

[15]Crown-5: An Unsymmetrical Bifacial Hydrogen-Bond Acceptor in Crystal Engineering

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Abstract: Reaction of [15]crown-5 with erbium nitrate and a range of nickel salts results in the formation of the hydrogen-bonded chain species $[\text{Er}(\text{NO}_3)_3(\text{H}_2\text{O})_3] \cdot [15]\text{crown-5} \cdot \text{H}_2\text{O}$ (**3**), $[\text{Ni}(\text{H}_2\text{O})_6]\text{Br}_2 \cdot [15]\text{crown-5} \cdot 2\text{H}_2\text{O}$ (**4**), $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2 \cdot [15]\text{crown-5} \cdot 2\text{H}_2\text{O}$ (**5**), $[\text{Ni}(\text{H}_2\text{O})_6](\text{NO}_3)_2 \cdot [15]\text{crown-5} \cdot 2\text{H}_2\text{O}$ (**6**) and $[\{\text{Ni}(\text{H}_2\text{O})_4\}_2(\mu\text{-Cl})_2]\text{Cl}_2 \cdot [15]\text{crown-5}$ (**7**). Complexes **3–5** exhibit low symmetry structures with 2–4 unique crown ether molecules, whereas **6** and **7** are more symmetrical. The factors contributing to this behaviour are discussed within the wider context of [15]crown-5 structures in the Cambridge Structural Database.

Keywords: aqua complexes • crown compounds • crystal engineering • hydrogen bonds

Introduction

At the current state of the art it is not usually possible to predict the finer details of solid-state structure (e.g., space group, unit-cell dimensions etc.).^[1] However, as the field of crystal engineering matures,^[2,3] it has become possible to rationalise, and indeed predict qualitatively, the effects of dominant intermolecular interactions, notably moderate to strong hydrogen bonds.^[4] As a result significant progress has been made towards the rational design of crystalline structures with consistently conserved gross structural features (e.g., the $\mathbf{R}_2^2(\mathbf{8})$ motif^[5] in unhindered carboxylic acid dimers^[6]), and with an understanding of the origins of such motifs comes the ability to disrupt them by incorporation of steric bulk or competitive groups.^[7] It has become clear that one almost essential prerequisite to crystal design is the *isolation* of particular intermolecular interactions so that the design process is not subject to interference by a wide spectrum of competing intermolecular forces.^[8] Our approach to this has been to examine the solid-state chemistry of the crown ethers.^[9–12] In crystal engineering terms crown ethers are effective hydrogen-bond acceptors by virtue of their electronegative sp^3 oxygen atoms, while they are only weak hydrogen-bond donors as a result of the presence of the very weakly acidic $-\text{CH}_2-$ groups. It was our anticipation, sup-

ported by earlier work,^[13–18] that the donor and acceptor properties of the crown ethers may be essentially decoupled, allowing scope for structure prediction as a result of moderate strength hydrogen bonds to the ether oxygen atoms, while retaining the high degree of crystallinity associated with the much less directional weak hydrogen bonds to the $-\text{CH}_2-$ groups. The crown ethers also have the advantage of a high degree of flexibility, allowing them to adapt to the properties of more rigid hydrogen-bond donor units.

As part of this programme we have previously examined the interaction of uranyl salts with [15]crown-5,^[10,19] isolating the hydrogen-bonded chain complexes $(\text{H}_5\text{O}_2)[\text{UO}_2\text{Cl}_3(\text{H}_2\text{O})_2] \cdot [15]\text{crown-5}$ (**1**; Figure 1) and $[\text{UO}_2\text{Cl}_2(\text{H}_2\text{O})_3] \cdot [15]\text{crown-5}$ (**2**; Figure 2). Both compounds show the characteristic unsymmetrical bifacial conformation of uncoordinated [15]crown-5; this involves a “3-up, 2-down” arrangement of the ether oxygen atoms such that three hydrogen-bond acceptors are available on one face of the molecule and two on the other. Formally this may be described by a torsion angle sequence $(g^+)aa(g^-)aa(g^+)aa(g^-)ag^-(g^-)aa$ with O–C–C–O torsion angles alternating \pm gauche (generally $\pm 60^\circ$) except for two that must retain the same sign as a consequence of molecular symmetry.^[15] For simplicity this con-



Figure 1. The hydrogen-bonded chain structure of $(\text{H}_5\text{O}_2)[\text{UO}_2\text{Cl}_3(\text{H}_2\text{O})_2] \cdot [15]\text{crown-5}$ (**1**) that exhibits two unique half crown ethers. Spheres represent oxygen atoms of the H_5O_2^+ unit.

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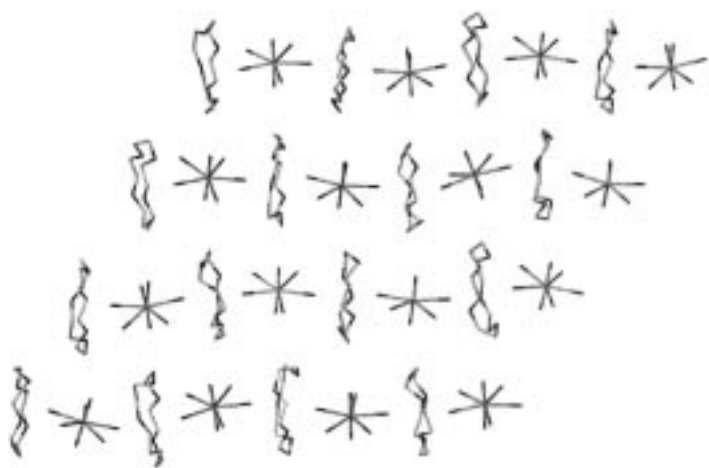


Figure 2. The unique 4×4 hydrogen-bonded array in $[\text{UO}_2\text{Cl}_2(\text{H}_2\text{O})_3]_{16} \cdot 16([\text{15}]\text{crown-5})$ (**2**).

formation will be denoted “+ + - + -”. This bifacial behaviour is consistent with the observation of two unique (half) crown ethers for **1** (space group $C2/c$); however, compound **2** exhibits a total of *sixteen* unique crown-ether/metal-complex pairs ($P3_2$). This latter result was rationalised in terms of the rigidity of the multiple hydrogen-bonding interactions between five of the six aqua OH protons of the $[\text{UO}_2\text{Cl}_2(\text{H}_2\text{O})_3]$ molecule and the [15]crown-5 acceptor; this leads to “frustration” between the conflicting driving forces of crystal close-packing and maximisation of strongly directional hydrogen bonds. The presence of five non-bifurcated^[20] interactions exerts a marked orientational preference of the acceptor, in turn defining the orientation of the next donor in the chain, resulting in a non-repeating pattern. In the case of **1**, however, the presence of only four aqua protons on the $[\text{UO}_2\text{Cl}_3(\text{H}_2\text{O})_2]^-$ anion apparently results in the need for a much less sterically demanding bifurcated interaction and hence a more symmetrical structure.

The characteristically unsymmetrical conformation of [15]crown-5 has led us to investigate its chemistry with a wide range of other moderate to strong hydrogen-bond donors based on metal aqua complexes in anticipation of conserving the unsymmetrical features of the structures, and we now report the results of these investigations along with supporting data from the Cambridge Structural Database (CSD).^[21]

Results and Discussion

Co-crystallised complexes were prepared with a variety of metal aqua ions and [15]crown-5 from aqueous solution. In all cases hydrogen-bonded chain-type structures were obtained, exhibiting a wide variety of crystal-packing arrangements. (Crystal data are given in Table 2 in the Experimental Section.) Of the greatest relevance to the observed frustration in **2** was the complex $[\text{Er}(\text{NO}_3)_3(\text{H}_2\text{O})_3] \cdot [\text{15}]\text{crown-5} \cdot \text{H}_2\text{O}$ (**3**), which was obtained from the reaction of hydrated erbium nitrate with [15]crown-5 in water. The neutral, nine-coordinate $[\text{Er}(\text{NO}_3)_3(\text{H}_2\text{O})_3]$ complex possesses a “T-shaped”

arrangement of water molecules with O–Er–O angles of $76.6(2)^\circ$, $85.0(2)^\circ$ and $147.8(2)^\circ$ (averages). Ostensibly equivalent angles in crystallographically independent molecules cover a range of about 3° , highlighting the effects of hydrogen bonding on molecular structure. This overall geometry gives a total of six water protons available to interact with the five crown ether acceptors. This situation is highly reminiscent of that found for **2**, although in that case the O–U–O angles are less evenly distributed, giving a distorted “Y-shaped” geometry for the “ $\text{U}(\text{H}_2\text{O})_3$ ” unit. Also as with **2** the crown ethers adopt an unsymmetrical + + - + - conformation, and the result is again a structure requiring multiple complexes in the asymmetric unit in order to simultaneously satisfy the requirements of close packing and maximisation of hydrogen-bonded interactions, in this case to give a unique 2×2 array of erbium complex/crown pairs, Figure 3. Each erbium

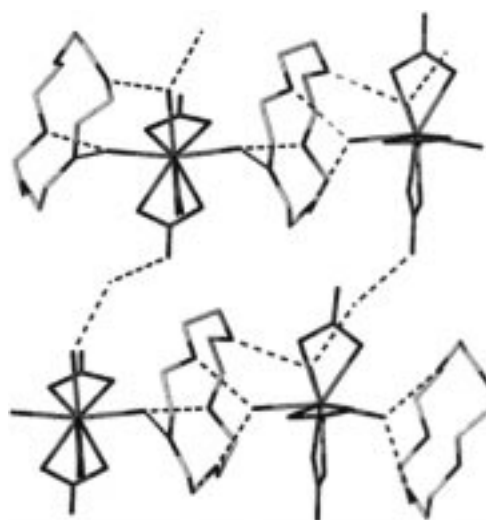


Figure 3. The 2×2 asymmetric unit in $[\text{Er}(\text{NO}_3)_3(\text{H}_2\text{O})_3]_4 \cdot [\text{15}]\text{crown-5} \cdot (\text{H}_2\text{O})_4$ (**3**). Selected bond lengths: Er–O_{water} 2.309(4) average; Er–O_{anion} 2.429(4) average; Er(1)–O \cdots O_{crown} 2.713, 2.706, 2.797, 2.672 and 2.678 Å.

complex forms a total of five hydrogen bonds to crown ether acceptors with O \cdots O contacts ranging from 2.67–2.89 Å, which are typical of this kind of system.^[20] The remaining aqua proton forms a hydrogen bond to lattice water, which in turn interacts with an adjacent stack of complex/crown units. While this Z' value¹⁾ of 4 is significantly lower than that of 16 encountered for **2**, it firmly establishes that the asymmetry encountered for the latter may be linked to the combination of packing factors encountered in these systems leading to packing “frustration”. Compound **3** also exhibits some well-defined disorder of all four unique crown ethers. The large

¹⁾ Z' is defined as the number of conventional formula units (Z) divided by the number of independent general positions. This value may be misleading as an asymmetry indicator in compounds such as **1**, which possesses two unique half crown ethers resulting in $Z' = 1$ despite the presence of two independent crowns. Its application to supramolecular chemistry needs particular care since the definition of “formula unit” is generally a molecular one. The parameter Z' has been introduced recently to indicate the number of independent molecular units or fragments (B. P. van Eijck, J. Kroon, *Acta Crystallogr. Sect. B* **2000**, 56, 535).

differences in the coordinates of pairs of disordered conformations suggests that this disorder may be static and, hence, also suggests the possible existence of a further supercell in which disorder need not be present. Interestingly, the triclinic α and γ angles for **3** are very close to 90° (89.644° and 89.832° , respectively) suggesting the presence of monoclinic pseudosymmetry. Pseudosymmetry has been observed extensively in various structures of cholesterol and has been discussed in depth for cholesterol monohydrate ($Z' = 8$, $P1$).^[22] As with the present work it was established that strong intermolecular interactions were responsible for distortions away from strict crystallographic symmetry. This is also the case for the largest Z' value recorded in the Cambridge Structural Database (CSD)^[21, 23] of 32 for Me_2SnOH .^[24] This material reduces to an orthorhombic subcell that contains only two discrete molecules. The choice of the true monoclinic cell, ($Z = 64$, $Z' = 32$, Pn (No. 7)) is dictated by the presence of an 8_3 helical molecular chain arising from $\text{Sn} \cdots \text{O} \cdots \text{Sn}$ interactions.^[24]

Hydrogen-bonded chain structures were also observed from the reaction of a variety of nickel salts with [15]crown-5. In the cases of nickel bromide, perchlorate and nitrate the structures all involve alternating $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ cations and [15]crown-5 acceptors, situated axially, with hydrogen bonds to the non-coordinated anions that are found in the equatorial plane of the cations. Despite the fact that these gross structural features and even the number of enclathrated water molecules are conserved, the bromide complex $[\text{Ni}(\text{H}_2\text{O})_6]\text{Br}_2 \cdot [15]\text{crown-5} \cdot 2\text{H}_2\text{O}$ (**4**) possesses four unique crown ether molecules, six unique nickel cations (two whole and four situated on crystallographic inversion centres) and eight unique water molecules ($Z' = 4$), Figure 4. However the

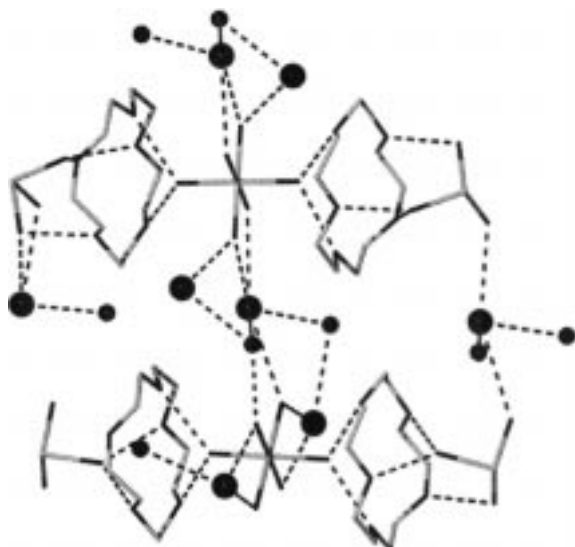


Figure 4. The asymmetric unit of $[\text{Ni}(\text{H}_2\text{O})_6]\text{Br}_2 \cdot [15]\text{crown-5} \cdot 2\text{H}_2\text{O}$ (**4**) ($Z' = 4$). Selected bond lengths: $\text{Ni}(1) - \text{O}_{\text{water}} 2.041(5) - 2.078(5)$; $\text{Ni}(3) - \text{O}_{\text{water}} 2.035(5) - 2.071(5)$; $\text{Ni}(1) - \text{O} \cdots \text{O}_{\text{crown}} 2.724, 2.740, 2.706, 2.731 \text{ \AA}$; $\text{Ni}(3) - \text{O} \cdots \text{O}_{\text{crown}} 2.732, 2.748, 2.772 \text{ \AA}$.

perchlorate species $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2 \cdot [15]\text{crown-5} \cdot 2\text{H}_2\text{O}$ (**5**) exhibits only two unique complex/crown pairs ($Z' = 2$), while the nitrate complex $[\text{Ni}(\text{H}_2\text{O})_6](\text{NO}_3)_2 \cdot [15]\text{crown-5} \cdot$

$2\text{H}_2\text{O}$ (**6**) exhibits a high symmetry structure with $Z' = 1$ and a single unique crown. In compound **4** hydrogen-bonded chain propagation occurs along the abc body diagonal, while in **5** the alternating crown ether acceptors and metal-complex donors stack along the crystallographic ac diagonal. In compound **6** chain propagation is along c and this axis length is essentially identical to that found for the chain-propagation direction in **3** along the a axis ($16.0457(6)$ and $16.0389(5) \text{ \AA}$, respectively).

Perhaps the most interesting comparison in these systems is that between bromide **4** and perchlorate salt **5**. Compound **4** possesses two unique, parallel hydrogen-bonded chain segments (each containing two unique crown ethers), whereas compound **5** exhibits only one. In the latter case there is only a single hydrogen bond through the perchlorate anions that links the water ligands of one chain to those adjacent in one dimension, but not in the second dimension perpendicular to the direction of chain propagation. The chains are thus relatively isolated from one another in terms of the existence of strong, multiple intermolecular interactions. In contrast, in **4** multiple $\text{OH} \cdots \text{Br} \cdots \text{HO}$ bridges link chains in two dimensions perpendicular to chain propagation giving rise to a three-dimensional hydrogen-bonded network ($\text{O} \cdots \text{Br}$ distances $3.30 - 3.42 \text{ \AA}$). This feature is shared by **3**, in which coordinated nitrate ligands are linked by bridging enclathrated water molecules to aqua ligands in two dimensions, and by **2**, in which $\text{OH} \cdots \text{Cl}$ hydrogen bonds ($\text{O} \cdots \text{Cl}$ distances $3.18 - 3.36 \text{ \AA}$) link the three symmetry equivalent components of the 3_2 screw. Such inter-chain communication is not observed for the symmetrical **1**. However, if hydrogen-bonding interactions from one chain to another are important for the observation of low-symmetry structures, they are not the sole factor at work. The highly symmetrical **6** ($Z' = 1$) has similar inter-chain hydrogen bonding as in **3** mediated by enclathrated water molecules, albeit with rather long hydrogen bond distances. Furthermore **5** does exhibit two unique crown ethers within the same chain, an observation apparently independent of strong inter-chain hydrogen bonds. It is useful, therefore to look at the structures of individual chains.

Clearly the observation of more than one unique crown ether per chain, as is the case for compounds **1**–**5**, cannot be a property intrinsic to [15]crown-5 itself in the solid state, nor to any particular [15]crown-5/metal-complex hydrogen-bonded pair (compare **5** and **6**, $Z' = 2$ and 1 respectively, both of which contain the “ $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} \cdot [15]\text{crown-5}$ ” unit). As a result the interactions of the individual chains to the anions must also be involved in the case of **5** at least. A close comparison of the octahedral metal ions in **5** and **6** reveals none of the axial $\text{Ni}-\text{O}$ bond-length shortening found in the analogous [18]crown-6 complexes.^[11] Indeed the $\text{Ni}-\text{O}$ bond lengths in **6** fall into a narrow range $2.0352(11) - 2.0593(10) \text{ \AA}$. A wider range is observed for both nickel cations in **5** $2.034(7) - 2.081(6) \text{ \AA}$, which suggests greater strain on the complex arising from intermolecular interactions. Indeed, while both species form pairwise hydrogen bonds to the perchlorate and nitrate anions, it is only in the case of **5** that equatorial water ligands interact with both anions and are also hydrogen bonded to the crown ethers, Figure 5. In the case of **6** only one such simultaneous hydrogen-bonding pattern occurs, Figure 6. It is possible that this is enough to displace $\text{Ni}(2)$ some 0.14 \AA

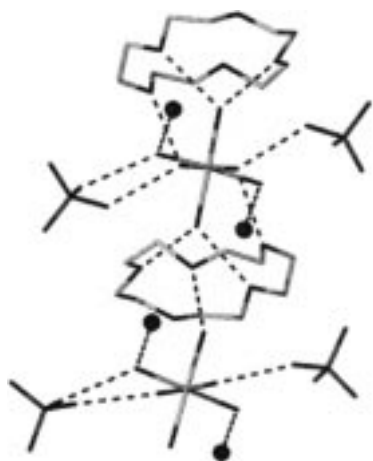


Figure 5. The asymmetric unit of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2 \cdot [15]\text{crown-5} \cdot 2\text{H}_2\text{O}$ (**5**) ($Z' = 2$). Selected bond lengths: $\text{Ni}(1)\text{--O}_{\text{water}}$ 2.041(7)–2.081(6); $\text{Ni}(2)\text{--O}_{\text{water}}$ 2.034(8)–2.080(8); $\text{Ni}(1)\text{--O}\cdots\text{O}_{\text{crown}}$ 2.725, 2.752, 2.829, 2.691, 2.742, 2.769 Å; $\text{Ni}(2)\text{--O}\cdots\text{O}_{\text{crown}}$ 2.634, 2.884, 2.630, 2.823 Å.



Figure 6. The single unique metal-complex/crown-ether pair in the nitrate complex $[\text{Ni}(\text{H}_2\text{O})_6](\text{NO}_3)_2 \cdot [15]\text{crown-5} \cdot 2\text{H}_2\text{O}$ (**6**). Selected bond lengths: $\text{Ni}\text{--O}_{\text{water}}$ 2.0352(11)–2.0593(10); $\text{Ni}\text{--O}\cdots\text{O}_{\text{crown}}$ 2.753, 2.737, 2.773, 2.797, 2.811 Å.

away from the coordinates (0.5, 0, 0.5), which would result in a centric structure. It is also possible that in maximising this double, geometrically constrained interaction the crown ether is constrained to adopt a conformation impossible to repeat in an adjacent site along the chain.

A much more striking difference between the symmetrical compound **6** and the unsymmetrical compounds **4** and **5** is seen in the orientations of successive crown ether molecules within a chain. In the case of **4** the nickel ions may be divided into two classes; firstly Ni(1) and Ni(2), which hydrogen bond to the crown ethers *only* through two *trans* (axial) water ligands to form a total of four hydrogen bonds to crown ethers per metal complex, and secondly Ni(3)–Ni(6), which use both *axial* and *equatorial* water to interact with the crown ether to give a total of six hydrogen bonds to crown oxygen atoms. Similarly in **5** Ni(1) exhibits a total of six hydrogen bonds to crown ethers, Ni(2) only four. Thus, in **4** and **5** the crown ethers alternate the orientation of their “3-oxygen” and “2-oxygen” faces, while adopting the usual “+ + – + –” conformation. This packing mode is also observed for the [18]crown-6 analogue of **4** (a species which also exhibits an unusual unsymmetrical chain structure) in which the [18]crown-6 adopts an unusual conformation exhibiting “4-oxygen” and “2-oxygen” faces.^[11] In contrast, in compound **6**, the crown ether acceptors pack in parallel fashion such that

each metal complex forms a total of five hydrogen bonds. With regard to this feature, compound **2** appears to adopt an irregular structure in which the majority of crown ether units parallel **6**, but with occasional “intermediate cases” in which the orientation of particular oxygen atoms is approximately within the plane of the crown ether; disorder between the two possibilities is observed for **3**. Compound **1**, which contains two unique (half) crown ether molecules, alternates as for **4** and **5**.

As a final example we examined the reaction of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with [15]crown-5 in anticipation of observing a structure similar to the bromide analogue **4**. Surprisingly, however, the greater coordinating ability of the Cl^- ligands results in the formation of a chloride-bridged structure of composition $[\{\text{Ni}(\text{H}_2\text{O})_4\}_2(\mu\text{-Cl})_2]\text{Cl}_2 \cdot [15]\text{crown-5}$ (**7**), Figure 7. Despite the presence of a binuclear metal complex the

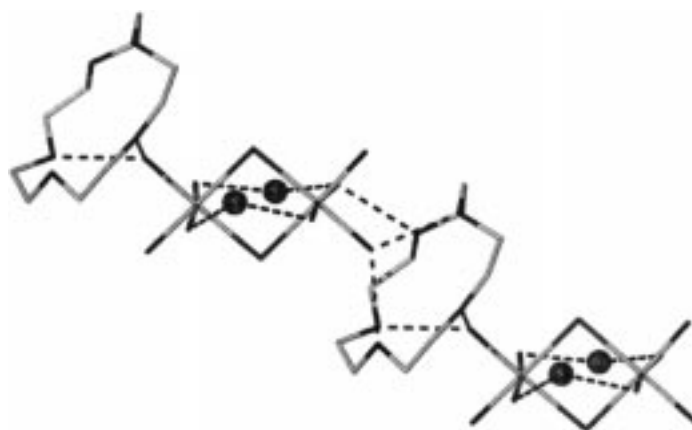


Figure 7. The symmetrical complex $[\{\text{Ni}(\text{H}_2\text{O})_4\}_2(\mu\text{-Cl})_2]\text{Cl}_2 \cdot [15]\text{crown-5}$ (**7**) (two asymmetric units showing chain structure). Selected bond lengths: $\text{Ni}(1)\text{--O}_{\text{water}}$ 2.0426(18)–2.079(2); $\text{Ni}(1)\text{--Cl}(2)$ 2.3828(6); $\text{Ni}(1)\text{--Cl}(1)$ 2.4174(6) Å; $\text{Ni}\text{--O}\cdots\text{O}_{\text{crown}}$ 2.753, 2.766, 2.707, 2.821, 2.876 Å.

basic hydrogen-bonded chain structure is retained with chain propagation along the *ab* diagonal, with a longer repeat distance (10.72 Å vs 7.96–8.03 Å in **5** and **6**, and 8.51 Å in **3**). Each crown ether accepts a total of five non-bifurcated hydrogen bonds in the usual, non-disordered + + – + – conformation, while individual chains link by short hydrogen bonds to non-coordinated Cl^- anions ($\text{O}\cdots\text{Cl}$ 3.02–3.08 Å). The “2-oxygen” face of the crown forms hydrogen bonds only to the axial O(1) of Ni(1), while the “3-oxygen” face interacts with both axial and equatorial water ligands of Ni(2). This is a similar situation to that encountered for the symmetrical **6**, but distinct from the more unsymmetrical perchlorate salt **5** and bromide **4**. This leads to a tentative conclusion that the observation of more than one unique crown ether within a chain is linked to the alternating structure observed in **4** and **5**. Gratifyingly, this observation is corroborated by the structure of the mixed hexaaqua, oxo-bridged species $[\text{Fe}(\text{H}_2\text{O})_6]_2^{2-}[\{\text{Fe}(\text{H}_2\text{O})_5\}_2(\mu\text{-O})](\text{NO}_3)_{10} \cdot 4[15]\text{crown-5} \cdot 6\text{H}_2\text{O}$ (**8**).^[25, 26] This remarkable complex involves an $[\{\text{Fe}(\text{H}_2\text{O})_5\}_2(\mu\text{-O})]^{4+}$ ion sandwiched between a discrete pair of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+} \cdot 2[15]\text{crown-5}$ buffers, Figure 8. Crucially each of the (equivalent) hexaaqua ions closely resemble Ni(1) in **4** and **5** in that they exhibit a total of six hydrogen bonds, three to each crown

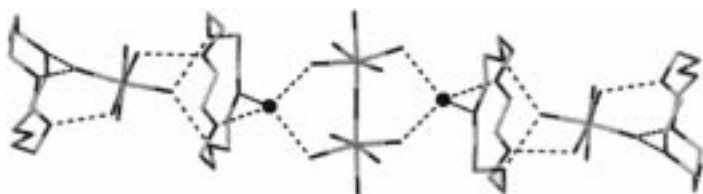


Figure 8. Two asymmetric units of $[\text{Fe}(\text{H}_2\text{O})_6]_2[\text{Fe}(\text{H}_2\text{O})_5]_2(\mu\text{-O})\text{-}(\text{NO}_3)_{10} \cdot 4([\text{15}]\text{crown-5}) \cdot 6\text{H}_2\text{O}$ (**8**)^[25, 26] showing the tetrametallic array that represents the supramolecular building block of the structure (nitrate anions and some lattice water omitted for clarity).

ether. The crown ethers are of two quite distinct types. The “inner” symmetry-equivalent pair are of the usual $++--$ conformation and possess two hydrogen bonds to a water molecule through the “2-oxygen” faces. This water molecule in turn interacts with the large $[\text{Fe}(\text{H}_2\text{O})_5]_2(\mu\text{-O})^{6+}$ unit. The outer pair of crown ethers adopt an unusual $++++$ conformation with no interactions to the outer face. The hydrogen-bonded chain is thus finite and represents a “slice” of the infinite structures seen for **4** and **5**. Once again alternation results in the presence of two unique crown ethers. Inter-chain interaction is by means of sparse hydrogen bonds to nitrate anions and is apparently insufficient to cause more than one-dimensional asymmetry.

A search of the CSD^[23] reveals some 37 structures (with available coordinates) that contain unsubstituted [15]crown-5 in which the crown ether acts solely as a hydrogen-bond acceptor (as opposed to coordinated to a metal cation). These structures are detailed in Table 1. The overwhelming observation that comes from this analysis is the confirmation that low-symmetry structures (i.e., $Z' > 1$) are *not* an intrinsic property of [15]crown-5 itself, but depend on the coincidence of a number of factors, of which the bifacial nature of the [15]crown-5 acceptor is one. To this may be added the need for *multiple* intermolecular interactions with a marked orientational preference. In the examples studied these interactions include both intra- and inter-chain.

Closely related to compounds **2** and **3** are structures LIGVUS,^[27] SONRIW,^[28] FUVFIL,^[29] KOKDIX,^[30] VEDHOB^[31] and the series $[\text{M}(\text{H}_2\text{O})_{8/9}]\text{Cl}_3 \cdot [\text{15}]\text{crown-5}$ ($\text{M} = \text{Y}, \text{Gd}, \text{Lu}, \text{Nd}$ and Er) typified by FAYVEG01 ($\text{M} = \text{Y}$)^[32] (LIGVUS = $[\text{La}(\text{NO}_3)_3(\text{H}_2\text{O})_2(\text{MeOH})(2,2'\text{-bipyridyl})] \cdot [\text{15}]\text{crown-5}$, SONRIW = $[\text{La}(\text{NO}_3)_3(\text{H}_2\text{O})_2(1,10\text{-phenanthroline})] \cdot [\text{15}]\text{crown-5}$, FUVFIL = $[\text{UO}_2(\text{H}_2\text{O})_5](\text{ClO}_4) \cdot \text{MeCN} \cdot \text{H}_2\text{O} \cdot 3([\text{15}]\text{crown-5})$, KOKDIX = $[\text{Y}(\text{H}_2\text{O})_3(\text{NO}_3)_3]_2 \cdot 2\text{Me}_2\text{CO} \cdot 3([\text{15}]\text{crown-5})$, VEDHOB = $[\text{Eu}(\text{NO}_3)_3(\text{H}_2\text{O})_3] \cdot 2([\text{15}]\text{crown-5}) \cdot 2\text{MeCN}$). Of all these hydrogen-bonded chain structures only FUVFIL^[29] and KOKDIX^[30] exhibit more than one independent crown ether moiety. Both represent special cases in which the hydrogen-bonded structure is a discrete unit, as for **8**, rather than part of chain structure. In the case of KOKDIX one central crown links two metal complexes, which are in turn capped by two terminal crown ether moieties. The central crown ether is thus necessarily distinct from the two terminal units and additional symmetry is not possible without disorder. Complex FUVFIL exhibits a trigonal array of crown ethers surrounding a single $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ unit.

Structure SONRIW,^[28] however, despite the Z' value of 1, is a very remarkable compound in which the crystallographic asymmetric unit corresponds to a small section of a vast helical structure (space group $P6_3$) with a pitch of 43.769 Å, requiring six molecules to complete one helical turn, Figure 9.



Figure 9. Sixfold helical array in $[\text{La}(\text{NO}_3)_3(\text{H}_2\text{O})_2(1,10\text{-phenanthroline})] \cdot [\text{15}]\text{crown-5}$.^[28] The degree of helical twist corresponds with the crystallographic 6_3 symmetry resulting in a single unique metal-complex/crown-ether pair in the crystallographic asymmetric unit, $Z' = 1$.

The helicity is apparently a consequence of the same strong and directional $\text{OH}_2 \cdots$ crown hydrogen-bonds seen in all of the other examples discussed so far, with the additional influence of the disparity in width of the planar phenanthroline ligand on one side of the metal cation and the three nitrate ligands on the other. In order to close pack efficiently the hydrogen-bonded chain must kink at every link. It is perhaps fortuitous that the degree of bending required corresponds exactly to the crystallographic 6_3 symmetry. This may be compared to much less pronounced non-crystallographic 8_3 helicity in Me_3SnOH which results in a total of 32 unique complexes.^[24]

Closely related to SONRIW is LIGVUS.^[27] This material, based on 2,2'-bipyridyl, is not helical and possesses an additional methanol ligand removing the size disparity between the planar pyridyl portion of the molecule and the three nitrate ligands. This results in the more usual linear chain structure and again $Z' = 1$. Interestingly, comparing LIGVUS with **2** and **3**, the two last compounds possess six hydrogen bond donors, whereas LIGVUS exhibits a perfect match of five donors to the five crown ether acceptor atoms. This again points to the inter-chain communication resulting from this sixth “free” proton that may contribute towards the unsymmetrical structure.

One final interesting case is structure KUPHEI^[33] $\{[\text{Cu}(\text{H}_2\text{O})_4]_2[\text{Cu}_3\text{Cl}_8(\text{H}_2\text{O})_2] \cdot 2([\text{15}]\text{crown-5})\}$ which exhibits the face alternation seen for **4** and **5**, but has only one unique crown ether. In this case there are two different types of metal complex, however.

Conclusion

After analysis of the large body of available data it is possible to state with some confidence that there is no simple, single factor responsible for the observation of low-symmetry, high Z' structures in these [15]crown-5-based systems. Low symmetry is apparently a result of a subtle additive effect of three

Table 1. Hydrogen-bonded structures containing [15]crown-5.

Refcode	Formula	No. unique uncoord. crowns	Crown conformation	H-bonds per crown (O...O < 3.0 Å)	H-bonded structure type
CAGTIN	[Sm(H ₂ O) ₄][15]crown-5)(ClO ₄) ₂ · [15]crown-5 · H ₂ O	1	++++-	5 ^[c]	chain through anions
CIGSAM	[CuCl ₂ (H ₂ O) ₂ (MeOH)] · [15]crown-5	2 ^[e]	++-+-	5	chain
DUCNEU	[ZnCl ₂ (H ₂ O) ₂] · [15]crown-5	1	++++-	4	chain
FANRUH	[SnCl ₄ (H ₂ O) ₂] · [15]crown-5	1	++-+-	4	chain
FAYVEG01	[Y(H ₂ O) ₈]Cl ₃ · [15]crown-5	1	++++-	5	chain
FILVOL ^[a]	[Gd(H ₂ O) ₈]Cl ₃ · [15]crown-5	1 ^[b]	++++-	5	chain
FILVUR ^[a]	[Lu(H ₂ O) ₈]Cl ₃ · [15]crown-5	1 ^[b]	++++-	5	chain
FUVFIL	[UO ₂ (H ₂ O) ₅](ClO ₄) · MeCN · H ₂ O · 3([15]crown-5)	3	++++-	4 ^[c]	discrete
			++++-	4 ^[c]	
			++++-	4 ^[c]	
GARLUG	[NH ₄][15]crown-5 ₂ [UO ₂ Cl ₄] · MeCN	2	++++-	5 ^[d]	discrete
GEMXIF	[ThCl ₄ (H ₂ O) ₂ (MeOH) ₂] · MeCN · [15]crown-5	1	+0-+-	6	chain
GOHTAY	[Nd(H ₂ O) ₈]Cl ₃ · [15]crown-5	1	++++-	6	chain
GOHTEC	[NdCl ₂ (H ₂ O) ₆]Cl · [15]crown-5	1	++-+-	5	chain
JOTQOY	(H ₂ O) ₃ · [15]crown-5[AuCl ₄]	2	++++-	5 ^[c]	chain
KOGSII	SO ₃ NH ₂ · [15]crown-5	2	++++-	5 ^[c]	discrete
KOKDIX	[Y(H ₂ O) ₃ (NO ₃) ₃] ₂ · (Me ₂ CO) ₂ · 3([15]crown-5)	3	++++-	4	discrete
			++++-	3	
			++++-	3	
KUPHAE	[CuCl ₂ (H ₂ O) ₂] · [15]crown-5	1	++++-	- ^[b]	chain
KUPHEI	[Cu(H ₂ O) ₄] ₂ [Cu ₃ Cl ₈ (H ₂ O) ₂] · 2([15]crown-5)	1	++++-	5	chain
KUZJEU	[Mg(H ₂ O) ₆] ₂ [Cu ₃ Cl ₈ (H ₂ O) ₂] · 2([15]crown-5) · 2H ₂ O	1	++++-	5	chain
LIGVUS	[La(NO ₃) ₃ (H ₂ O) ₂ (MeOH)(2,2'-bipyridyl)] · [15]crown-5	1	++++-	5	chain
NASSUV	[Cd(H ₂ O) ₂][15]crown-5][CdI ₃ (H ₂ O)] · [15]crown-5 · MeCN	1	++-+-	4	chain
POGDUK01	[SnCl ₂ Me ₂ (H ₂ O) ₂] · [15]crown-5	1	++++-	- ^[f]	- ^[f]
PUJIG ^[a]	[Yb(H ₂ O) ₈]Cl ₃ · [15]crown-5 ^[b]	1	++++-	5	chain
PXCDCB	[CuBr ₂ (H ₂ O) ₂] · [15]crown-5 ^[b] (isostructural with KUPHAE)	1	++++-	5	chain
				(2 bifurcated)	
SONRIW	[La(NO ₃) ₃ (H ₂ O) ₂ (1,10-phenanthroline)] · [15]crown-5	1	++-+-	5	P6 ₃ helical chain
				(2 bifurcated)	
SOQXEB	[Na ₄ Br][15]crown-5 ₄ [TlBr ₄] ^[b]	1	- ^[b]	- ^[b]	double shell clathrate
TEDZEH	[MeCCINH ₂][TaCl ₆] · [15]crown-5	1	+++++	5	discrete
				(bifurcation)	
TEDZIL	[Et ₃ NH][TaCl ₆] · [15]crown-5	1	++++-	1	discrete
TONFEH	[La ₂ Cl ₆ (H ₂ O) ₄ (1,10-phenanthroline) ₂] · [15]crown-5 · MeCN	1	++++-	5	chain
				(2 bifurcated)	
TUKVAW	[NH ₄][15]crown-5 ₂ [Cd(SCN) ₃]	2 × ½	+++++	5	discrete
				(bifurcation)	
VANFUL	[Eu(NO ₃) ₃ (H ₂ O) ₂][15]crown-5] · [15]crown-5	1	- ^[b]	- ^[b]	discrete
VEBWUU	[Zr(C ₅ H ₅)Cl ₃ (H ₂ O) ₂] · [15]crown-5	2 × ½	++++-	4 ^[b]	chain
VEDHOB	[Eu(NO ₃) ₃ (H ₂ O) ₃] · 2([15]crown-5) · 2MeCN	1	++-+-	3	discrete
VILMOS	[MoCl ₄ (dme)] · [15]crown-5	1	++++-	0	
	discrete			(long CH...O)	
VUKKOB	[InCl ₃ (H ₂ O) ₂] · [15]crown-5	1	++-+-	4	chain
WIDPOO	[VOCl ₂ (H ₂ O) ₂] · [15]crown-5	1	++++-	4	chain
YICCIW ^[a]	[Er(H ₂ O) ₈]Cl ₃ · [15]crown-5	1	++++-	5	chain
ZEGSAF10 ^[a]	[La(H ₂ O) ₄][15]crown-5)(ClO ₄) ₃ · [15]crown-5 · H ₂ O	1	- ^[b]	- ^[b]	discrete
ZOCYUL ^[b]	[FeCl ₃ (H ₂ O) ₂] · [15]crown-5	1	++-+-	4	chain

[a] Isostructural with FAYVEG01. [b] Crown disordered. [c] Two bifurcated hydrogen bonds. [d] NH...O < 3.1 Å with bifurcation. [e] Space group *Pn*. [f] Coordinates incorrect? [g] Isostructural with CAGTIN. [h] Isostructural with VUKKOB.

dimensional interactions. Individual contributing circumstances may be identified and it is clear from the present study that the unsymmetrical shape of the [15]crown-5 molecule itself is one such factor. It is also clear that molecular parameters such as *Z'* entirely fail to adequately represent supramolecular structure. Instances of large *Z'* values are *de facto* indications of the presence of a greater supramolecule or hierarchy of supramolecules. In the final analysis it is curious to note that as many unsymmetrical species based on [15]crown-5 have been reported in the present work than were previously known in the entire Cambridge Structural Database. If

metaphysical explanations are discounted, then it may be that this is partially due to recent improvements in area-detector technology and the routine use of very low-temperature data collection facilities. Such instrumental factors must undoubtedly greatly increase the chances of indexing weak reflections characteristic of “supramolecular supercells” that display subtleties of the crystal packing unobservable on a conventional instrument at room temperature. If this is the case, it is likely that many more low-symmetry species will appear in the literature over the next few years. A more wide-ranging survey of this phenomenon is planned.

Experimental Section

Instrumental: [15]Crown-5 was purchased from Fluka and hydrated metal salts were purchased from Aldrich; these 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. Infrared spectra were performed as Nujol mulls in NaCl plates on a Nicolet Nexus FTIR spectrophotometer. All products displayed some degree of moisture sensitivity when exposed to the atmosphere. For this reason yields were not measured in order to protect crystals for the X-ray experiment, but are estimated to be about 50–70% based on metal salt.

Preparations: In all experiments, a 1:1 mixture of hydrated metal salt (~0.12 g, 0.45 mmol) and [15]crown-5 (0.10 g, 0.45 mmol) were dissolved in a minimum of water (ca. few mL) and allowed to slowly evaporate. Infrared spectra confirmed the presence of [15]crown-5 with bands near 945 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.

[Er(NO₃)₃(H₂O)₃]·[15]crown-5·H₂O (3): Small pink plates of **3** deposited from solution. M.p. 179–82 °C; elemental analysis calcd (%) for C₁₀H₂₈ErN₃O₁₈: C 18.60, H 4.37, N 6.51; found C 18.8, H 4.6, N 6.5; IR (Nujol): $\tilde{\nu}$ = 3360 (m, br), 1654 (m), 1350 (s), 1306 (m), 1091 (m, br), 1025 (m), 938 (s), 840 (m), 815 cm⁻¹ (m).

[Ni(H₂O)₆Br₂]·[15]crown-5·2H₂O (4): Long green needles of **4** deposited from solution. M.p. 115–8 °C; elemental analysis calcd (%) for C₁₀H₃₆Br₂NiO₁₃: C 20.61, H 6.23; found C 20.8, H 6.5; IR (Nujol): $\tilde{\nu}$ = 3359 (s, br), 1620 (s), 1354 (s), 1295 (w), 1250 (m), 1097 (s), 943 (m), 840 cm⁻¹ (m).

[Ni(H₂O)₆(ClO₄)₂]·[15]crown-5·2H₂O (5): Long green acicular crystals of **5** deposited from solution. M.p. 46–8 °C; elemental analysis calcd (%) for elemental analysis calcd (%) for C₁₀H₃₆Cl₂NiO₂₁: C 19.31, H 5.83; found C 19.4, H 5.2; IR (Nujol): $\tilde{\nu}$ = 3384 (m, br), 1635 (m), 1354 (s), 1296 (m), 1104 (m, br), 945 (m), 829 cm⁻¹ (w).

[Ni(H₂O)₆(NO₃)₂]·[15]crown-5·2H₂O (6): Small green acicular crystals of **6** deposited from solution. M.p. 62–6 °C; elemental analysis calcd (%) for C₁₀H₃₆N₂NiO₁₉: C 21.95, H 6.63, N 5.12; found C 22.0, H 6.7, N 5.1; IR (Nujol): $\tilde{\nu}$ = 3360 (m, br), 1646 (m), 1355 (s), 1294 (w), 1097 (s), 1040 (m), 946 (m), 828 cm⁻¹ (w).

[[Ni(H₂O)₆]₂(μ-Cl)₂Cl₂]·[15]crown-5 (7): Small green acicular crystals of **7** deposited from solution. M.p. = 139 °C (decomp); elemental analysis calcd (%) for C₁₀H₃₆Cl₄Ni₂O₁₃: C 19.26, H 5.82; found C 21.67, H 6.52. The sample was relatively unstable with respect to loss of water of crystallisation and retained uncomplexed crown ether tenaciously. This proved impossible to remove, while keeping the crystalline sample hydrated. IR (Nujol): $\tilde{\nu}$ = 3358 (m, br), 1614(s), 1356(s), 1306 (w), 1260 (m), 1096 (s), 1040 (m), 943 (s), 840 cm⁻¹ (m).

Crystallography: Crystal data and data collection parameters are summarized in Table 2. Crystals were mounted by using a fast setting epoxy resin on the end of a glass fibre and cooled on the diffractometer to 100 K with an Oxford Cryosystems low-temperature attachment. All crystallographic measurements were carried out with a Nonius KappaCCD equipped with graphite monochromated MoK_α radiation by using ϕ and ω rotations of 2° frame width and a detector-to-crystal distance of 30 mm. Integration was

Table 2. Crystallographic data for new complexes.

	3	4	5	6	7
formula	C ₁₀ H ₂₈ ErN ₃ O ₁₈	C ₁₀ H ₂₀ Br ₂ NiO ₁₃	C ₁₀ H ₃₆ Cl ₂ NiO ₂₁	C ₁₀ H ₃₆ N ₂ NiO ₁₉	C ₁₀ H ₃₆ Cl ₄ Ni ₂ O ₁₃
<i>M</i> _r [g mol ⁻¹]	645.61	566.79	622.00	547.12	623.16
<i>T</i> [°C]	-150	-100	-173	-100	-173
λ [Å]	0.7107	0.7107	0.7107	0.7107	0.7107
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	16.0389(5)	10.3367(5)	10.5028(7)	12.0882(4)	8.1536(6)
<i>b</i> [Å]	16.5839(3)	17.8842(9)	17.3496(12)	12.6690(6)	10.2145(7)
<i>c</i> [Å]	17.1986(6)	26.5018(13)	13.8394(7)	16.0457(6)	15.4698(8)
α [°]	89.644(1)	104.516(1)			81.028(2)
β [°]	79.744(1)	93.829(1)	99.373(4)	101.344(1)	77.394(2)
γ [°]	89.832(1)	102.314(1)			70.380(2)
<i>V</i> [Å ³]	4501.4(2)	4596.1(4)	2488.1(3)	2409.32(17)	1179.54(13)
<i>Z</i>	8	8	4	4	2
ρ_{calcd} [g cm ⁻³]	1.905	1.638	1.660	1.508	1.756
μ [cm ⁻¹]	38.17	43.72	10.84	8.91	21.05
<i>F</i> (000)	2568	2256	1304	1160	648
θ range [°]	3.44–26.00	3.34–25.00	1.49–25.00	3.47–26.00	3.45–26.00
index ranges	–19 ≤ <i>h</i> ≤ 19 –19 ≤ <i>k</i> ≤ 19 –21 ≤ <i>l</i> ≤ 21	–12 ≤ <i>h</i> ≤ 12 –20 ≤ <i>k</i> ≤ 21 –31 ≤ <i>l</i> ≤ 31	–12 ≤ <i>h</i> ≤ 12 –20 ≤ <i>k</i> ≤ 20 –15 ≤ <i>l</i> ≤ 16	–14 ≤ <i>h</i> ≤ 14 –15 ≤ <i>k</i> ≤ 15 –19 ≤ <i>l</i> ≤ 19	–10 ≤ <i>h</i> ≤ 10 –12 ≤ <i>k</i> ≤ 12 –18 ≤ <i>l</i> ≤ 19
reflections collected	27947	38304	14925	20860	7378
independent reflections	16526	15082	8396	4643	4331
parameters	1028	944	614	292	387
goodness-of-fit on <i>F</i> ²	1.081	1.055	1.046	1.034	1.050
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)] ^[a]	0.0576	0.0824	0.0659	0.0294	0.0312
<i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)] ^[a]	0.1455	0.2207	0.1546	0.0881	0.0712
<i>R</i> 1 (all data) ^[a]	0.0637	0.1109	0.0970	0.0335	0.0406
<i>R</i> 1 (all data) ^[a]	0.1502	0.2420	0.1786	0.0925	0.0751
largest diff. peak [e Å ⁻³]	2.18 ^[b]	1.42 ^[b]	1.07	0.522	0.417

[a] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] Close to heavy atom.

carried out by the program DENZO-SMN.^[34] Data sets were corrected for Lorentz and polarization effects and for the effects of absorption with the program Scalepack.^[34] Structures were solved by using the direct methods option of SHELXS-97^[35] and developed with conventional alternating cycles of least-squares refinement and difference Fourier synthesis (SHELXL-97^[36]) with the aid of XSeed.^[37] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were fixed in idealized positions and allowed to ride on the atom to which they were attached. Hydrogen-atom thermal parameters were tied to those of the atom to which they were attached. Acidic protons were located on final difference Fourier maps and their positional and isotropic displacement parameters refined freely wherever possible. For **5–7** water hydrogen atoms were located experimentally and then allowed to ride on the parent atom. All calculations were carried out either on a Silicon Graphics Indy R5000 workstation or an IBM-PC compatible personal computer. For details of refinements see Table 2.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147469–CCDC-147473. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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