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Divalent Metal Halide Double Salts in Equilibrium with Their Aqueous Solutions

II. Factors Determining Their Crystal Structures

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The double salts of many divalent metal halides that exist in equilibrium with their saturated aqueous solutions are composed of discrete or polymerized complex ions in simple ratios (e.g., 1 : 1 or 1 : 2). By treating the complex ions as spheres, ellipsoids, or cylinders whose dimensions can be easily estimated, one can predict possible crystal structures for these compounds. The observed cell dimensions generally lie within 0.8 Å of those predicted by the model. We show that the existence of some compositions can only be understood when crystal packing is considered. In particular, we are able to predict why interstitial water appears in some compounds. © 1991 Academic Press, Inc.

1. Introduction

In the first paper of this series Duhlev *et al.* (*1*) showed that, using six simple assumptions it is possible to predict the chemical structures and compositions of most of the metal halide double-salt phases ($xMeX_2 \cdot yMe'X_2 \cdot z\mathrm{H_2O}$; Me,Me' = Mg,Ca,Mn,Fe,Co,Ni,Cu,Zn,Cd; X = Cl,Br) that exist in equilibrium with their saturated aqueous solutions. In this paper we show that in many cases it is also possible to predict the crystal structures (including lattice dimensions and symmetries) of these phases. Two new features appear when the space filling requirements of crystal packing are considered: the existence of two new classes of compound and the presence of interstitial water.

The earlier paper (*1*) predicted that there should be seven basic types of double-salt structures (labeled A to G and listed in (*1*, Table I)) and that these fall into two classes. Four structures (A–D) are composed of discrete complex ions and three (E–G) have complex anions that are polymerized. In addition when Ca is present as the harder metal atom, we expect structures (indicated by the labels A* to G*) that are derived from the above structures by the fusion of the complex cation with either the anion or other cations. Two further structures (H–I) having hydrated polymeric anions are observed

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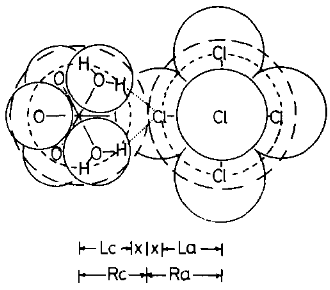

FIG. 1. The packing of a complex anion with a complex cation. The circle of short dashes indicates the first coordination sphere, the circle of long dashes indicates the effective size of the ion. Note that the two ions are projected down different octahedral axes.

but are not directly predicted in (*1*). This paper shows that these are the only two such structures that are consistent with the assumptions of (*1*) when crystallographic restraints are taken into account.

In Section 2 we discuss the principles that underlie the crystal structures adopted by these compounds. In the following three sections we apply these principles to the prediction of crystal structures of compounds with discrete complex ions, of those with polymerized octahedral anions and of those with polymerized tetrahedral anions respectively.

2. Structural Principles

To a first approximation, the discrete ions can be treated as spheres and the polyanions as cylinders. As shown in Fig. 1, their radii (R) can be calculated from

$$R = L + x, \qquad (1)$$

where L is the metal-ligand bond length (calculated from the predicted bond valences (*2*)) and x represents the distance the ligand projects beyond the first coordination sphere. The value of x will be less than the Van der Waals radius of the ligand because each ion will pack with its ligands pointing between the ligands of its neighbors and they will be linked by hydrogen bonds that are directed (ideally) 71° away from the radial direction (assuming an Me–O–H angle of 109°). In the compounds that are the subject of this paper, we observe that the first coordination spheres can approach to within 1.1 Å of each other, a distance that, to first order, is independent of size of the ligand atom. The value of x is taken to be half this amount (0.55 Å). Values of L and R for the complexes discussed in this study are given in Table I. (In this paper the terms cation and anion are assumed to refer to complex cations and complex anions and are differentiated by the subscripts c and a, respectively.)

If the compound contains a polymeric anion chain, one of the crystallographic axes is determined by the intrapolymer repeat, which can be easily calculated. All the other axes are determined by packing, which includes the influence of the hydrogen bonds between the coordinated water molecules of the cation and the halogen atoms of the anion.

3. Structures Containing Discrete One-Centered Ions—Structures A–D

In these systems each ion, treated as a sphere, consists of a single metal atom sur-

TABLE I

METAL LIGAND DISTANCES (L) AND COMPLEX ION RADII (R) IN Å FOR COMPLEX IONS

		$Me(H_2O)_n$		$Me'Cl_n$		$Me'Br_n$	
		L_c	R_c	L_a	R_a	L_a	R_a
Ni		2.06	2.61	2.39	2.94	2.60	3.15
Co		2.10	2.65	2.44	2.99	2.64	3.19
Mg		2.10	2.65	2.43	2.98	2.64	3.19
Zn	Octahedral	2.11	2.66	2.43	2.98	2.65	3.20
Zn	Tetrahedral	1.96	2.51	2.28	2.83	2.50	3.05
Fe		2.14	2.69	2.47	3.02	2.68	3.23
Mn		2.20	2.75	2.54	3.09	2.74	3.29
Cd		2.31	2.86	2.62	3.17	2.85	3.40
Ca		2.37	2.92	2.71	3.26	2.92	3.47

Note. All ions are octahedral unless otherwise stated. For anions with water replacing X as a ligand, a weighted mean of R_c and R_a can be used. All values of L are calculated from the bond valence using the method of Brown and Altermatt (*2*).

rounded by four to six halogen atoms or water molecules. Cations and anions are present in the ratios of 2 : 1, 1 : 1, or 1 : 2 and the cation/anion radius ratios (about 0.90 for the chlorides and 0.84 for the bromides) correspond to the packing of 8 to 12 anions around each cation. When the ions are present in equal numbers, the CsCl structure is expected as this gives the highest possible cation coordination number of 8. Since the ions are in contact along the body diagonal, the length of the cubic cell is

$$a = 2(R_c + R_a)/\sqrt{3} = 1.155(R_c + R_a). \tag{2}$$

For compounds with ions present in the ratio 1 : 2 the ionic structure with the highest coordination number is fluorite (antifluorite for 2 : 1 compounds) with a cell edge given by

$$a = 4(R_c + R_a)/\sqrt{3} = 2.309(R_c + R_a). \tag{3}$$

The coordination number of 8 found in these structures is the largest which is possible without ions of the same charge coming into contact, but because the complex ions in these structures are large, repulsion between ions of like charge is smaller than it would be if the ions were simple. Close-packed structures with coordination numbers of 12 may therefore be favored even though they bring like ions into contact. Close-packed layers of the kind illustrated in Fig. 2a give a cell with the correct 1 : 2 stoichiometry and are more compact, offering a volume reduction of 23–45% relative to the fluorite structure. The length of the unit cell edge in such a hexagonal layer is (see Fig. 3b)

$$a = 2(R_c + R_a)(\sqrt{3}/2) = 1.732(R_c + R_a). \tag{4}$$

Where the ions have high enough symmetry, we may expect the compounds to crystallize in a space group that reflects the symmetry of the underlying cubic or hexagonal lattice, but in many cases the symmetry will be lowered, either because some of the ions have low internal symmetry or because of the restrictions imposed by the hydrogen bond network.

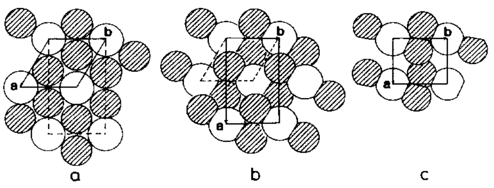

FIG. 2. A and A* structures projected down c (compare with (*1*, Fig. 4)). The actual cell is shown with a solid line, the pseudocell with a broken line. The cations are shaded, the anions unshaded. (a) A structure ($P31c$ or $R\bar{3}$). (b) A* ($C2/c$). The cation is linked to the anion by a halogen bridge. (c) A* ($P2_1/c$). The cations are linked as in b) and additionally to another cation through a double H_2O bridge to form chains along b.

3a. *Structure A—$[Me(H_2O)_6]_2[Me'X_6]$*

Compounds with the chemical structure A have a cation : anion ratio of 2 : 1. Both ions have O_h (or close to O_h) symmetry. They are expected to form an antifluorite structure or a structure based on hexagonal layers of the type shown in Fig. 2a. The antifluorite structure will be fully ordered in the cubic space group $F23$ with a cell edge given by Eq. (3). Each cation will have four anion neighbors and six cation second neighbors.

The hexagonal layer structure will have a basal plane unit cell edge given by Eq. (4).

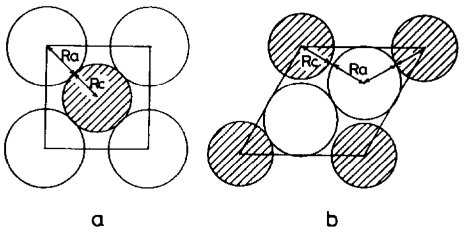

FIG. 3. (a) Square packing (Eq. 12). (b) Hexagonal packing (Eq. 4).

TABLE II

Comparison of Observed (and Calculated) Crystal Lattices

Compound		Cell dimensions (Å)	
Two-layer structures	Space group	*a*	*c*
	Compounds of Type A		
$[Ni(H_2O)_6]_2[CdCl_6]$ (*3*)	*P*3	9.95	11.24
	(*P*31*c*	10.01	11.56)
$[Mg(H_2O)_6]_2[MnCl_6]$ (*4*)	*P*3	9.46	11.11
	(*P*31*c*	9.94	11.48)
$[Mg(H_2O)_6]_2[CdCl_6]$ (*5*)	*P*31*c*	9.98	11.56
	(*P*31*c*	10.08	11.64)
Three-layer structures			
$[Mg(H_2O)_6]_2[CaCl_6]$ (*6*)	$R\bar{3}$	10.14	17.32
	($R\bar{3}$	10.24	17.12)
$[Mg(H_2O)_6]_2[CdBr_6]$ (*7*)	$R\bar{3}$	10.37	17.76
	($R\bar{3}$	10.48	17.40)
$[Ni(H_2O)_6]_2[CdBr_6][H_2O]_{0.67}$ (*8*)	$R\bar{3}$	10.16	19.15
	($R\bar{3}$	10.41	17.24)

Two-layer structures		*a*	*b*	*c*	*β*	*γ*
		Compounds of Type A*				
$[Ca(H_2O)_6]_2[CdCl_6]$ (*9*)	$P2_1/c$	8.84	10.11	12.71	114.0	90
		(9.13	10.55	12.18	90.0	120)
$[Ca(H_2O)_6]_2[CaCl_6]$ (*10*)	$P2_1/c$	8.95	10.22	12.79	117.2	90
		(9.27	10.70	12.36	90.0	120)
$[Ca(H_2O)_6]_2[CdBr_6]$ (*11*)	$C2/c$	18.29	10.34	13.53	117.0	90
		(18.96	10.95	12.64	90.0	120)

		a	*b*	*c*	*β*
	Compounds of Type B*				
$[Ca(H_2O)_6][MnBr_4(H_2O)_2]$ (*12*)	$C2/m$	9.06	9.58	9.40	113.0
		(9.84	9.84	6.96	90.0)
	Compounds of Type C				
$[Mg(H_2O)_6][MnBr_3(H_2O)_3]_2$ (*13*)	$C2/m$	13.48	10.03	8.43	111.0
(Fluorite		16.06	9.26	9.26	90.0)
(Close packed hexagonal layer		9.82	11.34	9.82	120.0)

		a	*b*	*c*	*α*	*β*	*γ*
		Compounds of Type D					
$[Mn(H_2O)_6][ZnBr_4]$ (*14*)	*Pbam*	12.44	12.95	8.00			
		(13.40	13.40	6.70)			
$[Mg(H_2O)_6][ZnCl_4]$ (*15*)	$P\bar{1}$	6.56	6.60	14.10	88.6	89.4	84.4
		(6.33	6.33	12.66	90.0	90.0	90.0)
$[Mg(H_2O)_6][ZnBr_4] \cdot H_2O$ (*16*)	$P2_1/n$	8.33	12.60	14.05		97.9	
		(6.58	13.16	13.16		90.0)	

		a	*b*	*c*	*β*
	Compounds of Type F				
$[Co(H_2O)_6][Cd_2Cl_6]$		(Structure not known)			
	($C2/c$	10.08	22.50	6.42	90.0)

TABLE II—*Continued*

		a	b	c	β
	Compounds of Type F*				
$[Ca(H_2O)_6][Cd_2Cl_6]$ (*17*)	*C*2/*m*	21.94	3.84	9.40	111.4
(Disordered subcell		24.50	3.70	10.55	120.0)

		a	b	c
	Compounds of Type G			
$[Mg(H_2O)_6][Zn_2Br_6]$ (*18*)	*Immm*	10.45	10.32	8.00
		(11.40	11.40	7.57)
$[Zn(H_2O)_6][Zn_2Br_6]$ (*19*)	*Immm*	10.44	10.37	7.96
		(11.42	11.42	7.58)
	Compounds of Type H			
$[Ni(H_2O)_6][Cd_2Cl_6(H_2O)_2] \cdot 4H_2O$ (*20*)	*Fdd*2	24.42	22.34	7.54
		(23.12	23.12	7.40)
$[Mg(H_2O)_6][Cd_2Cl_6(H_2O)_2 \cdot 4H_2O$ (*21*)	*Fdd*2	24.59	22.42	7.56
		(23.28	23.28	7.40)

		a	b	c	β
	Compounds of Type I				
$[Ni(H_2O)_6][Cd_4Cl_{10}(H_2O)_2] \cdot 2H_2O$ (*22*)	*P*2$_1$/*c*	6.63	12.01	16.08	108.7
		(6.42	11.56	17.43	100.8)

The stacking arrangement of the layers is less easy to predict. A close-packed stacking gives each cation five anion and seven cation neighbors but, because the ions are not all identical, the threefold crystallographic axis is lost. The highest possible symmetry is monoclinic and the cell dimensions and space group will depend on the stacking sequence. In any case the crystal will not be able to incorporate the high symmetry of the ions.

A stacking in which the ions lie directly one above the other preserves the threefold axis and can, depending on the stacking, give each cation four anion and four cation neighbors. The simplest stacking (all layers identical) is unlikely as it would result in each cation having only three anion neighbors. An alternating stacking of two layers results in half the cations having three and a half five anion neighbors. Such a structure is trigonal (*P*31*c*) with the unique *c* axis given by

$$c = 2(R_a + R_c) \tag{5}$$

This structure contains columns of ions stacked along the *c* axis, with one-third of the columns consisting only of cations, and two-thirds having alternating cations and anions leading to the correct 2 : 1 stoichiometry.

In a three-layer sequence, the $R\bar{3}$ structure has all the columns identical (two cations followed by one anion) and all the cations have four anion neighbors. The expected length of the *c* axis (hexagonal setting) is

$$c = 2(2R_c + R_a). \tag{6}$$

In all the three high-symmetry structures (*F*23, *P*31*c*, and $R\bar{3}$) the anions have eight cation neighbors and the cations (on average) four anion neighbors, but the antifluorite structure has a molecular volume 18% larger than the trigonal ones, which in turn have a molecular volume 23% larger than the fully close-packed monoclinic structure.

There are five compounds of Type A known (see Table II) and none have the antifluorite or monoclinic structures. Two have the rhombohedral structure and three the trigonal (two with the symmetry lowered to $P3$). The standard deviation between the predicted and observed lattice parameters is 0.3 Å.

Because the layers are not close packed, trigonal prismatic cavities are formed between the layers that can be large enough to enclose an interstitial water molecule. The nominal diameter of these cavities is about the size of the mean radius of the ions, which ranges from 2.80 to 2.90 Å. Interstitial water is found in $[Ni(H_2O)_6]_2[CdBr_6][H_2O]_{0.67}$ near this cavity but shifts toward a point between the two cations (*8*). Although this compound is not strictly of Type A it is listed in Table II for comparison.

*3b. Structure A**

This structure has the same formula as the A structure and is obtained from it by polymerizing the cations with the anions, other cations, or both, in order to increase the coordination number around *Me*, in this case Ca. The threefold symmetry axis of the ions is lost and the resulting crystal structure has only monoclinic symmetry. The details of the crystal structure and space group depend on the nature of the polymerization but the lattice parameters are related to those predicted for the A structures. Three crystal structures of A* compounds are known and these are compared with the crystal structure of A in Fig. 2. The monoclinic cell dimensions are given by

$$a = a_{\mathrm{h}} \cos 30° \quad \text{or} \quad 2a_{\mathrm{h}} \cos 30°$$
$$b = a_{\mathrm{h}}$$

with c given by Eq. (5). The standard deviation between the calculated and observed lattice parameters (Table II) is 0.5 Å.

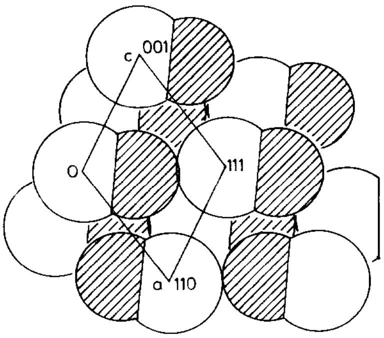

FIG. 4. The B* structure of $[Ca(H_2O)_6][MnBr_4(H_2O)_2]$. The cation is fused to the anion by Ca coordinating to a Br and an H_2O of the anion. The projection is down the monoclinic b axis and corresponds to a view of the $(1\bar{1}0)$ plane of the parent CsCl cell whose directions are indicated by the Miller indices. The Mn atoms shown at the cell corners are fixed but the cations are disordered, being attached randomly to the left and right side of the anion.

3c. Structures B and B—* $[Me(H_2O)_6][Me'X_4(H_2O)_2]$

As these compounds have equal numbers of cations and anions the *CsCl* structure is expected but the crystal symmetry will be less than cubic because of the low symmetry of the anion. Monoclinic or orthorhombic crystals are most likely with a pseudo-cubic cell dimension given by Eq. (2). Three B compounds are known (see Table I of (*1*)) but the crystal structure of none has been reported. The structure of $[Ca(H_2O)_6][MnBr_4(H_2O)_2]$, which is known, has the expected B* structure with the Ca atom of the cation bonded directly to both a Br and an O atom of the anion. It is monoclinic with the severely distorted *CsCl* structure shown in Fig. 4. The a and b axes correspond to the cubic 110 and $1\bar{1}0$ directions and c to the cubic 001.

3d. Structure C— $[Me(H_2O)_6][Me'X_3(H_2O)_3]_2$

The compounds with the C structure have a cation : anion ratio of 1 : 2. The possible

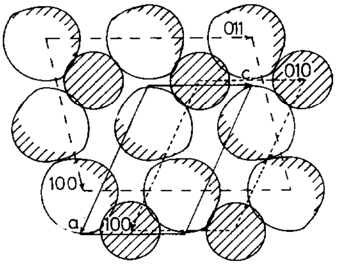

FIG. 5. Structure C, $[Mg(H_2O)_6][MnBr_3(H_2O)_3]_2$. The actual cell (solid line) is $C2/m$. The $0\bar{1}1$ projection of the pseudo-fluorite cell is shown with the broken line, and the basal plane of the pseudohexagonal cell is shown with a dotted line. The side of the anion containing the water is shaded.

crystal structures are, by analogy with the A structures, fluorite and structures based on close-packed layers, with lattice parameters calculated by Eqs. (3), (4). In this case, because of the lower symmetry of the anion, only low-symmetry structures (monoclinic) are expected. The anion acts as both a donor and an acceptor of hydrogen bonds and bonding occurs between anions as well as between anions and cations. The only crystal structure of this type that is known, $[Mg(H_2O)_6][MnBr_3(H_2O)_3]_2$ shown in Fig. 5, has a fluorite structure with $a = d_{1\overline{22}}$, $b = d_{(0\bar{1}1)}/2$, and $c = d_{(011)}/2$ distorted toward a two-layer hexagonal structure with $a = d_{100}$, $b = d_{001}$, and $c = d_{010}$. The standard deviation between the observed lattice parameters (Table II) and the average of the two cells calculated with $R_a = (3.29 + 2.75)/2$ Å is 0.7 Å.

3e. Structure D—$[Me(H_2O)_6][Me'X_4]$

Like compounds with structure B, those with structure D have a cation : anion ratio of 1 : 1 but with tetrahedral rather than octahedral anions. A *CsCl* symmetry is expected (cell dimensions given by Eq. (2)) but with lowered symmetry, because it it not possible in a cubic space group to form ordered hydrogen bonds from the 12 hydrogen atoms of the cation to the 8 neighboring anions. The asymmetry of the hydrogen bonding causes the ions to twist away from the cubic symmetry directions. The structure of $[Mn(H_2O)_6][ZnBr_4]$, is orthorhombic (*Pbam*) with a unit cell consisting of four *CsCl* cells related by glide planes so that ions in adjacent cells are rotated in opposite directions. $[Mg(H_2O)_6][ZnCl_4]$ is triclinic with a double *CsCl* cell. The standard deviation between the calculated and observed lattice parameters of both crystals is 0.9 Å.

$[Mg(H_2O)_6][ZnBr_4] \cdot H_2O$ has a structure similar to D but it includes two interstitial water molecules, shared by two formula units, in one of the octahedral cavities of the structure. Its unit cell and structure are similar to that of $[Mn(H_2O)_6][ZnBr_4]$ as shown in Table II but it has a lower symmetry ($P2_1/n$).

4. Structures with Polyanions based on Octahedra

When one of the metal ions, Me'^{2+}, is particularly soft, e.g., Zn^{2+} or Cd^{2+}, the anions will tend to polymerize into chains. One unit cell dimension will necessarily correspond to the anion chain repeat, or a multiple of the repeat. Five types of chain identified in (*1*) are illustrated in (*1*, Fig. 3) and four of these are based on condensed octahedra: (a) the straight single chain, (b) the staggered single chain, (c) the straight double chain, and (d) the staggered double chain. For both sets of straight chains the anion repeat is given by Eq. (7) as shown in (*1*, Fig. 3a and 3c).

$$d_1 = 2L_a \cos 45° = \sqrt{2}\,L_a = 1.414\,L_a. \quad (7)$$

The corresponding quantity for the staggered chains shown in (*1*, Fig. 3b and 3d) is

$$d_2 = 2L_a \cos 45° \times 2 \cos 30° = 2.449\,L_a. \quad (8)$$

TABLE III

REPEAT DISTANCES (d) AND LONG RADII OF POLYANIONS (R_l) IN Å

	Chloride		Bromide	
	d	R_l	d	R_l
Cd straight single chain (d_1, R_a)	3.70	3.17	4.03	3.40
Cd staggered single chain (d_2, R_{l_1})	6.42	4.10	6.98	4.41
Cd straight double chain (d_1, $R_{l_{21}}$)	3.70	4.77	4.07	5.14
Cd staggered double chain (d_2, $R_{l_{22}}$)	6.42	5.95	6.98	6.42
Zn tetrahedral chain (d_3, R_a)	3.72	2.83	4.08	3.05
Zn dimer (R_l)		4.15		4.50

Note. In each case the polyanion will also have a short radius equal to the radius of the discrete anion (Table I). See (*1*, Fig. 3) for the definition of d_1, d_2, and d_3.

Of the metal ions studied only Cd^{2+} is expected to form octahedral polyanions. Values of d_1 and d_2 for the Cd halides are given in Table III.

The cations will form columns between the chains and, since the distance between cation centers along the columns must be greater than $2R_c$ (= 5.2 Å for $Ni(H_2O)_6$), straight chains will only occur if the d_1 lattice spacing (3.70 Å for Cd–Cl) is doubled to $2d_1$ (7.42 Å) in order to be greater than $2R_c$. The d_2 spacing (6.42 Å) is already larger than $2R_c$. In either case a single anion chain will contain two metal atoms within the crystallographic repeat distance giving it the formula $Me'_2X_8^{4-}$. By the same argument the double chains will contain four metal atoms in the crystallographic repeat giving the polyanion the formula $Me'_4X_{12}^{4-}$. In both cases, because the polyanion has a charge of -4, the cation : polyanion ratio will be 2 : 1 and the $Me : Me'$ ratio will be 1 : 1 and 1 : 2, respectively. This difference between the cation : polyanion ratio and the $Me : Me'$ ratio leads to new possible structures that cannot be predicted from chemical considerations alone. For example, with a cation : polyanion ratio of 1 : 2 (consistent with (*1*, Assumption 2)) $Me : Me'$ ratios of 1 : 4 and 1 : 8 might, in principle, be found. However, surprisingly few of the additionally predicted compounds are consistent with the other assumptions. A single-chain anion composed of corner-shared octahedra, $Me'_2X_{10}^{6-}$, is consistent but is not expected as Cd halides normally only form edge-shared polymers.

Further possibilities occur if the X atoms in the above chains are replaced by H_2O. Because the polyanions carry a charge of -4, up to three X atoms could be replaced without the charge on the polyanion being reduced to zero. Replacing one halogen leads to a polyanion with a charge of -3 and a cation : polyanion ratio of 3 : 2 which violates Assumption 2 of (*1*). Replacing two halogens leads to the single- and double-chain polyanions $Me'_2X_6(H_2O)_2^{2-}$ and $Me_4X_{10}(H_2O)_2^{2-}$, both of which give a cation : polyanion ratio of 1 : 1 and compounds with an $Me : Me'$ ratio of 1 : 2 and 1 : 4, respectively. These are the only two hydrated polyanion structures that have been observed. They were not predicted in the earlier paper (*1*) but were assigned as Types H and I respectively on the grounds that several examples of each were known. Replacing three halogens yields singly charged anions and therefore compounds with a cation : polyanion ratio of 1 : 2. Although the ratio is satisfactory the anions themselves lack any symmetry and could only form crystals with triclinic symmetry. For this reason we do not think these structures are likely to form.

In most of the polyanion compounds, d_2, and particularly $2d_1$, is appreciably larger than $2R_c$. The result is the formation of an intercation cavity whose diameter varies from 1.20 Å for staggered Cd–Cl chains to 2.84 Å for straight Cd–Br chains, large enough to hold interstitial water molecules (see, for example, Figs. 9 and 10). How many water molecules will be included in the cavity will depend on the exact packing arrangements: the longer straight chains and larger Br atoms should favor interstitial water, but structures with double cation columns, where the cations in one column are opposite the cavities of the adjacent column, will tend to suppress them.

The straight single chain has a circular cross section but the other three chains have elongated cross sections with the larger radius given by Eqs. (9) (staggered single chain), (10) (straight double chain), or (11) (staggered double chain),

$$R_{l_1} = R_a + L_a/(2\sqrt{2}) = R_a + 0.354L_a \quad (9)$$

$$R_{l_{21}} = R_a + \sqrt{3}L_a/(2\sqrt{2}) = R_a + 0.612L_a \quad (10)$$

$$R_{l_{22}} = R_a + 3L_a/(2\sqrt{2}) = R_a + 1.061L_a, \quad (11)$$

the second term in each equation being the distance between the two columns of *Me'* atoms within the polyanion. Radii for the Cd halides are given in Table III. The symmetries of the chains are shown in (*1*, Fig. 3).

The polyanion chains and the cation columns in compounds with a cation : polyanion ratio of 1 : 1 pack in the square illustrated in Fig. 3a with a unit cell edge given by

$$a = \sqrt{2}(R_c + R_a) = 1.414(R_c + R_a). \quad (12)$$

In these structures each polyanion chain is surrounded by a square of cation columns. In the 2 : 1 and 1 : 2 cases the packing will be based on hexagonal close packing, which contains three chains or columns in the unit cell (Fig. 3b). The hexagonal cell dimension perpendicular to the chains is given by Eq. (4).

In order to provide uniform bonding along the anion chain one-half of the cation columns will be displaced along the chain direction by d_1 (or $d_2/2$) relative to the other half. This is easily accomplished in the hexagonal cell that contains two independent cation columns but in the square cells, where there is only one cation column, the cell must be doubled in size by rotation of the axes by 45° (compare Figs. 3a and 6). The unit cell dimensions are

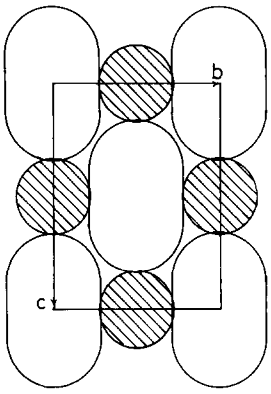

FIG. 6. Projection of the structures of Type H, $[Ni(H_2O)_6][Cd_2Cl_6(H_2O)_2] \cdot 4H_2O$, and Type I, $[Ni(H_2O)_6][Cd_4Cl_{10}(H_2O)_2] \cdot 2H_2O$, derived from Fig. 3a by an elongation of the anion and a rotation of the axes by 45°. The axes labels are for structures I; for H the *b* and *c* axes should be replaced by *a* and *b*, respectively.

$$a = 2(R_c + R_a) \quad (13)$$

$$b = 2(R_c + R_l), \quad (14)$$

where R_l is the larger radius of the chain cross section.

4a. *Structure E*—$[Me(H_2O)_6]_2[Me'_2X_8]$

Compounds with the structure E contain one of the single polyanion chains shown in (*1*, Figs. 3a–3b). In both cases there are two columns of cations for each anion chain giving rise to the hexagonal arrangement shown in Fig. 7 (*a* and *b* axes reversed).

The straight chains have *mmm* symmetry but only one mirror plane can be used crystallographically, leading, for a hypothetical $[Mg(H_2O)_6]_2[Cd_2Cl_8]$ salt, to a cell in space group *C*2/*m* with $a = 2(2R_c + R_a) = 16.94$ Å, $b = 10.08$ Å (Eq. (4)), $c = 2d_1 = 7.40$ Å, and $\beta = 90°$. Less likely would be a structure in *P*2/*m* with $a = c = 10.08$ Å, $b = 7.40$ Å, and $\beta = 120°$. With staggered chains the crystals would be monoclinic,

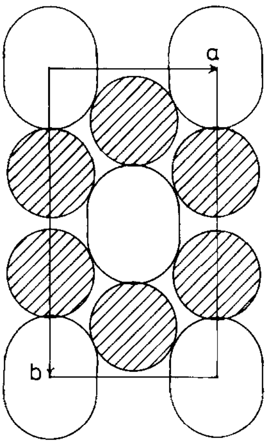

FIG. 7. Packing expected in the Types E and F structures. The axes correspond to the $C2/c$ structures.

$C2/c$ with a = 10.08 Å (Eq. (4)), $b = 2(2R_c + R_{l_1})$ = 18.80 Å, $c = d_2$ = 6.42 Å, and β = 90°. No compounds with structure E are known.

4b. Structure F—$[Me(H_2O)_6]_2[Me'_4X_{12}]$

Compounds with structure F have an $Me : Me'$ ratio of 1 : 2 and double chains of the kind illustrated in (*1*, Figs. 3c and 3d) giving a cation : polyanion ratio of 2 : 1 since there are 4 Me' atoms in one repeat unit of the polyanion chain. The crystal structures will be based on hexagonal packing (Fig. 7) with the symmetry of the staggered chain structure being $C2/c$ (similar to the E staggered chain structure). The cell dimensions for $[Co(H_2O)_6]_2[Cd_4Cl_{12}]$, calculated in the same way as the $C2/c$ E structure, are given in Table II. The alternative straight chain structure could be in either space group $I2/m$ or $P2/m$. The body-centered cell would be similar to the $C2/c$ cell calculated with $R_{l_{21}}$ instead of $R_{l_{22}}$ and $2d_1$ instead of d_2 but would have c as the unique axis. The $P2/m$ cell, $a = b$ = 11.26 Å, c = 7.40 Å, and γ = 120°, has its a and b axes along the 110 and $1\bar{1}0$ directions of the $I2/m$ cell. Although two F compounds are known, nothing is known about their crystal structure, although the apparent absence of interstitial water (as determined from their composition) suggests that they have the staggered chains with the shorter chain axis.

4c. Structure F*

The crystal structures of F* compounds will be similar to those of F compounds but with Me (= Ca) bonded directly to one or more terminal ligands of the anion. The only known crystal structure of this kind is $[Ca(H_2O)_6]_2[Cd_4Cl_{12}]$. It contains the straight double chain that provides a prominent terminal Cl to which the Ca can bond. It is triclinic but there is a disordered monoclinic cell (shown in Fig. 8) in $C2/m$ (equivalent to the $I2/m$ structure) with the chain axis (b) halved.

The calculated cell has $a = 2(2R_c + R_{l_{21}})/\sin(120°)$, $b = d_1$, c given by Eq. (4), and β = 120°. Although the lattice spacing along the chain is large enough to accommodate interstitial water, none is found because the cavity is occupied by the second terminal Cl atom, the one that does not bond to Ca.

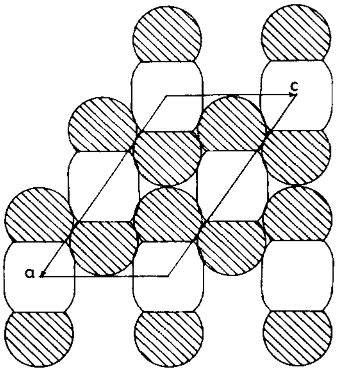

FIG. 8. Structure of Type F*, $[Ca(H_2O)_6]_2[Cd_4Cl_{12}]$. Compare with the proposed Type F structure given in Fig. 7. The two chains in the unit cell are displaced by $b/2$ relative to each other.

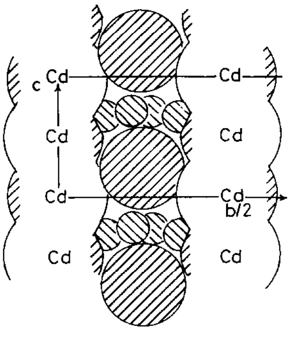

FIG. 9. The straight single-chain structure of H. The interstitial water molecules are shaded in the opposite direction to the shading used on the cation and on the water of the anion.

4d. Structure H—$[Me(H_2O)_6][Me'_2X_6(H_2O)_2]$

This structure contains one column of cations for each polyanion chain and a rectangular arrangement is expected as shown in Fig. 6. The cell dimensions are given by

$$a = 2(R_c + R_a) \qquad (15)$$

$$b = 2(R_c + R_a) \quad \text{or} \quad 2(R_c + R_{l_1}) \qquad (16)$$

$$c = 2d_1 \quad \text{or} \quad d_2, \qquad (17)$$

the second values being used if the chains are staggered. Five compounds of this type are known and the crystal structures of two have been determined. They contain straight single chains and have the a and b axes doubled in the space group $Fdd2$. With the straight chains there is a large cavity (2.12 Å) between the cations and this contains four interstitial water molecules (Fig. 9).The standard deviation between the predicted and observed lattice parameters shown in Table II is 0.9 Å.

4e. Structure I—$[Me(H_2O)_6][Me'_4X_{10}(H_2O)_2]$

This double-chain structure also has a cation : polyanion ratio of 1 : 1 and will adopt the rectangular structure perpendicular to the polymer chain axis shown in Fig. 6 with a and b given by Eq. (17) and (15), respectively, and c by

$$c = 2(R_c + R_{l_{21}})/\sin(\beta) \quad \text{or} \quad 2(R_c + R_{l_{22}})/\sin(\beta). \qquad (18)$$

Several I compounds are known but the crystal structure of only one has been determined. It has a staggered chain and the standard deviation between its observed and calculated lattice parameters, given in Table II, is 0.7 Å. Figure 10 shows the projection down the monoclinic axis, b. In order to provide a suitable cavity for the cation, adjacent polymer chains must be translated by $a/2$ giving rise to the predicted monoclinic angle, $\beta = 110.8°$. Although the cavity between the cations is relatively small (1.20 Å) two interstitial water molecules are found as shown in Fig. 10.

5. Structures with Polyanions based on Tetrahedra

The structural chemistry of polyanions composed of tetrahedra is much less extensive than that based on octahedra because the polyanions composed of tetrahedra contain fewer halogen atoms per metal. Zn is the only element of those considered here that is expected to form these compounds.

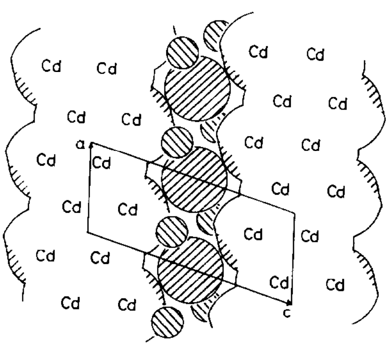

FIG. 10. The staggered double-chain structure of I using the same conventions as those in Fig. 10.

The only chain that can be formed is the corner-sharing chain with the composition $Me'_2X_6^{2-}$ shown in (*1*, Fig. 3f). The chain repeat, d_3, given by Eq. (19), is 3.72 Å for Zn–Cl (Table III).

$$d_3 = 2L_a \sin(54.7°) = 1.63L_a. \quad (19)$$

The crystallographic repeat along this direction will therefore be twice this value ($2d_3 = 7.44$ Å). Replacement of one of the halogens by H_2O would give the polyanion $Me'_2X_5(H_2O)^-$ whose low internal symmetry would restrict any compounds it forms to a triclinic space group. For this reason, and because the complex would have bonds around Zn of unequal strength (see (*1*, Assumption 5)), hydrated tetrahedral polyanions are not expected.

5a. Structure G—[Me(H₂O)₆][Me′₂X₆]

Compounds with the G structure have tetrahedral anions and two crystal structures could occur, one with chains composed of corner-sharing tetrahedra (*1*, Fig. 3f), the other with dimers (*1*, Fig. 3e).

The chains will have a repeat given by Eq. (19) and the cation : polyanion ratio will be 1 : 1. The structure is based on a square lattice perpendicular to the chains with *a* and *b* given by Eq. (13) and $c = 2d_3$. For $[Mg(H_2O)_6][Zn_2Br_6]$ the cell dimensions would be $a = 11.40$ Å, $b = 11.40$ Å, $c = 8.16$ Å. Because of the large *c* axis the structure would probably contain several molecules of interstitial water (compare with Fig. 9). Although the cell is compatible with the *mm*2 symmetry of the chain, the hydrogen bond requirements would likely reduce this symmetry. Such a crystal structure is not known.

The alternative crystal structure is one which contains a discrete dimeric anion, the radius of whose long axis is

$$R_l = R_a + L_a \cos(54.7°) = R_a + 0.578L_a. \quad (20)$$

The structure is composed of equal numbers of spherical cations and elliptical anions. The dimeric anion has an average radius larger than that of the corresponding monomeric anion, giving, for $[Mg(H_2O)_6][Zn_2Br_6]$, a radius ratio to 0.75, close to the value (0.732) that divides the CsCl from the NaCl arrangements. In this range the NaCl structure can be stabilized by its ability to form ordered hydrogen bonds without lowering its symmetry (c.f. the CsCl structure D in which this is not possible). A structure that preserves the full symmetry of the anion can be constructed in space group *Immm* by orienting the long axis of the anion along the NaCl [011] direction and rotating the cell 45° around *a*. For this cell, $a = 2(R_c + R_a)$ lies along the NaCl *a* axis, $b = 2(R_c + R_a)\cos\theta + 2L_a \cos(54.7°)$, and $c = 2(R_c + R_a)\sin\theta$, where θ is the angle between the Mg–Zn vector and the *b* axis. Assuming $a = b$, the standard deviation between the predicted and observed lattice parameters (Table II) is 0.9 Å.

6. Conclusions

The first paper in this series (*1*) identified seven chemical structures that were expected for the double salts featured in this study. By taking into account crystal packing requirements we predict two further structures containing hydrated polyanions. Compounds of eight of these nine chemical structure types are known and in most cases at least one crystal structure of each type has been determined. By treating the ions as spheres, cylinders, or ellipsoids whose dimensions are easily predicted, we show that the known unit cell dimensions can be reproduced within an average standard deviation of 0.7 Å from a knowledge of the repeat distance along the chains of polyanions and a consideration of possible ionic packing. We also predict the crystal structures of those compounds whose structure is not yet known and we have shown why some of these salts contain interstitial water molecules.

Acknowledgments

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