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[$M(H_2O)_2$(15-crown-5)]$(NO_3)_2$: A System Rich in Polymorphic and Modulated Phases[†]

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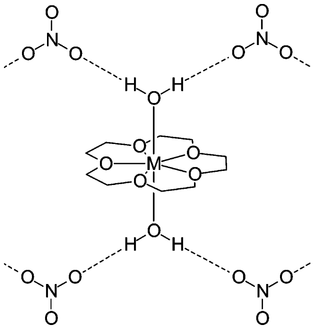
ABSTRACT: The series of structurally related compounds [$M(H_2O)_2$(15-crown-5)]$(NO_3)_2$, M = Cu, Mg, Zn, and Co (four phases) has been extended to include three new phases for M = Mn and two new phases for M = Fe. Two new structure types have been discovered, so nine phases of two basic types (two- or three-dimensional H-bonding pattern) are now known. For the 2-D H-bonded (or layered) structure type, four variants having different modulation patterns have been observed. All phases have more than one crystallographically independent formula unit ($Z' > 1$) The cation conformations of all the independent units in all the structures are essentially identical. Reversible phase transitions during which crystallinity is preserved link the two layered structures of the Mn compound and of the Fe compound. A reason for the existence of so many related phases has been identified.

Introduction

The compound [$M(H_2O)_2$(15-crown-5)]$(NO_3)_2$, M = Cu,



was initially reinvestigated[1] at room temperature and below because we wondered whether the two closely related structures that had been reported previously[2,3] were actually different. (We concluded they are not.) Analogous compounds having M = Mg,[4] Zn,[5] and Co[6] were also reinvestigated. Problems (overlooked inversion symmetry, missed weak reflections, misplaced origin) were found in all the published structures,[1] which include the basic structural unit shown above. The Co crystal ($P4_1$, $Z' = 2$) has a three-dimensional (hereafter, 3-D) H-bonding network that involves the water ligands and the nitrate anions. The other three compounds all have very similar two-dimensional (or 2-D) H-bonding networks, but the Mg and Zn compounds have three independent sets of ions in the unit cell ($P2_1/c$, $Z' = 3$), and the Cu compound has five ($P2_1/n$, $Z' = 5$). The important difference between the $Z' = 3$ and $Z' = 5$ structures is the pattern of alternation of the conformational enantiomers of the cations, which are related by pseudoinversion and pseudotranslation. No phase changes were observed when the crystals were cooled from 294 to 90 K.

Consideration of M−O distances[7] and searches of the Cambridge Structural Database[8] (hereafter, the CSD) indicated that Mn^{2+}, Fe^{2+}, Cd^{2+}, and perhaps Ni^{2+} ions should also fit inside the 15-crown-5 ligand. This paper describes the five phases found for the Mn and Fe compounds. Three of the phases have structure types already known, and two have new structure types that are closely related to those found previously. No compound containing a Ni^{2+} ion coordinated within a 15-crown-5 ligand was isolated.

The Mn compound initially precipitates at room temperature in a new variant of the 2-D H-bonded structure type; when the crystals are cooled they transform, without loss of crystallinity, to the $Z' = 3$ pattern known for the Mg and Zn compounds. The room-temperature phase of the Fe compound is yet another variant of the 2-D structure type, this time with $Z' = 8$. Crystals of the Mn compound that are left in contact with mother liquor over a period of weeks or months transform to the 3-D H-bonded structure type previously known for the Co compound ($Z' = 2$).

The system of compounds [$M(H_2O)_2$(15-crown-5)]$(NO_3)_2$ is then rich in related structures, some of which are polymorphic[9] and all of which modulated. Modulated structures are those in which there are at least two crystallographically independent formula units ($Z' > 1$) and in which relatively small displacements or reorientations of those units would make them crystallographically identical in a smaller unit cell. The lengths of the modulation waves, which describe the distortions from the smaller unit, can be integral multiples of the unit-cell lengths, in which case the modulation is commensurate, or nonintegral multiples, in which case the modulation is incommensurate and the crystal aperiodic.[10] We have studied a number of commensurately modulated molecular structures ($Z' = 4$,[11] 5,[12,13] 9,[14] and 10[15]) and have always been able to identify a structural reason for the increased size of the unit cell. We have also found unusually high frequencies of $Z' > 1$ structures among monoalcohols, C_nH_mOH[16] and *vic*-diols $C_nH_m(OH)_2$.[17] Steed reviewed the subject of high-Z' structures and noted the role of competing packing requirements (e.g., strong directional interactions such as H-bonds in conflict with space-filling considerations).[18] A recent paper about incommensurately modu-

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[†] Dedicated to J. Michael McBride on the occasion of his 65th birthday.

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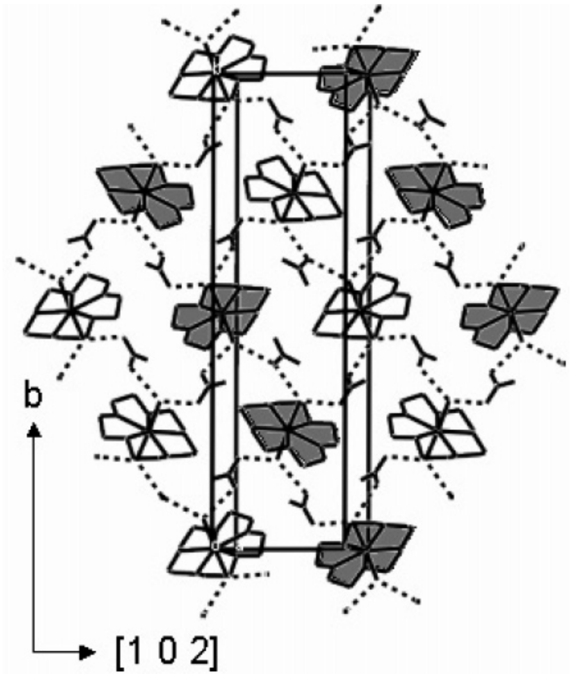

Figure 1. Drawing of a layer perpendicular to $(20\bar{1})$ of the triclinic structure of the Mn compound. Light- and dark-colored cations are conformational enantiomers. Cations adjacent in the horizontal direction, which is the vector [102], are related by inversion centers; cations in adjacent rows are crystallographically independent. The O−H···O H-bonds are shown as dotted lines. Adjacent layers are related by inversion centers.

lated structures suggests that modulations occur when competing noncovalent interactions between nearest and next-nearest neighbors are of similar importance.[19]

A careful consideration of the $[M(H_2O)_2(15\text{-crown-}5)](NO_3)_2$ structures suggests a structural reason for the large number (nine) of related structures, all of which are unusual[18,20,21] in having $Z' > 1$. The observation that complexes of the 15-crown-5 ligand are often disordered is also explained.

Results

Phases Observed. The first crystals of the Mn compound obtained by evaporation at room temperature from water solutions approximately equimolar in $Mn(NO_3)_2$ and 15-crown-5 are triclinic with the 2-D H-bond pattern shown in Figure 1. Comparisons with the layered phases known previously are simplified if the nonstandard space group $C\bar{1}$ is used instead of $P\bar{1}$ (all crystallographic data are given in Table 1). When the group is changed to $C\bar{1}$ the α and γ angles are very close to 90°, and the H-bonded layers are parallel to the reciprocal-lattice plane $(20\bar{1})$, which contains the direct-space vector [102]. In a row of cations that extends along [102] (i.e., the horizontal direction in Figure 1), adjacent cations are related by inversion centers and so must be (conformational) enantiomers. Cations in adjacent rows are crystallographically independent so that $Z' = 2$.

No phase change occurs if the triclinic Mn crystals are flash cooled to 90 K, but if the crystals are cooled slowly (e.g., at 0.2 K/min), there is a change not far below room temperature (see Experimental Section) to the $P2_1/c$, $Z' = 3$, phase already known for the Mg and Zn compounds (see Figure 2). No additional transition was observed when the crystal was cooled to 160 K at the same rate or when it was cooled from 160 to 90 K at 5 K/min.

A vial containing crystals of the Mn compound that also contained a small amount of mother liquor was examined again after several months had passed. The crystals, which had previously been chunky with obvious acute and obtuse angles, had changed to thick plates that appeared to have a square cross section. These new crystals were found to be isostructural with those of the Co compound, which has a 3-D pattern of H-bonding.[1] No phase transition was found for this tetragonal phase between 294 and 90 K.

Unlike the wet crystals, triclinic crystals of the Mn compound that had been dried carefully could be stored indefinitely without change.

Table 1. Crystallographic Data

identifier	Mn I	Mn II	Mn III	Fe I	Fe II
formula	$C_{10}H_{24}MnN_2O_{13}$	$C_{10}H_{24}MnN_2O_{13}$	$C_{10}H_{24}MnN_2O_{13}$	$C_{10}H_{24}FeN_2O_{13}$	$C_{10}H_{24}FeN_2O_{13}$
molar mass	435.25	435.25	435.25	436.16	436.16
crystal system	triclinic	monoclinic	tetragonal	monoclinic	monoclinic
space group; Z; Z'	$C\bar{1}$; 8; 2	$P2_1/c$; 12; 3	$P4_1$, $P4_3$; 8; 2	$B2_1$; 32; 8	$P2_1/c$; 12; 3
a (Å)	14.544(3)	14.647(3)	11.355(2)	14.521(1)	14.541(1)
b (Å)	28.470(6)	14.127(3)	11.355(2)	14.229(1)	14.191(1)
c (Å)	10.646(2)	25.823(5)	27.183(5)	68.443(3)	25.647(3)
α (deg)	89.78(3)	90	90	90	90
β (deg)	126.43(4)	96.22(3)	90	96.26(1)	96.21(1)
γ (deg)	89.98(3)	90	90	90	90
temp (K)	90.0(2)	90.0(2)	90.0(2)	90.0(2)	90.0(2)
V; V/Z (Å^3)	3546.7(12) 443.34(15) [V/Z = 454.9(2) at 294 K]	5311.8(18) 442.65(15) [V/Z = 451.70(6) at 263 K]	3504.9(10) 438.1(1) [V/Z = 451.9(1) at 294 K]	14057(2) 439.29(5) [V/Z = 450.2(1) at 287 K]	5261.2(12) 438.4(1) [V/Z = 448.1(1) at 263 K]
D_{calc} (g cm^{-3})	1.630	1.633	1.650	1.649	1.652
μ (mm^{-1})	0.82	0.82	0.82	0.93	0.93
θ max (deg)	27.5	27.5	27.5	27.4	25.0
reflns					
measured	11 181	43 531	22 952	133 546	18 103
independent	8102	12135	7972	31488	9276
$I > 2\sigma(I)$	7133	5238	6494	14989	6100
no. of params	495	740	495	795	703
no. of restraints	12	18	13	1	0
R_1 [$I > 2\sigma(I)$]	0.028	0.051	0.036	0.046	0.035
wR_2 (all)	0.069	0.126	0.076	0.134	0.098
Flack param			−0.006(13)		

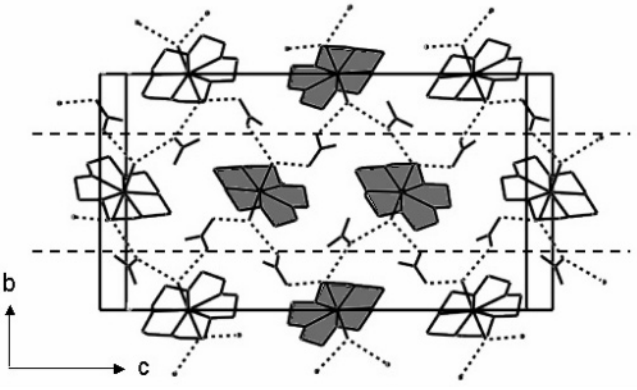

Figure 2. Drawing of a layer of the $P2_1/c$, $Z' = 3$, structure of the Mn and Fe compounds at x ca. $^1/_4$. Light- and dark-colored cations are conformational enantiomers. The O−H···O H-bonds are shown as dotted lines. The Mn and Fe structures are very similar, but one of the nitrate−water H-bonds in the Mn structure should probably be viewed as bifurcated. The traces of the c glide planes are shown as dashed lines. The first three cations in the middle row (from left to right) are the three crystallographically independent cations. The nitrate ions at y ca. $^1/_4$ and ca. $^3/_4$ form two crystallographically independent groups. Adjacent layers are related by 2_1 screw axes and by inversion centers.

Crystals of the Fe compound grown at room temperature have a surprisingly large unit cell ($P2_1$, $Z' = 8$). Comparison with the other layered structures known ($P2_1/n$, $Z' = 5$ for Cu; $P2_1/c$, $Z' = 3$ for Mg, Zn, and Mn; $C\bar{1}$, $Z' = 2$ for Mn) was simplified if the $P2_1$ structure was described in a nonstandard $B2_1$ cell (see Figure 3). It was fortunate that this phase, like the triclinic phase of the Mn compound, could be studied at 90 K if flash-cooled because the reflections at room temperature of this large modulated superstructure are too weak to give a good independent-atom refinement.

If crystals of the Fe compound are cooled slowly, they undergo a phase transition not far below room temperature (see Experimental Section) to the $P2_1/c$, $Z' = 3$, phase already known for the Mg, Zn, and Mn compounds. An overlay of the four $P2_1/c$, $Z' = 3$, structures made with the structure visualization program Mercury[22] shows that they are so similar that the only difference between the overlay and a picture of one of the single structures is the width of the lines used to represent the chemical bonds.

Cation Geometry. The conformation of the crown ligand is essentially identical in all the known structures that have a 2-D H-bond arrangement and is only a little different in the structures that have a 3-D H-bond arrangement. For the layered structures (Cu, $P2_1/n$, $Z' = 5$; Mg, Zn, Mn, Fe, $P2_1/c$, $Z' = 3$; Mn, $C\bar{1}$, $Z' = 2$; Fe, $P2_1$, $Z' = 8$), a 16-point match (C and O atoms of the crown ligand plus metal ion) of the 27 independent cations as observed at 90 K gives a root-mean-square (hereafter, rms) deviation of 0.054 Å. This rms value is remarkably low given that the M−O distances are not the same (see below). The rms value rises to 0.061 Å if the O atoms of the water ligands are included but the two cations of the triclinic structure are left out. The water ligands in the triclinic Mn structure are in slightly different positions relative to the crown than they are in the monoclinic layered structures so that the rms deviation if the water O atoms are included for all 27 cations is 0.52 Å (although the average deviation is only 0.22 Å).

All of the cations have an approximate 2-fold axis that passes through the metal ion and one of the crown O atoms (here designated as O5; see Figure 4). This approximate symmetry is a consequence of the odd number of O atoms in the ring. In the favorable conformation for a coordinated $(CH_2OCH_2)_n$ ligand, the O atoms are roughly coplanar and each has one lone pair directed toward the metal. The attached C atoms should then be located well above or below the approximate plane of the O atoms and the M ion. Since the O−C−C−O torsion angles should be about 60°, adjacent C atoms should be on opposite sides of the MO_5 plane. If the number of CH_2OCH_2 units is even, then there is no problem achieving this conformation, which is normal for complexes of 18-crown-6, but if the number of CH_2OCH_2 units is odd, there must be one O atom (denoted as O5 in these structures) that is next to C atoms with axial H atoms that point toward opposite

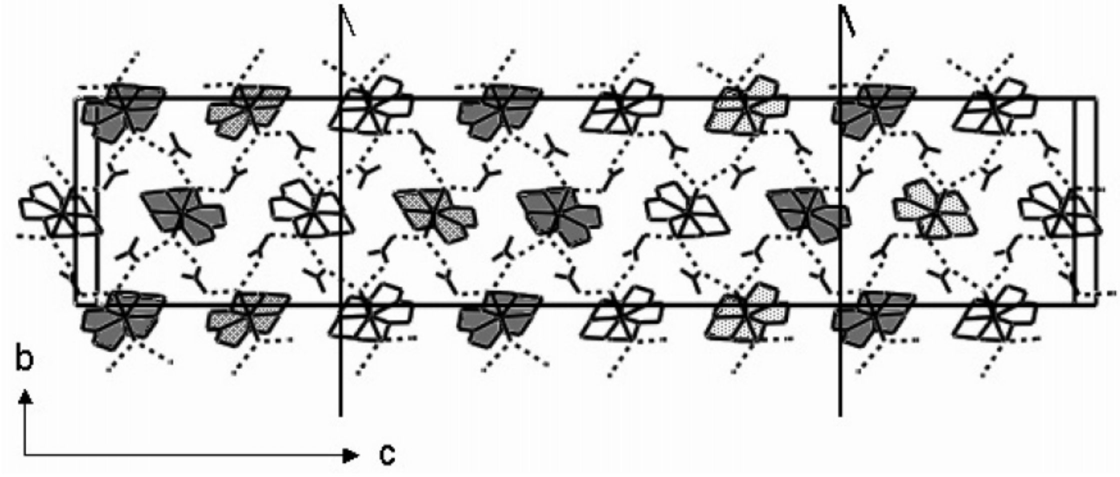

Figure 3. Drawing of a layer of the $B2_1$, $Z' = 8$, structure of the Mn compound at x ca. $^1/_4$. Light- and dark-colored cations are conformational enantiomers; cations that are sometimes disordered are less light and less dark. The O−H···O H-bonds are shown as dotted lines. The locations of the 2_1 screw axes are shown. The first eight cations in the middle row (from left to right) are the eight crystallographically independent cations. Adjacent layers are related by translation.

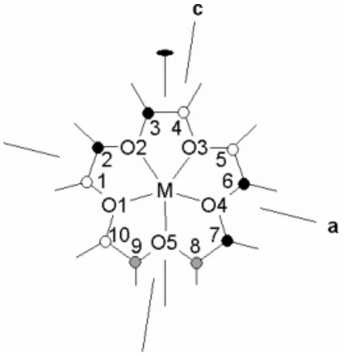

Figure 4. Drawing showing the observed cation conformation, the atom-numbering scheme, and the approximate orientation of the cations relative to the *a* and *c* axes in the layered structures that are monoclinic.

Table 2. M−O Distances (Å) Averaged over the Five Equatorial Ether O Atoms and Two Axial Water O Atoms for the Structures Determined at 90 K[a]

	Mn $P2_1/c$, $Z' = 3^b$	Fe $P2_1/c$, $Z' = 3^b$	Zn $P2_1/c$, $Z' = 3^c$	Mg $P2_1/c$, $Z' = 3^c$
$M-O_{ether}$	2.252(11)	2.226(6)	2.227(13)	2.193(11)
$M-O_{water}$	2.121(2)	2.064(3)	1.992(3)	2.010(3)

	Mn $C\bar{1}$, $Z' = 2^b$	Fe $B2_1$, $Z' = 8^b$	Cu $P2_1/n$, $Z' = 5^c$
$M-O_{ether}$	2.251(14)	2.227(11)	2.253(14)
$M-O_{water}$	2.121(3)	2.065(2)	1.910(3)

	Mn $P4_3$, $Z' = 2^b$	Co $P4_1$, $Z' = 2^c$
$M-O_{ether}$	2.247(6)	2.211(5)
$M-O_{water}$	2.149(3)	2.059(5)

[a] Numbers in parentheses are estimated standard deviations of the means. These deviations are relatively large for the $M-O_{ether}$ distances because those distances vary systematically around the crown (see text). [b] This work. [c] Reference 1.

sides of the MO_5 plane. The atoms C8, C9, O5, and M are then more coplanar than they would be otherwise (numbering as in Figure 4), and the associated strain leads to values of the O−C−C−O* angles that are in the range 43°−54° [average 48.9(4)° for 27 cations] rather than close to 60° [range 52°−63°; average 58.5(2)°]. The exceptionally good fit of the overlay of 27 independent cations known for layered structures shows that the minimum-energy conformation is well defined.

The conformations of the two independent Mn and Co[1] cations in each of the tetragonal structures with 3-D H-bonding are very similar to each other and to those of the cations in the layered structures except for small differences around the strained O atom of the crown (see Experimental Section) and small displacements of the water ligands.

Bond Lengths. The $M-O_{ether}$ and $M-O_{water}$ distances are normal (see Table 2).[7] The averages of the $M-O_{ether}$ and $M-O_{water}$ distances are the same for the three Mn structures and for the two Fe structures; this equality indicates that the bond lengths do not change with structure type. Detailed comparisons of the 27 independent cations in the seven layered structures show that the M−O5 bonds are, on average, 0.075(8) Å shorter than the average $M-O_{ether}$ distance in the same structure and that the adjacent M−O1 and M−O4 bonds are just a little longer [0.037(11) and 0.032(11) Å] than the average. The shorter M−O5 distance is not a consequence of a shift of the M ion away from the centroid toward O5; in all the cations, the M ion is actually shifted slightly (by an average of 0.015 Å and a maximum of 0.030 Å) from the centroid away from O5 and toward O2 and O3. It appears that the shorter M−O5 bond length signals a distortion of the crown ligand that keeps the crown "flatter" in the region of O5, C8, and C9 than it would be otherwise.

Over the whole series (Cu, Mg, Zn, Co, Mn, Fe), the average of the $M-O_{ether}$ distances varies by 0.060 Å (the Mg−O bonds are shortest, and the Mn−O bonds are longest), and the average $M-O_{water}$ distance varies by 0.240 Å (the Cu−O distances are shortest, and the Mn−O distances are longest). The only feature worth noting is the shortness of the $Cu-O_{water}$ bonds.

Overview of the Packing. The four types of layered phase all contain H-bonded layers that include the directions *b* and *c* when the crystal is monoclinic and the directions *b* and [102] when the crystal is triclinic. The cations are in van der Waals contact along a row in the layer (i.e., along *c* or [102]). The cations in adjacent layers are also in van der Waals contact along *a*. Two kinds of layers must then be considered: the H-bonded layer (defined by *b* and either *c* or [102]) and the cation layer (defined by *a* and either *c* or [102]).

Enantiomeric Alternation. The cations have 2-fold symmetry and are therefore chiral, although the reversibility of two phase transitions shows that enantiomers can interconvert readily within the crystal as well as in solution, at least at temperatures above ca. 270 K. In the projection that shows the layers of H-bonds (see Figures 1−3), the cations look like thick arrows. Atoms C3 and C4, which are nearly superimposed, are at the head of the arrow, and atoms C8, O5, and O9 define the tail of the arrow. Cations in a row along which they are in contact (horizontal direction in Figures 1−3) are enantiomeric when the arrows point in opposite directions.

M = Ni. No analogous compound was found for M = Ni, which is probably not surprising. The only structure in the CSD with a Ni^{2+} ion complexed by a 15-crown-5 ligand (refcode BIHFED) was reported in a meeting abstract only and was archived without coordinates. We have, however, found seven phases containing Ni^{2+}, $2NO_3^-$, 15-crown-5, and water (including the compound $[Ni(H_2O)_6](NO_3)_2 \cdot 15\text{-crown-}5 \cdot 2H_2O$,[23] but the Ni^{2+} ion is not coordinated by the crown ligand in any of them. Two additional phases containing these three components are known, but these last two phases also include a solvent molecule (e.g., acetonitrile) that was included in the synthesis in an attempt to reduce the number of water ligands coordinated to the Ni^{2+} ion. The M = Ni phases will be described in a separate paper.

Related Structures. A search of the CSD found 53 different structures with a metal ion other than a 1A alkali or 2A alkaline-earth metal ion within a 15-crown-5 ligand. Of these 53, 16 (30%) are affected by major disorder of the crown ligand and 5 (9%) have $Z' > 1$.

Fourteen well-determined structures (excluding the nitrate salts) were found in which $[M(H_2O)_2(15\text{-crown-}5)]^{2+}$ ions are linked by H-bonding anions. In six of these 14 structures, the H-bonding pattern is 1-D, in three, it is 2-D, and in four, it is 3-D, but three of the four 3-D structures include extra water molecules that are part of the H-bonding pattern.

Discussion

Phase with 3-D H-Bonding. The tetragonal structure found for Mn (and for Co) must be the most stable phase, at least for those two metals. Nucleation of this phase is very slow for the Mn compound (weeks or months near 300 K), but once it occurs, all of the triclinic phase is transformed if at least a small amount of saturated aqueous solution is present. Furthermore, the molar volume for the tetragonal phase is smaller (see Table 1) than for the other Mn phases at the same temperature. It appears that the 3-D H-bonding arrangement in this phase is more favorable than the 2-D arrangement in the layered phases. The 3-D H-bonding pattern might seem to be complicated enough to explain the slow nucleation, but crystals of the isostructural Co compound, for which no other phase has been found, grow readily. While the tetragonal phase has not been observed for M = Cu, Mg, Zn, or Fe, it may yet be found.

Phases with 2-D H-Bonding−Alternation Patterns. The important differences between the four types of layered structures (i.e., the structures with 2-D H-bonding) are the patterns of alternation of conformational enantiomers along the direction in the H-bonded layer in which the cations are in contact (i.e., [102] in the triclinic structure, and *c* in the three monoclinic structures [Z' = 3 (Mg, Zn, Mn, Fe), 5 (Cu), and 8 (Fe)]). Within such a row cation “arrows” (see above and Figures 1−3) that point in opposite direction are related by real or approximate inversion and by pseudotranslation.

In the triclinic structure seen for the Mn compound (see Figure 1) at room temperature, the alternation within a row parallel to [102] is perfect. In the $P2_1/c$, Z' = 3, structure seen for the Mn, Fe, Mg, and Zn compounds (see Figure 2), the alternation pattern within a row parallel to *c* is R R S R R S R R S (or S S R S S R S S R); that is, the enantiomer fails to alternate once in every three contacts. In the higher-temperature $B2_1$ phase of the Fe compound (see Figure 3), the alternation faults are reduced to one in four if the minor (14%) disorder is ignored.

Phase Transitions. The two reversible phase transitions described here both give a structure with a more perfect pattern of enantiomeric alternation at the higher temperature. We have found that the same principle (more perfect alternation in the phase stable at higher temperature) holds for transitions observed above 300 K for the Cu, Mg, and Zn compounds.[24] All these phase transitions can be reversible because the atomic displacements required to change the cation conformation are so small that a change can occur in place without the introduction of stresses large enough to fracture the crystal.

The reversible transitions found below room temperature for the Mn and Fe compounds have, as is expected, the same sign for ΔV (see Table 1) and ΔH (see Experimental Section). When a crystal is heated through the transition temperature the slightly larger molar volume of the phase stable at higher temperature lowers the vibrational frequencies of the lattice modes just enough that a favorable $T\Delta S$ term offsets the unfavorable ΔH term. The DSC measurements show that the hysteresis for these transitions is very large.

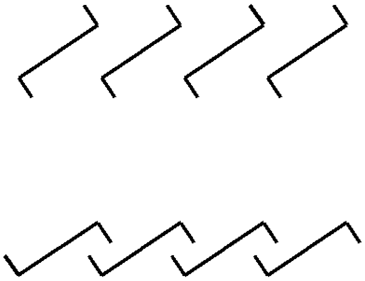

Figure 5. Drawing showing a favorable (top) and unfavorable (bottom) packing of planar fragments with small protrusions.

Packing Problems in the Cation Layers. The van der Waals surfaces of crown ligands have the approximate shape of a thick, but somewhat uneven, disk. The disk axes must be tilted away from the layer normal if the stacking of layers is to be favorable. If there are protrusions from one side of the disk (e.g., the axial H atoms), then these should be aligned (see Figure 5) so that they point into the space between layers rather than toward another disk in the same layer.

Within the cation layer, each cation has four nearest neighbors because that is the arrangement most compatible with the (indirect) linking of adjacent cations by H-bonds to nitrate ions (see Figures 2 and 3). The H-bonding requires that the M ions be lined up in a reasonably straight line.

If the packing is to be tight then the axial H atoms of the methylene groups that are in van der Waals contact must point in opposite directions, and the axial H atoms on opposite sides of the same cation must point in opposite directions (see Figure 5). Cations adjacent along *a* and *c* (or [102] if the crystal is triclinic) could be related by either inversion (or pseudoinversion) or translation (or pseudotranslation), but the former is more common than the latter and can therefore be assumed to be more favorable. In all observed layered structures, all cations adjacent along *a* are related by inversion or pseudoinverson, as are most cations adjacent along *c* (or [102]).

The combination of translational symmetry with these packing requirements means that vectors between metal ions adjacent along *a* and *c* (or [102]) must pass through the crown such that axial H atoms nearest the vector and on opposite sides of the crown ligand point in opposite directions. Furthermore, the angle between these two vectors must be large (i.e., near 90°).

Consideration of Figure 4 shows that there are not many possible choices for these vectors. Since the crown layers in a number of structures are very similar, it must be that there is one choice that is clearly best. That choice has one vector passing near atoms C1 and C6 and the other passing near atoms C4 and C9 (numbers as in Figure 4). The closest contacts along *a* between adjacent cations then involve the H atoms attached to C1 and C6, and the closest contacts along *c* involve the H atoms attached to C4 and C9.

Along *a*, the cations within a cation layer are always related by a true or pseudo inversion center. Because there are two kinds of contacts (C1⋯C1 and C6⋯C6), there are two different M⋯M distances for each independent M ion. In the triclinic structure (Z' = 2), the Mn1⋯Mn1 distance for the longer contact (C6⋯C6) is

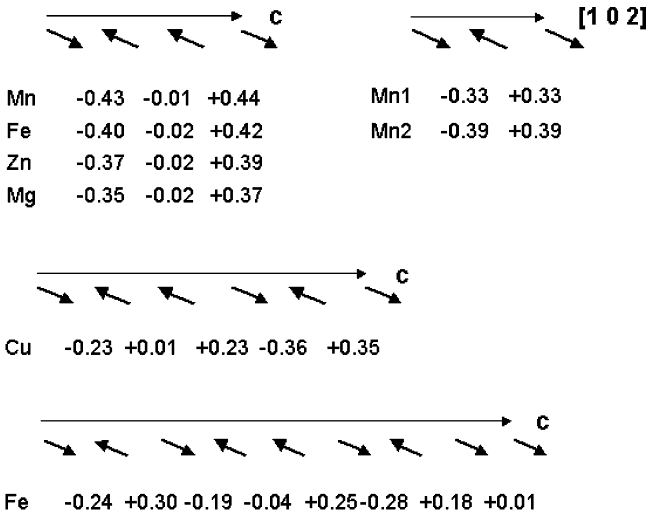

Figure 6. Drawing showing the four different patterns of enantiomeric alternation in the layered structures; data for the Zn, Mg, and Cu structures are from ref 1. The directions of the arrows correspond to the cation orientations in the rows shown in Figures 1–3. The distances (in Å) shown below the arrows are the deviations of the M···M distances from the average M···M distance of that structure. The distance is short when two arrows point toward each other (C4···C4 contact), long when the arrows point away from each other (C9···C9 contact), and intermediate when the arrows point in the same direction (C4···C9 contact). In the triclinic Mn structure (only), there are two crystallographically independent rows.

0.33 Å longer than the distance for the shorter contact (C1···C1); for Mn2···Mn2, the distance difference is 0.14 Å. The differences in the other structures are similar.

Along the other direction in the cation layer (*c* or [102]), the important contacts are C4···C4, C9···C9, and, when the cations are related by pseudotranslation rather than pseudoinversion, C4···C9. Participation of the C9 methylene group in close contacts causes problems because the axial H atom attached to C9 does not point straight up and because the equatorial H atom attached to C9 points more down than do the equatorial H atoms on C1–C8. In the triclinic Mn structure, in which the enantiomeric alternation is perfect, the Mn···Mn separations along the row are 0.66 and 0.78 Å longer when the H atoms of C9 are in contact than when the H atoms of C4 are in contact. This pattern is also found in the other 2-D H-bonded structures (see Figure 6). The M···M separations are relatively short for the C4···C4 contacts (i.e., the head-to-head contacts of the cation "arrows"), are relatively long for the C9···C9 contacts (the tail-to-tail contacts of the arrows), and are intermediate in length for the C4···C9 contacts. The crown distortion mentioned above can be understood as allowing the C4···C4 and C9···C9 contacts to have more similar lengths than they would otherwise.

Since the M···M distances vary, so do the distances between the axial water ligands that are bridged, through H-bonding, by a nitrate anion. The orientations of the crystallographically independent nitrate ions vary slightly so that the N–O···O–M distances can remain similar while the M–O···O–M distances vary. When the M–O···O–M distance is very short, a single nitrate O atom interacts with two different water ligands. This arrangement occurs when, for example, a cation in one row is shifted to the left because of a head-to-head contact and the cation above (or below) it is shifted to the right because of a tail-to-tail contact. In the triclinic structure, one of the four independent nitrate ions uses only one of its O atoms to form H-bonds. In the $P2_1/c$, $Z' = 3$, structures, two of six nitrate ions do the same, and in the $P2_1$, $Z' = 8$, structure, five of 16 nitrate ions bond this way.

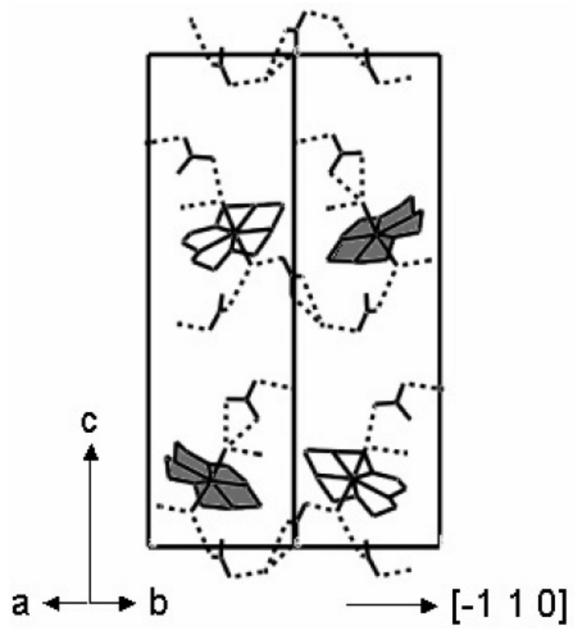

Figure 7. Drawing of a "layer" perpendicular to (110) of the $P4_3$ (or $P4_1$), $Z' = 2$, structure of the Mn compound. Light- and dark-colored cations are conformational enantiomers and are crystallographically independent.

Another indication of the reorientation of the nitrate ions to compensate for uneven spacing of the metal ions is the occurrence of bifurcated H-bonds in which the axial O atom of the complex is approximately equidistant from two O atoms of a nitrate ion. No such bond is shown in the figures drawn here, but bifurcated H-bonds occur in all four layered structures that were determined near room temperature and in the 90 K Mn $P2_1/c$, $Z' = 3$, structure.

When the temperature is raised, the M···M distances become more similar; the differences in M···M distances for the head-to-head and tail-to-tail contacts are reduced by 10–25%.

Tetragonal Structures. Rows of cations are also found in the tetragonal structures (see Figure 7), but there is no close-packed cation layer like those in the 2-D structures. Within the rows, which are parallel to $[1\bar{1}0]$, there is perfect alternation of conformational enantiomers. The spacing of cations in the rows is ca. 7% smaller at 90 K for the tetragonal Mn structure than for the monoclinic or triclinic Mn structures. The contacts within the rows are between methylene groups C1 and C6 of cation 1 and C5 and C10 of cation 2 (numbering as in Figure 4). The shorter spacing is possible because neither the C9 nor C8 methylene groups are involved in the contacts. The disorder of conformational enantiomers (see Experimental Section) is consistent with loose packing in the region of O5.

The rows in the tetragonal structure are just 3–4% less than twice as far apart as in the layered structure, but the cations are more than twice as far apart in the third direction. Overall the Mn structure with 3-D H-bonding is just over 1% denser at 90 K than are the Mn structures that have 2-D H-bonding.

Conclusions

The $[M(H_2O)_2(15\text{-crown-}5)](NO_3)_2$ system is remarkable for having nine structures in five space group/Z' combinations, all of which have $Z' > 1$ and two of which have unusually large Z' values (5 and 8). The 15-crown-5 ligand is also known to be likely to disorder. What structural features of the 15-crown-5 ligand lead to this behavior?

Occurrence of Modulated ($Z' > 1$) Structures. This system is an example of the principle that conflicts between optimum spacings for two (or more) different kinds of noncovalent interactions can lead to modulated structures. In the $[M(H_2O)_2(15\text{-crown-}5)](NO_3)_2$ structures, the competition is between the cation spacings that optimize O−H···O bonding and the spacings that optimize the filling of space. The even spacing in a row of M ions is probably more favorable for the formation of a 2-D H-bonding pattern, but the shape of the van der Waals surface of the crown ligand prevents the spacing from being even (see above).

The role of temperature is also important. With increased thermal motion, the effective van der Waals surface of a cation becomes smoother (and also a little larger, which is why crystals expand with T). Conversely, as the temperature is lowered and motion decreases, the effective van der Waals surface develops small hollows. If an adjacent cation can nestle into one of these hollows, the crystal density can be increased and the crystal energy lowered.

The 15-crown-5 ligand is unusual because the conformational enantiomers of the (presumed) minimum-energy conformation of the complexed ligand can interconvert in the crystal, at least at temperatures not too far below 295 K. If the ligand could not interconvert the $P2_1/c$, $Z' = 3$, structures for the Mn and Fe compounds would not have been found. The possibility of enantiomer conversion makes possible the occurrence of multiple phases.

Likelihood of Disorder. If the van der Waals surfaces of the two conformational enantiomers of the complexed 15-crown-5 ligand are similar enough that they can interconvert in a crystal without causing crystal fracture, then it is not surprising that disorder might be common, especially if the ligands are not in good van der Waals contact with each other or if the temperature is relatively high. It is, however, also possible that in at least some cases the disorder is apparent rather than real and was found because the weak reflections signaling a modulated superstructure were overlooked.[1]

Polymorphs or Not? It is clear that the tetragonal Mn structure, which has a 3-D H -bonding pattern, should be considered as being a different polymorph than the Mn structures with 2-D H-bonding patterns. It is less obvious that the triclinic ($Z' = 2$) and monoclinic ($Z' = 3$) Mn structures or the two monoclinic Fe structures ($Z' = 3$ and $Z' = 8$) should be considered to be polymorphic; perhaps they should just be considered to be different modulations of the same basic structure. The powder patterns calculated with Mercury[22] for the two Mn structures with 2-D H-bonding are very similar, while the pattern for the structure with 3-D H-bonding is clearly different. On the other hand, the powder patterns for the two layered Fe structures are not the same; the $Z' = 8$ Fe structure has four strong peaks at low angles that are missing from the pattern for the $Z' = 3$ structure.

Experimental Section

Reagents. All reagents and solvents were used as purchased.

Crystal Growth. Crystals of the Mn complex were grown at room temperature from water solutions approximately equimolar in $Mn(NO_3)_2$ and 15-crown-5. Crystals of the Fe complex were produced in the same general way except that the $Fe(NO_3)_2(aq)$ was synthesized from $Fe(NO_3)_3(aq)$ by reduction with iron powder in 3 M $HNO_3(aq)$ before the 15-crown-5 was added. The reaction mixture was warmed for a time to 333−343 K to hasten removal of some of the water, but crystals were then grown at room temperature.

Differential Scanning Calorimetry Measurements. The reversible phase transitions for the Mn and for the Fe compound were studied by differential scanning calorimetry (DSC) using a DSC 822^e apparatus manufactured by Mettler Toledo. For the Mn compound, 3.27 mg of powdered sample was used, and the heating rate was 10 K/min. For the Fe compound, 2.0 mg of powdered sample was used and the heating rate varied from 1 to 20 K/min. The transition for the Mn compound showed very significant hysteresis with the onset and peak temperatures determined during heating and cooling differing by ca. 20 K; average values are $T_{Tr} = 285$ K and $\Delta H_{Tr} = 0.19(2)$ kJ/mol. The transition for the Fe compound was not observed when the sample was cooled (although the transition must have taken place since it was observed when the sample was subsequently heated); the values obtained during heating are $T_{Tr} = 278$ K and $\Delta H_{Tr} = 0.06(1)$ kJ/mol.

Crystallography. All X-ray data were collected on a Nonius KappaCCD diffractometer with a Mo Kα fine-focus tube and equipped with a CRYOCOOL-LN2 low-temperature system (CRYO Industries of America, Manchester, NH). In all cases, the detector distance (in mm) was at least twice the largest cell dimension (in Å), which we have found to be a useful guide for dealing with large unit cells. All corrections, including an absorption correction based on spherical-harmonic analysis of symmetry-related measurements, were applied automatically using SCALEPACK.[25] Phase purity was checked by examining slices of the reciprocal lattice reconstructed from the pixel values of original data frames using the PRECESSION routine in the Nonius data-processing package COLLECT[26] to be sure no extra diffraction peaks were present. The structures were solved without difficulty using SHELXS-97[27] and were refined on F^2 using SHELXL-97.[28] All non-H atoms were refined anisotropically except as described below. All methylene H atoms were placed at calculated positions and allowed to ride on the attached C atom. The H atoms of the water ligands for the low-temperature structures were located in difference Fourier maps and refined with restraints. Refinements of data collected at or near room temperature started from the parameters determined at low temperature, and the coordinates of the H atoms of the water ligands were held fixed.

The atom-numbering schemes and the choices of the asymmetric units are all consistent with those described previously for other structures in the series.[1]

The triclinic phase of the Mn compound was described in the space group $C\bar{1}$ rather than the standard group $P\bar{1}$ to facilitate comparisons with the other structures. The transformation is given by $a(C\bar{1}) = (-1\ -1\ 0/-1\ -1\ -2/1\ 0\ 0)\ a(P\bar{1})$; the cell constants at 90 K of the primitive cell are 10.646(2), 11.874(2), and 15.983(3) Å and 108.16(3)°, 105.87(3)°, and 99.75(3)°. In the $C\bar{1}$ cell, the H-bonded layers are parallel to $(20\bar{1})$, which contains the vector [102].

The room-temperature phase of the Fe compound was described by the space group $B2_1$ rather than the standard group $P2_1$ to make comparisons with the $P2_1/c$ structure easier. The transformation is given by $a(B2_1) = (1\ 0\ 0/0\ {-1}\ 0/{-1}\ 0\ {-2})a(P2_1)$; for the primitive cell at 90 K, $c = 34.200(2)$ Å and $\beta = 95.92(1)°$. This structure presented several crystallographic challenges. Data were collected at a detector distance of 68 mm, that is, twice the length (after conversion from Å to mm) of the longest axis of the primitive cell. We then checked the reconstructed slices of the reciprocal lattice very carefully to make sure that all diffraction maxima had integral indices and that there were no unusual absence conditions that might indicate twinning. It was fortunate that this phase was stable at 90 K if flash cooled, because the reduction in thermal motion raises the intensities of many of the weak superstructure reflections above background level. Even so, the data did not include sufficient information to allow independent refinement of displacement parameters for all the independent atoms; atoms related by pseudotranslation and pseudoinversion were constrained to have the same displacement parameters. Another complicating factor was the minor enantiomeric disorder [occupancy factors 0.866(2) and 0.860(2) for the major components] found at two cation sites; the two minor components were treated as rigid groups. The crystals seem to be inversion twinned, so no determination of the absolute structure was possible. Convergence was smooth, and final agreement factors were very satisfactory (see Table 1). The largest correlation coefficient had an absolute value <0.79. The agreement within the sets of distances related by pseudotranslation and pseudoinversion was good; the estimated standard deviations for the sets of eight distances for the cations and 16 distances for the anions averaged about 1.8 times the average uncertainty of an individual measurement.

No special difficulties were encountered in refinement of the $P2_1/c$, $Z' = 3$, structures for the Mn and Fe compounds even though the pseudosymmetry is so strong that the fraction of reflections with $I > 2\sigma(I)$ is unusually low. Refinements of the isostructural phases of the Mg and Zn compounds, which have been discussed previously,[1] were also problem free.

Crystals of the tetragonal ($P4_1$ or $P4_3$, $Z' = 2$) Mn compound with the 3-D H-bonding network are, like the isostructural crystals of the Co compound,[1] very pseudosymmetric. The Mn crystal chosen for study happened to have space group $P4_3$ rather than $P4_1$ (the group found for the specific Co crystal sudied), and the x and y coordinates for the two crystals happen to be switched. If the structure is viewed down c when the a, b, and c axes of the Mn structure are aligned with the $-b$, a, and c axes of the Co structure, then corresponding atoms are aligned, although their z coordinates have opposite signs. These atom numbers do not follow the scheme shown in Figure 4 for reasons that have been explained previously.[1] Atoms O21 and O32 (which are not related by the pseudosymmetry) correspond to the atom marked O5 in Figure 4.

There is clear evidence in the tetragonal Mn structure of up/down disorder of atoms C3n and C4n, $n = 1$ and 2, and perhaps O2n and O3n. The ellipsoids are elongated in the direction perpendicular to the plane of the crown O atoms and the C3n−C4n distances are too short.

The tetragonal Mn crystals, like the Co crystals, are also twinned by merohedry (a mirror plane perpendicular to c), but the smaller individual of the Mn twin occupied less than 9% of the crystal volume.

Data for the five phases measured at 90 K are given in Table 1. Crystallographic data for the determinations at or near room temperature (see Table 1) are available in the Supporting Information.

Superpositions of independent cations were made using version 2.1 of the program *CrystMol* by David J. Duchamp.[29]

Pseudocell refinements were important in the identification of the important van der Waals interactions between cations. For the $Z' = 3$ and $Z' = 5$ phases, the $l \neq Z'n$ reflections were discarded, the value of c was divided by Z', and the z values for one cation and one pair of anions were multiplied by Z'. The refinements of the disordered structures in the smaller centrosymmetric unit cells gave a few rather eccentric atomic displacement ellipsoids but were otherwise very satisfactory. Examination of the resulting structures with the program Mercury then allowed identification of van der Waals contacts that are short in the average pseudocell structure but normal in the modulated supercell structure.

CSD Searches. Searches were made on the database as available in June 2005 (version 5.26 of November 2004 plus the updates of February and May 2005). Structures were considered to be well determined if the R factor was less than 0.075 and a full set of coordinates had been archived.

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Supporting Information Available: X-ray crystallographic data for **1**−**5** both at 90 K and at or near room temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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