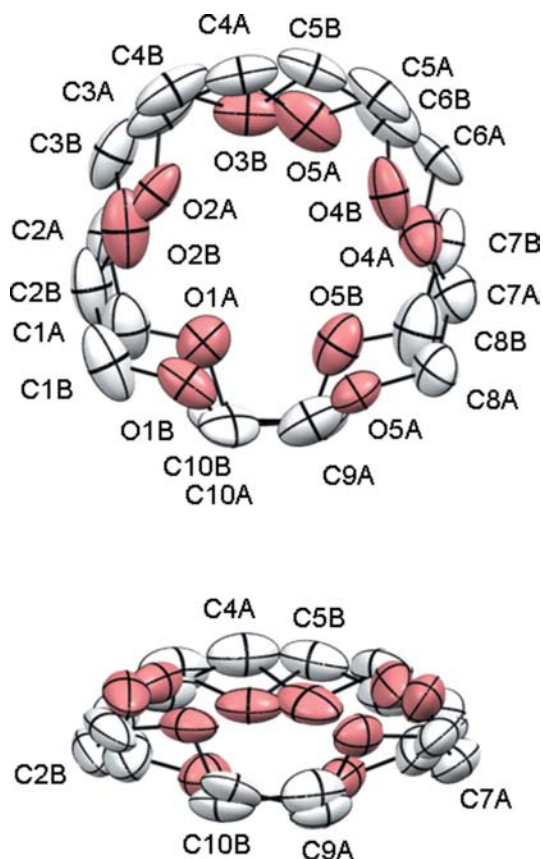

Figure 4
Ellipsoid plot (50% probability level) for all non-H atoms except the atoms of the 15-crown-5 molecules, of one formula unit of $[Cr(H_2O)_5(NO_3)](NO_3)_2 \cdot 1.5(15\text{-crown-5}) \cdot H_2O$ at 90 K. The disordered atoms are shown in light gray; most of the atoms with occupancies below 0.5 were refined isotropically. The atom-numbering scheme is shown. The hydrogen bonds are not shown.

Figure 5
Ellipsoid plots (50% probability level) for the outer rings (see Fig. 1) of $[Cr(H_2O)_5(NO_3)](NO_3)_2 \cdot 1.5(15\text{-crown-5}) \cdot H_2O$ at 90 K. The lower drawing is related to the upper drawing by a rotation of 50° around the horizontal.

were both solved in space group $P1$ and then converted to the centrosymmetric group. The presence of the extra nitrate group in the second structure [(5); see Figs. 1 and 7] was a surprise. The possibility of having formed a Pd[IV] complex was ruled out because Pd[II] is very common and almost always square planar, while Pd[IV] is uncommon and essentially always octahedral (Barnard & Russell, 1987). The similarity of the Pd—OH$_2$ and Pd—ONO$_2$ distances in the two structures (2.016, 2.009; 2.013 Å compared with 1.998, 1.993; 1.993 Å; all s.u.s 0.0013 Å or less) was further evidence that both structures contain Pd[II]. If Pd[II] rather than Pd[IV] were present at the inversion center then one more H atom needed to be located. When the refinement of the second Pd structure was nearly complete (R_1 = 0.025) the largest peak in the Fourier difference map had a height of 0.65 e Å^{-3} and was located approximately 0.94 Å from O16 of the nitrate counterion and 1.56 Å from O11 of the water molecule that is hydrogen-bonded to the crown; together with the angle O16–peak–O11 of 165° these distances strongly suggested an O—H$\cdots$O grouping. Furthermore, the N2—O16 distance was more than 0.1 Å longer than the N2—O14 and N2—O15 distances, which differed by only 0.002 Å. The remaining important peaks in the difference map were either near the Pd ion or near the centers of covalent bonds. Finally, there are two clear precedents in the CSD for an O$_2$NOH$\cdot$OH$_2\cdot$(crown ether) grouping: NEYBOI (Young & Sykes, 1998) and QADYAW01 (Calleja *et al.*, 2003; neutron diffraction study at 100 K). We therefore concluded that molecules of nitric acid had been included in the crystal. The coordinates of the acidic H atom could be refined without restraints; the final O16—H16 distance is 0.84 (2) Å.

In the Pd structure with infinite hydrogen-bonded chains (4), both Pd^{2+} ions are located on inversion centers and there is one independent 15C5 molecule. The Pd^{2+} ion in (5) is also located on an inversion center.

2.2.4. CSD search. The CSD was searched (version 5.30 + updates through May 2009) for structures containing both a 15C5 molecule and a H$_2$O—M–OH$_2$ group. The hits were then screened by hand to remove those structures that were obviously unreli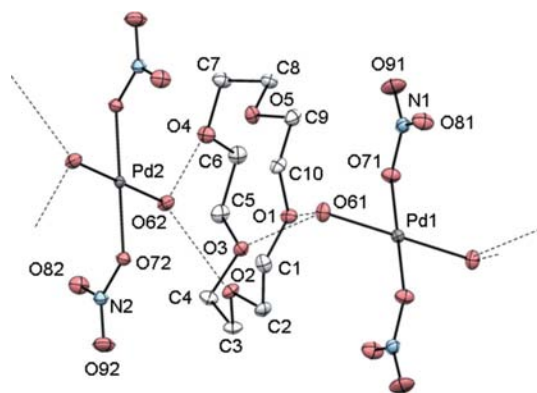able ($R > 0.10$ or coordinates missing) and those in which a metal atom or ion was linked directly to O atoms of the crown. The final number of structures was 41. A list of the refcodes, metal type, oxidation state, ion charge and M—O distance is available with the supplementary material.

3. Results

3.1. CSD search

Of the 41 structures containing 15C5 and an H$_2$O—M—OH$_2$ grouping 37 (90%) have infinite hydrogen-bonded chains. Simple infinite chains of the type 15C5$\cdots$H$_2$O—M—OH$_2\cdots$15C5$\cdots$H$_2$O—M—OH$_2\cdots$ are found in 32 of those 37 structures. The other five structures have more complicated chains of the type 15C5$\cdots$H$_2$O—M—OH$_2\cdots$15C5$\cdots B\cdots$, where B is a second type of H$_2$O—M—OH$_2$ unit in four cases and an H$_5$O$_2^+$ ion in the fifth. The last four of the 41 structures (10%) have discrete hydrogen-bonded aggregates that include two, three or four 15C5 molecules.

The formal oxidation states of the metals in the H$_2$O—M—OH$_2$ units vary from +2 to +6, but in 22 of the 41 structures (54%) the presence of coordinated anions makes the metal complex electrically neutral. In another 12 of the structures (29%) the charge on the complex is 1± or 2±. In only seven structures (17%) do the metal complexes have charges of 3+ or higher. Six of the M^{3+} structures have the formula
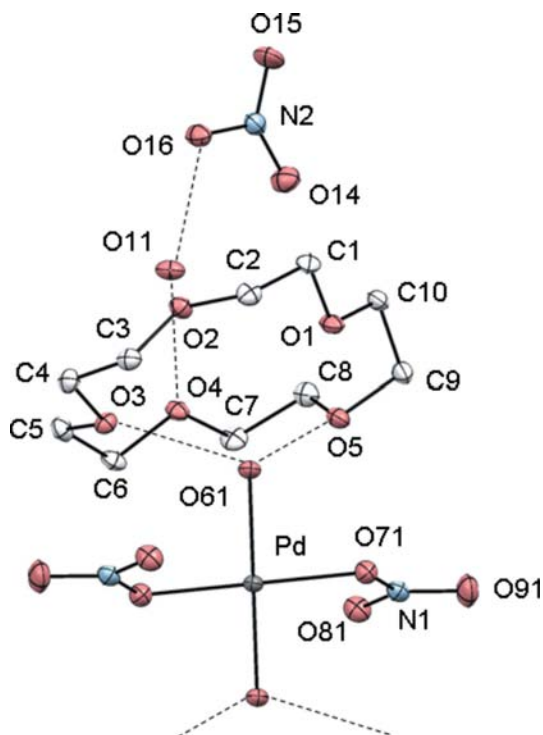

Figure 6
Ellipsoid plot (50% probability level) for one formula unit of the structure of [Pd(H$_2$O)$_2$(NO$_3$)$_2$]·(15-crown-5) at 90 K. Each Pd^{2+} ion is located on an inversion center. The atom-numbering scheme and the O—H$\cdots$O bonds are shown.

Figure 7
Ellipsoid plot (50% probability level) showing the unique part of the structure of [Pd(H$_2$O)$_2$(NO$_3$)$_2$]·2(15-crown-5)·2H$_2$O·2HNO$_3$ at 90 K. The Pd^{2+} ion is located on an inversion center The atom-numbering scheme and the O—H$\cdots$O bonds are shown. The hydrogen-bonded units in this structure are discrete.

$[M(H_2O)_n]Cl_3 \cdot 15C5$, where $n = 8$ for M = Y, Gd, Er, Yb and Lu, and $n = 9$ for M = Nd. The $n = 8$ compounds are all isostructural (*e.g.* FAYVEG01). In all six the chloride ions are located in positions consistent with the formation of hydrogen bonds to the coordinated water molecules. The overall packing unit (metal complex plus hydrogen-bonded chloride ions) is therefore electrically neutral. The seventh structure containing highly charged ions is XIGSEL (Junk *et al.*, 2002), which was grown from aqueous solutions equimolar in $Fe(NO_3)_3$ and 15C5 and contains an unusual, discrete, centrosymmetric aggregate formed by two $[Fe(H_2O)_6]^{3+}$ ions, one $[(H_2O)_5FeOFe(H_2O)_5]^{4+}$ ion and three 15C5 molecules.

In 23 of the 37 structures (62%) that have infinite hydrogen-bonded chains, these chains are crosslinked by good hydrogen bonds ($D \cdots A$ distances that are at least 0.2 Å shorter than the sum of the van der Waals radii; Bondi, 1964). Of the 14 structures without crosslinks, 13 have electrically neutral metal complexes. All structures having metal complexes with charges of 2+ or above are crosslinked.
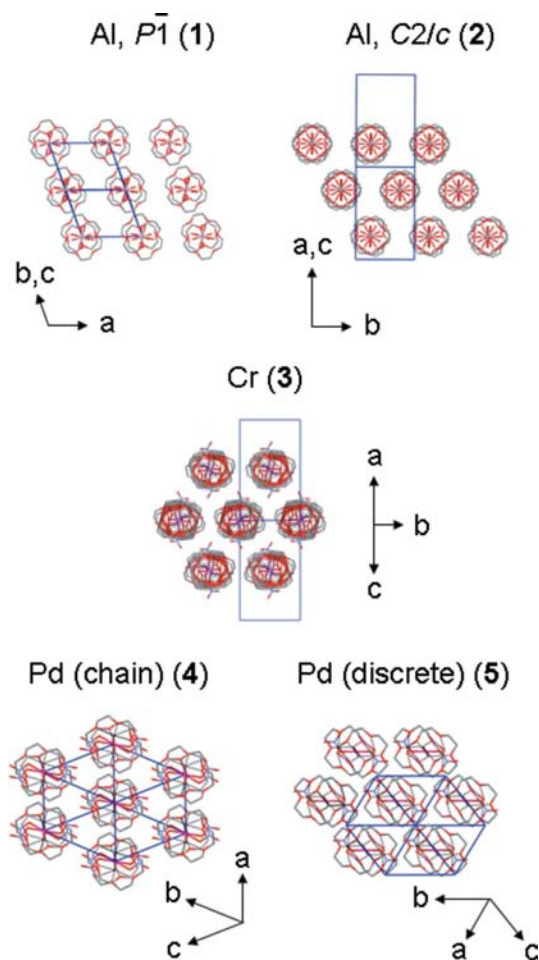

Figure 8
Projections showing the arrangements of the hydrogen-bonded stacks in the five structures. Neither lattice water molecules nor nitrate counterions are shown. The directions normal to the drawings are (1) [0 1 $\bar{1}$], (2) [1 0 $\bar{1}$], (3) [1 0 1], (4) [1 $\bar{1}$ 1] and (5) [1 $\bar{1}$ $\bar{1}$].

3.2. Al³⁺ structures

The hydrogen-bonded chains in the two $[Al(H_2O)_6]$-$(NO_3)_3 \cdot 15C5 \cdot 4H_2O$ polymers (see Fig. 1) are almost unique [XIGSEL (Junk *et al.*, 2002) is the other example] in including water spacers. In each Al structure there are two independent $[Al(H_2O)_6]^{3+}$ cations; one is directly hydrogen bonded to two 15C5 molecules, but the other is separated from the two closest 15C5 molecules by water spacers. The chain pattern is then $\cdots 15C5 \cdots H_2O - Al - OH_2 \cdots 15C5 \cdots W \cdots H_2O - Al - OH_2 \cdots W \cdots 15C5 \cdots H_2O - Al - OH_2 \cdots 15C5 \cdots W \cdots$, where W stands for lattice water.

The chain repeat distance is 4.5% shorter in the triclinic structure (18.73 Å along [0 1 $\bar{1}$]) than in the monoclinic structure (19.59 Å along [1 0 $\bar{1}$]). The molar volumes, however, differ by only 0.3% (see Table 1) because the chains in the monoclinic structure are more tightly packed in directions normal to the chain axis. In the monoclinic structure the chains are nearly straight (hence the longer repeat distance) and the array is nearly hexagonal (see Fig. 8), while in the triclinic structure the array is only very approximately hexagonal. In both polymorphs the hydrogen-bonded chains are crosslinked by hydrogen bonds involving the three nitrate ions and three lattice water molecules. The two crosslinking patterns are quite different.

In the triclinic structure the 15C5 molecules in the hydrogen-bonded chains are in direct contact along [0 1 1] only (see Fig. 8). The Al^{3+} ions are lined up along [0 1 $\bar{1}$]; in this direction $[Al(H_2O)_6]^{3+}$ ions hydrogen-bonded to water spacers alternate with $[Al(H_2O)_6]^{3+}$ ions hydrogen-bonded to 15C5 molecules (see Fig. 9). The water spacers can be
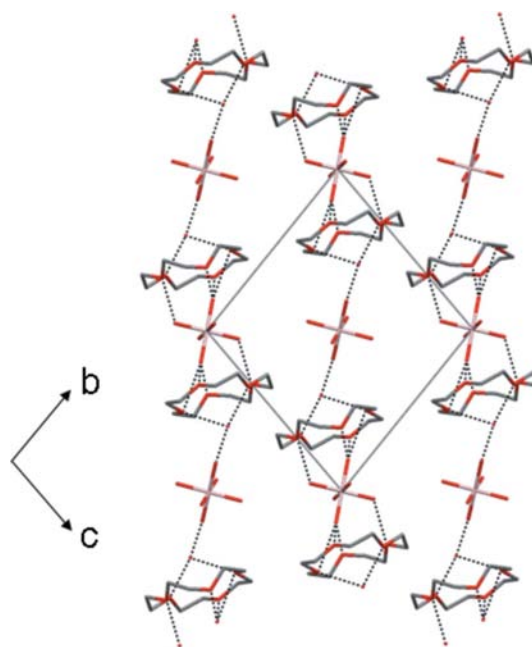

Figure 9
A layer of the triclinic Al structure perpendicular to **a**, which points into the paper; the axes **b** and **c** point somewhat out of the paper. This is the only layer in the structure in which the hydrogen-bonded chains, which run approximately vertically, are in direct contact (see Fig. 8).

Table 2
Distances of metal ions from O atoms of the water molecules.

	$M-O_{water, ax}$ (Å)	$M-O_{water, eq}$ (Å)	$M-ONO_2$ (Å)	Ionic radius† (M^{n+}, Å)
Al³⁺ ($P\bar{1}$)	1.888 (2)‡	1.864 (2), 1.877 (2)		0.535§
[$Z' = 2(\frac{1}{2})$] (1)	1.863 (2)¶	1.870 (2), 1.873 (2)		
Al³⁺ ($C2/c$)	1.883 (2)‡	1.868 (2), 1.884 (2)		0.535§
[$Z' = 2(\frac{1}{2})$] (2)	1.870 (2)¶	1.868 (2), 1.888 (2), 1.889 (2)		
Cr³⁺	1.936 (5), 1.983 (4)	1.943 (3), 1.960 (3), 1.986 (3)	1.958 (3)	0.615§
($Z' = 1$) (3)				
Pd²⁺	2.016 (2)		1.998 (2)	0.64††
[$Z' = 2(\frac{1}{2})$] (4)	2.009 (2)		1.993 (2)	
Pd²⁺ ($Z' = \frac{1}{2}$) (5)	2.013 (2)		1.993 (2)	0.64††
Ni²⁺‡‡	(2.02–2.05)	(2.04–2.07)	(2.00–2.05)	0.690§

† Shannon (1976). ‡ To H_2O_{ax} that is hydrogen-bonded to a 15-crown-5 molecule. ¶ To H_2O_{ax} that is hydrogen-bonded to a water molecule in the cation/water/15-crown-5 chain. § Octahedral radius. †† Square-planar radius. ‡‡ Siegler *et al.* (2008).

understood as facilitating packing by preventing direct 15C5···15C5 contacts. In the monoclinic structure each hydrogen-bonded chain is in direct contact with six others (see Fig. 8) and the role of the water spacers in the crystal packing is less easy to understand.

3.3. Cr³⁺ structure

In the Cr structure discrete, centrosymmetric, hydrogen-bonded units are formed from three 15C5 molecules that separate and surround two Cr-containing cations (see Fig. 1). Most [84.2 (3)%] of the cations have five water ligands and one nitrato ligand, but the other 15.8 (3)% have six water ligands (see Fig. 4). The crystals therefore contain two different compounds, $[Cr(H_2O)_5(NO_3)](NO_3)_2$·1.5(15C5)·$H_2O$ and $[Cr(H_2O)_6](NO_3)_3$·1.5(15C5)·H_2O that occupy the same site.

The cations are stacked along [1 0 1] to give an array that is nearly hexagonal (see Fig. 8). The outer 15C5 molecules of cation aggregates adjacent in a stack are related by an inversion center; the best molecular planes of the outer 15C5 rings in adjacent molecules are separated by 3.88 Å. Space-filling views drawn with *Mercury* (Macrae *et al.*, 2008) show that these two rings are in only loose contact. The loose contact explains at least some of the disorder. Stacks adjacent in the approximately hexagonal array are linked by hydrogen bonds.

3.4. Pd²⁺ structures

In the two Pd structures each square-planar Pd²⁺ ion is coordinated to two water molecules and two nitrato ligands; in both cases the ligand arrangement is *trans*. In the $[Pd^{II}(H_2O)_2(NO_3)_2]$·15C5 structure (*i.e.* the structure that does not include extra water and nitric acid) the typical hydrogen-bonded chain (parallel to [1 $\bar{1}$ 1]) includes two independent Pd^{II} complex ions, each located on an inversion center, alternating with one independent 15C5 molecule. The chains are packed in a distorted hexagonal array.

In the $[Pd(H_2O)_2(NO_3)_2]$·2(15C5)·$2H_2O$·$2HNO_3$ structure, however, there are discrete hydrogen-bonded units (see Figs. 1 and 7) $O_2NOH···OH_2···15C5···H_2O-Pd-H_2O···15C5···H_2O···HONO_2$, with the Pd²⁺ ion again located on an inversion center. Each water O atom makes three short O···O contacts: two to ether O atoms (2.72 and 2.74 Å) and one (2.48 Å) to the protonated O atom of the included nitric acid molecule.

The arrangement of the stacks is again basically hexagonal (see Fig. 8), but is not as symmetrical as in the monoclinic Al and Cr structures.

4. Discussion

4.1. General considerations

Crystals grown from aqueous solutions equimolar in $M(NO_3)_n$ and 15-crown-5 are expected to be those that are the most thermodynamically stable. The coordination of the metal ion must therefore be favorable, with octahedral coordination expected for Al³⁺ and Cr³⁺, and square-planar coordination for Pd²⁺. The arrangement of charges is also very important because electrostatic interactions are so much stronger than van der Waals interactions. Next, the hydrogen-bond donors and acceptors should be satisfied as much as possible. Finally, van der Waals interactions should be optimized and space filled densely.

All of the compounds reported here, and the 41 others found in the CSD search, include 15C5 and are therefore co-crystals. The 15C5 molecule provides a tidy and convenient package of hydrogen-bond acceptors for the water molecules that are coordinated to the metal ions. This advantage apparently more than offsets the disadvantage of having to optimize a much larger number of interatomic distances (see Siegler, Parkin *et al.*, 2008 and references therein). The failure of 15C5 to crystallize well by itself (Parsons, 2007) must also be a factor.

4.2. Coordination by a nitrato ligand

In solution the metal ions are coordinated by water molecules, which are better ligands than the ONO_2^- ion and are present in much greater concentration. Coordination of the metal by a nitrato ligand, as occurs in the Cr³⁺ (84% of the time) and the Pd²⁺ complexes, must occur because lowering the local charge makes it easier to find an electrostatically favorable arrangement in the solid state.

In this context we wondered if any of the protons of the four independent $[Al(H_2O)_6]^{3+}$ ions might have been transferred to one of the lattice water molecules. There is only limited information about the positions of the H atoms available, but we found no evidence in the short contacts that would indicate transfer of a proton from the $[Al(H_2O)_6]^{3+}$ cation to some other site.

4.3. Inclusion of extra water molecules in the chains of the Al structures

The Al—O distances (see Table 2) are, on average, 0.086 (1) Å shorter than the Cr—O distances, which are 0.051 (1) Å shorter than the Pd—O distances. The Ni—O distances in the three $[Ni(H_2O)_6](NO_3)_2 \cdot nH_2O$, $n = 1$, 2, structures are, on average, another 0.036 (1) Å longer than the Pd—O distances (Siegler, Parkin et al., 2008). These distances are consistent with the differences in ionic radii (see Table 2). We believe that the Al compound includes water molecules in the hydrogen-bonded chains because the resulting increase in the distance between 15C5 molecules allows the formation of a more stable structure of this quite ionic compound. All the structures found in the CSD search that have M—O_{ax} distances less than 2.00 Å contain neutral complexes, like $[Cu(H_2O)_2Cl_2]$ (refcode KUPHAE). The only other structure that includes water in the chain is XIGSEL, where the $[(H_2O)_5Fe(\mu\text{-}O)Fe(H_2O)_5]^{4+}$ ions, which have their Fe—Fe vectors perpendicular to the chain axis, form hydrogen bonds to water molecules, which are in turn hydrogen-bonded to 15C5 molecules.

4.4. Interchain interactions

Fitting the hydrogen-bonded chains together is an important packing problem. Chemical groups that are different
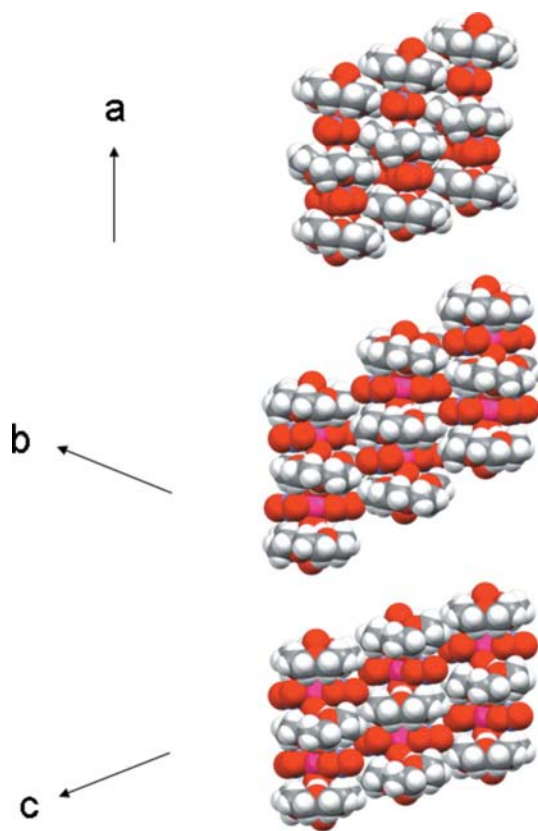

Figure 10
Space-filling drawings of the chain–chain alignment in the Pd structure with infinite chains. The arrows correspond to the directions in Fig. 8; the top, middle and bottom drawings include the axes **a**, **b** and **c**.

electronically are usually segregated in a crystal, so it might be expected that layers of 15C5 molecules would separate ionic layers. That expectation cannot, however, be fulfilled so easily because the van der Waals surface of a 15C5 molecule is wider than that of a $[M(H_2O)_6]^{n+}$ ion and less wide than that of a cation plus its anions. Strict segregation would result in too much empty space. A compromise must therefore be found between the dense filling of space and the segregation of electronically similar units. The M—O_{ax} distance must also play an important role in determining the final structure.

Many of the hydrogen-bonded chains pack in an array that is at least approximately hexagonal close-packed (see Fig. 8). In directions perpendicular to the stack (or chain) axes the 15C5 rings sometimes almost alternate with cations and sometimes are adjacent but tilted and overlapping. Fig. 10 shows the chain alignments of the infinite Pd chains for the three directions in which the chains are in contact.

Other indications of packing difficulties in these compounds are large asymmetric units (NIKZUC01 with $Z' = 16$; XEMFUQ and XEMGAX with $Z' = 4$; several more with $Z' = 2$) and unexpected co-crystals (e.g. NILBAL01, ROLBUQ, and ROLCAX). The unexpected inclusion of two molecules of nitric acid per Pd^{2+} ion in the structure reported here (5) is another sign of a packing problem. If the more normal Pd structure (4) were packed well, structure (5) would not exist, even if nitric acid had been present in the solution from which crystals were grown. Finally, if the Cr compound reported in this study had better crystal packing it would not be so disordered.

Discrete hydrogen-bonded aggregates (four from the CSD search; two more reported here) are much less common than infinite hydrogen-bonded chains). Discrete units are probably formed only when no satisfactory extended chain motif can be found.

Crosslinking of the chains by hydrogen bonds, especially hydrogen bonds between cations and anions, stabilizes many of the structures.

5. Summary

Co-crystals of 15C5 and metal complexes containing the fragment H_2O—M—OH_2 are common; they probably form because the crown provides a tidy package of hydrogen-bond acceptors for the water ligands. As the 15C5 molecule is an 'unsymmetrical bifacial hydrogen-bond acceptor' (Steed et al., 2001), inclusion of the crown makes possible the formation of extended hydrogen-bonded chains. Five new structures of this type have been determined and another 41 reliable structures have been found in the literature. While the formation of hydrogen-bonded chains almost always occurs, the length and detailed structure of the chain motif vary, probably because of the compromises that must be made if space is to be filled densely and the arrangement of charges is to be favorable.

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