JOURNAL OF SOLID STATE CHEMISTRY 95, 39–50 (1991)

Divalent Metal Halide Double Salts in Equilibrium with Their Aqueous Solutions

I. Factors Determining Their Composition

RUMEN DUHLEV* AND I. DAVID BROWN

Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1

AND CHRISTO BALAREW

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria

Received October 9, 1990

Using a few simple assumptions based on the hard and soft acid and base model and the bond-valence model, we explain why the five most common double salt compositions $xMeX_2 \cdot yMe'X_2 \cdot z\mathrm{H_2O}$ (Me, Me' = Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd; X = Cl, Br) found in equilibrium with the corresponding saturated solutions at room temperature will have $x:y:z$ equal to 2 : 1 : 12, 1 : 1 : 8, 1 : 1 : 6, 1 : 2 : 6, and 1 : 4 : 10 and predict that these will belong to nine structural types. About 90% of the double salts observed under these conditions have one of these compositions and the remainder have closely related structures. We also make predictions about the chemical species expected in saturated solutions. © 1991 Academic Press, Inc.

1. Introduction

More than 40 double salts of the type $xMeX_2 \cdot yMe'X_2 \cdot z\mathrm{H_2O}$ [$= Me_xMe'_yX_{2(x+y)} \cdot z\mathrm{H_2O}$] have been reported to exist in equilibrium with the saturated solution in ternary MeX_2–$Me'X_2$–$\mathrm{H_2O}$ systems, where Me and Me' = Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd; and X = Cl or Br (*1–7*). Although double salts are not formed in all systems, they are found in all systems in which at least one of the metal ions has zero ligand field stabilization energy (*1, 6*). The double salts found in equilibrium saturated solution show a variety of compositions ($x:y:z$) namely: 2 : 1 : 12 [16],[1] 1 : 1 : 8 [7], 1 : 2 : 6 [6], 1 : 1 : 6 [5], 1 : 4 : 10 [4], 1 : 1 : 5 [2], 2 : 1 : 12.67 [1], 1 : 1 : 7 [1], and 1 : 1 : 4 [1], the numbers in brackets being the number of known occurrences.[2]

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* On leave from the Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria. Present address: Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, England.

[1] If, following the conventions used later in this paper, x refers to the harder, and y to the softer cation, group 2 : 1 : 12 divides (*7, 8*) into two groups: 2 : 1 : 12[9] and 1 : 2 : 12[7].

[2] Not considered in this paper is a series of Ca–Cd double-salt phases that do not occur in the equilibrium phase diagram, viz: $2\mathrm{CaCl_2} \cdot 3\mathrm{CdCl_2} \cdot 18\mathrm{H_2O}$ (*9*), $\mathrm{CaCl_2} \cdot 3\mathrm{CdCl_2} \cdot 8.5\mathrm{H_2O}$ (*10*), $\mathrm{CaCl_2} \cdot 5\mathrm{CdCl_2} \cdot 11.5\mathrm{H_2O}$ (*11*), and $\mathrm{CaBr_2} \cdot 2\mathrm{CdBr_2} \cdot 7\mathrm{H_2O}$ (*12*). Further work is needed on these systems. Recent work (*13*) suggests that the latter compound may be the equilibrium phase previously described as $\mathrm{CaBr_2} \cdot 2\mathrm{CdBr_2} \cdot 6\mathrm{H_2O}$. We also exclude from consideration compound of the larger alkaline earths, Sr and Ba, as their weaker Lewis acid strength leads to structures that are not directly related to those discussed here.

0022-4596/91 $3.00

The question that these results pose is: Why should these, and only these, compositions be found? Part of the answer is given in this paper, which examines the chemical factors involved, and part in the following paper, which examines the crystallographic factors.

In this paper we select candidate structures on the basis of six chemical assumptions drawn from, *inter alia,* Pearson's (*14*) hard and soft acid and base concept and the bond-valence model (*15*). According to Pearson (*14*), Lewis acids (cations) and Lewis bases (anions) can be divided into two classes, soft (polarizable) and hard (nonpolarizable). The essence of Pearson's concept is that hard acids show a preference for bonding to hard bases and soft acids to soft bases. Balarew and Duhlev (*16*), using Klopman's (*17*) scale of hardness, have shown that the most favored arrangement in these double salts is the one that maximizes the sum of $H_a \times H_b$, where H_a is the hardness of the cation and H_b is the hardness of its ligand.[3] Thus the hard cations Mg^{2+} and Ca^{2+} usually bond to the hard ligand H_2O and the soft cations Zn^{2+} and Cd^{2+} usually bond to the softer ligands Cl^- or Br^-. Cations with intermediate hardness such as Mn^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, and Cu^{2+} may bond to either H_2O or halogen depending on the hardness of the second cation and the relative proportions of H_2O and halogen. In any case the harder cation bonds to the H_2O and the softer cation to the halogens. Using Pearson's hard and soft acid and base concept (*14*) and Pauling's rules (*19*), Balarew and Duhlev (*16*) explained the observed structural motifs in known double-salt structures and predicted them for a number of compounds whose structures had not yet been studied.

In the bond-valence model (*15*), the atomic valence (or formal charge) of an ion is assumed to be distributed between the bonds it forms. Each bond is thus assigned a valence which is found experimentally to correlate inversely with the bond length. Two rules govern the distribution of the valences between the bonds (*20*). The valence sum rule states that the sum of bond valences around each atom is equal to the atomic valence, and the equal-valence rule states that, subject to the valence sum rule being satisfied, the valences of the bonds formed by any given atom will be, as nearly as possible, equal to each other. The second rule is not universally obeyed but it is expected to be obeyed by all the atoms in the present structures except hydrogen (the hydrogen bond is expected to be asymmetric, see below) and copper (where a Jahn–Teller distortion is expected).

The valence sum and equal-valence rules suggest that a good estimate of the valence of any bond can be obtained by dividing the atomic valence of an ion by its coordination number. Thus a 4-coordinate divalent cation would form bonds of $\frac{2}{4} = 0.5$ valence units (v.u.), a 6-coordinate divalent cation would form bonds of $\frac{2}{6} = 0.33$ v.u., and an 8-coordinated divalent cation would form bonds of $\frac{2}{8} = 0.25$ v.u. Since the coordination numbers displayed by a given cation usually lie in a rather narrow range, the estimated bond valences will lie in a correspondingly narrow range, giving a value that scales as the Lewis acid strength of the cation (*21*). A similar treatment of anions leads to a corresponding scale of Lewis base strengths.

Since the Lewis acid strength of a cation and the Lewis base strength of an anion are both estimates of the valence of the bond between them, a bond will only form if these two strengths are approximately equal. This rule (known as the valence matching principle) is used to determine which complex anions and cations will form stable compounds.

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[3] The hardness values of the Lewis acids and bases use in this paper are Mg^{2+} (2.53), Ca^{2+} (2.33), Mn^{2+} (0.69), Fe^{2+} (0.64), Co^{2+} (0.44), Ni^{2+} (0.29), Cu^{2+} (−0.55), Zn^{2+} (−1.02), Cd^{2+} (−2.04), H_2O (1.73), Cl^- (0.94), and Br^- (0.22) (*18*).

As mentioned above, hydrogen needs special treatment. Steric effects force it to bond asymmetrically, the constraint being best relieved when the valence is distributed between the two H–O (or H–X) bonds in the ratio 0.83 : 0.17 (*22*). Thus $Me(H_2O)_6^{2+}$ cations, whose Lewis acid strength is $\frac{2}{12} = 0.167$ v.u., will be particularly favored as they will be able to form hydrogen bonds of optimum strength.

In the second section of this paper we list the six assumptions that we use to predict (in Section 3) the double-salt compositions we expect to find in equilibrium with the saturated solution at room temperature. Although some of these assumptions may seem self-evident or trivial, they are all logically necessary to exclude certain otherwise possible structures. In Section 4 we compare the predictions of the model with observation and in Section 5 we discuss the implications of the model for saturated solution structure. The second paper of the series (*23*) shows that it is possible to account not only for the chemical structures, but also for the crystal structures[4] of most double-salt phases, as well as to explain some of the anomalies in the chemical composition.

2. Assumptions Used in the Model

In predicting the chemical compositions and structures of the double salts that exist in equilibrium with a saturated solution we make the following assumptions:

Assumption 1. Solids crystallizing from saturated solutions will contain anions and cations (or possible neutral complexes) in proportions that lead to electroneutrality. The ions may be simple (e.g., Br^-) or complex (e.g., $Mg(H_2O)_6^{2+}$). Solids formed from anions and cations will be held together by electrostatic (or hydrogen) bonding or will condense. Solids formed from neutral complexes must be held together by condensation (e.g., sharing halogen atoms) or by hydrogen bonding. In the latter case the complex must contain coordinated water.

Assumption 2. The solids formed will usually have only one kind of anion and one kind of cation in simple proportions, or a single neutral species. This assumption corresponds to Pauling's principle of parsimony (*19*). If the neutral species contains only one metal atom it cannot form a double salt. Therefore double salts are expected to contain one kind of cation and one kind of anion in simple proportions (e.g., 1 : 1 and 2 : 1).

Assumption 3. Since there is a competition between H_2O and X^- ligands for bonding to the two metal cations, *the harder metal cation (Me^{2+}) will be mainly coordinated by the harder water molecules, and the softer metal cation (Me'^{2+}) mainly by the softer halide ions* (*16*). The harder metal ion will therefore form a complex ($Me(H_2O)_n^{2+}$, or possibly $Me(H_2O)_{n-1}X^+$), which will be a cation. The softer metal ion will form an anion complex with the halide ions and this complex may or may not also contain water ligands to complete the coordination sphere ($Me'X_{n-m}(H_2O)_m^{-n+m+2}$). If this complex is to be an anion, $n - m$ must be greater than 2 and less than or equal to the expected coordination number (n) for the metal (usually 6 but for some metals 4; see Fig. 2). If the cation is hydrated, any interaction between the complex anion and the complex cation will be through O–H . . . X (or possibly O–H . . . O) hydrogen bonds. Two possibilities occur if the number of halogen atoms available is less than the coordination number. For Me'^{2+} ions of intermediate hardness (e.g., Mn^{2+}, Co^{2+}) water may appear in the coordination sphere as shown in Fig. 2. With softer metal ions (e.g., Zn^{2+}, Cd^{2+}) the water will be eliminated and

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[4] We distinguish between the chemical structure and the crystal structure, the former being a description in terms of the complex ions that are present, the latter a description of the way in which these complex ions are arranged in space.

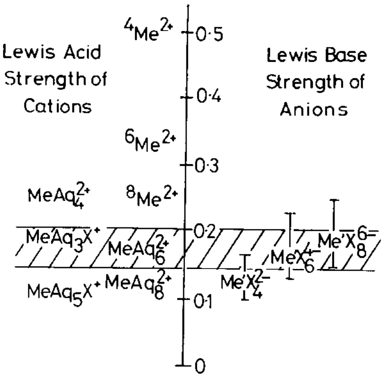

FIG. 1. Lewis acid strengths (left-hand side) and Lewis base strengths (right-hand side) of ions that could occur in double-salt structures. The shaded band represents the normal range of hydrogen bond strengths.

the complexes will condense into polymeric anions as shown in Fig. 3.

Assumption 4. In order to cocrystallize, *the complex cation and the complex anion must have similar acid and base strengths* (*15*). The acid strengths of metal cations, Me^{2+}, and their hydrated $Me(H_2O)_n^{2+}$ complexes and the base strengths of the anionic complexes $Me'X_n^{-n+2}$ are shown in Fig. 1.

These values represent the strengths (valences) of typical bonds formed by the ions and are calculated by dividing the oxidation state of the ion by the number of bonds it is expected to form. The units of acid and base strength in this model are valence units. Since the bonds formed by the cations will terminate on the anion, stable compounds will only form if the acid strength of the cation is close to the base strength of the anion (valence matching principle (*15*)).

The right-hand side of Fig. 1 shows the anion base strengths and, since a range of anion coordination numbers is possible, a corresponding range of base strengths is expected. The most likely value is assumed to be the one corresponding to each halogen atom forming five bonds, one to *Me*′ and four external bonds, but halogen coordination numbers of 4 and 6 are also possible.

The left-hand side of Fig. 1 shows the Lewis acid strengths of the cations and it is clear that, apart from 8-coordinated *Me* atoms, only hydrated cations have an acid strength suitable for bonding to the anions. There is a further restriction. Since the cation–anion bonds will be hydrogen bonds, only bonds that have the strength normally found for hydrogen bonds are expected (*22*). These are shown by the shaded band in Fig. 1. With these restrictions, the only cations that are expected to occur in double salts are $[Me(H_2O)_3X]^+$ and $[Me(H_2O)_6]^{2+}$.

All three of the anions shown are capable of receiving normal hydrogen bonds, but none of the metal atoms studied is expected to be 8-coordinate with Cl or Br. This leaves $[Me'X_4]^{2-}$ and $[Me'X_6]^{4-}$ as the only two possible anions.

Calculating the base strength of an anion with mixed halogen and H_2O ligands is more complex since the hydrogen atoms of the H_2O act as Lewis acids. Let the formula of the anion be $[Me'X_{n-m}(H_2O)_m]^{-n+m+2}$, where n is the coordination number of Me' and m is the number of X substituted by H_2O. Since the total valence of the external bonds formed by the X atoms equals the residual negative charge on the complex anion, and the total valence of the external bonds formed by the H atoms equals the residual positive charge, charge neutrality requires that

$$V(Me') + (n - m)V(X) = pS(X) + qS(\mathrm{H}),$$

where $V(Me')$ is the valence (charge) on the metal atom, $V(X)$ is the valence of each halogen ligand, $S(X)$ is the base strength (through the halogen), and $S(\mathrm{H})$ the acid strength (through H), of the complex. p is the number of base bonds formed and q the number of hydrogen bonds formed. Substituting +2 for $V(Me')$, −1 for $V(X)$, $4(n - m)$ for p, and $2m$ for q gives

$$4(n - m) \cdot S(X) + 2m \cdot S(\mathrm{H}) = 2 - (n - m).$$

Assuming that $S(H) = 0.17$, this equation gives $S(X) = -0.167$ v.u. for all values of m when $n = 6$, and $S(X) = -0.125$ and -0.112 v.u. for $m = 0$ and 1 respectively when $n = 4$. Thus the substitution of H_2O for X makes little or no difference to the base strength of the anion.

Another possibility exists that an 8-coordinated (hard) metal ion (e.g., Ca^{2+}) bonds directly to $[Me'X_6]^{4-}$ rather than through a water molecule. The base strength of the anion does not quite overlap the acid strength of the cation (0.25 v.u.), but bonds of this kind can be expected for the larger alkaline earths and, as shown below, are sometimes found for Ca.

Assumption 5. All the metal-ligand bonds within a complex will tend to have similar strengths. This is a consequence of the equal-valence rule (*20*). If a complex can only exist by being strongly distorted, it is unlikely to be found in double salts. For example, the 4-coordinated cation $[Me(H_2O)_3X]^+$ can only exist if either the water molecules form hydrogen bonds that lie outside the normal strength range (0.25 v.u.) or the bonds within the complex have very different strengths (weak Me–O of 0.33 v.u. and strong Me–X of 1.00 v.u.). Similar arguments suggest that other mixed ligand 4-coordinate complexes such as the anion $[Me'X_3(H_2O)]^-$ will also not be found.

Assumption 6. Stronger bonds will be established before the weaker bonds. In postulating structures it is first necessary to determine the strongly bonded species. Only when these structures are established can the structures produced by the weaker bonds be considered. The bonds found in these structures, in decreasing order of strength, are those in H_2O (0.83 v.u.), MeL_4 (0.50 v.u.), MeL_6 (0.33 v.u.), MeL_8 (0.25 v.u.), and hydrogen bonds (0.17 v.u.), where L may represent a halogen or water ligand. As a solid transforms to a liquid, the weaker bonds (<0.20 v.u.) will become labile but the strong bonds within isolated complexes will remain.

The bivalent metal ions under consideration are of similar size and most favor 6-coordination with both H_2O and X^-. Only Ca^{2+} shows a larger coordination number with H_2O (usually 7, 8, or 9). Zn^{2+} normally, and Co^{2+} and Cu^{2+} occasionally, are 4-coordinated by X^- in inorganic compounds (*21*).

3. Prediction of Possible Compositions and Chemical Structures

The above assumptions can be used to predict four basic chemical structures (A–D) composed of isolated complex ions. Other possible structures can be derived from these by polymerization or the addition of interstitial water.

3a. Structures Composed of Isolated Complexes

According to Assumptions 2, 3, and 4 there will be two different species (complex ions) in these structures, they will exist in the ratios 1 : 1 or 1 : 2 and they will be linked only by hydrogen bonds.

When Me^{2+} and Me'^{2+} are both 6-coordinated, the only chemical structures (and hence compositions) that satisfy Assumptions 1–6 are

A. 2 : 1 : 12 = $[Me(H_2O)_6]_2^{2+}[Me'X_6]^{4-}$ (Fig. 2a),

B. 1 : 1 : 8 = $[Me(H_2O)_6]^{2+}$ $[Me'X_4(H_2O)_2]^{2-}$ (Fig. 2c),

C. 1 : 2 : 12 = $[Me(H_2O)_6]^{2+}$ $[Me'X_3(H_2O)_3]_2^{2-}$ (Fig. 2d).

When Me^{2+} is 6-coordinated and Me'^{2+} 4-coordinated, the only possible combination is:

D. 1 : 1 : 6 = $[Me(H_2O)_6]^{2+}$ $[Me'X_4]^{2-}$ (Fig. 2e).

To the extent that the assumptions are valid and that the ionic complexes are discrete (i.e., not polymerized) the double salts formed from saturated solutions will have one of the above four compositions and all interionic bonds will be hydrogen bonds.

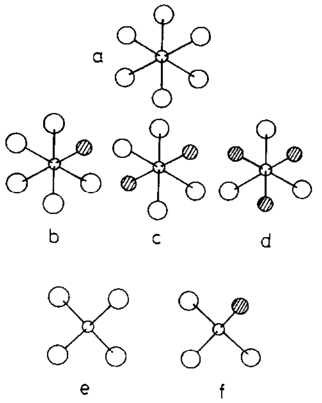

FIG. 2. Six possible types of discrete anion. Large circles are halogen, the shaded circles H_2O. Note that the predicted structures do not include *b* (eliminated by Assumption 2) or *f* (eliminated by Assumption 5).

3b. Prediction of Chemical Structures with Polymerized Anions

According to the discussion following Assumption 3, polymerization of the complex anions will occur when the softer metal ion shows a pronounced soft character (e.g., Zn^{2+} and Cd^{2+}) and requires more halogen ligands than are available from the composition to complete its coordination sphere. This leads to the prediction of the following three additional fully polymerized structures:

E. $1:1:6 = [Me(H_2O)_6]^{2+}[Me'X_4]^{2-}_{\infty}$, derived from B with the elimination of two water molecules. Me'^{2+} is 6-coordinated but four of the halogens are shared with neighboring $Me'X_6$ octahedra and the effective formula of the polyanion segment is $Me'X_4$ (see Fig.3a–3b).

F. $1:2:6 = [Me(H_2O)_6]^{2+}$ $[Me'_2X_6]^{2-}_{\infty}$, derived from C with the elimination of three water molecules. Most of the X^- around Me'^{2+} are shared (some between 3 Me' atoms) and the effective formula of the polyanion segment is $Me'X_3$ (see Fig. 3c–3d).

G. $1:2:6 = [Me(H_2O)_6]^{2+}$ $[Me'_2X_6]^{2-}$. Me'^{2+} is 4-coordinated and two of the halogens are shared (see Fig. 3e–3f).

Structures E and F are expected for the Cd salts where the polyanions are derived from the sheets of edge sharing octahedra

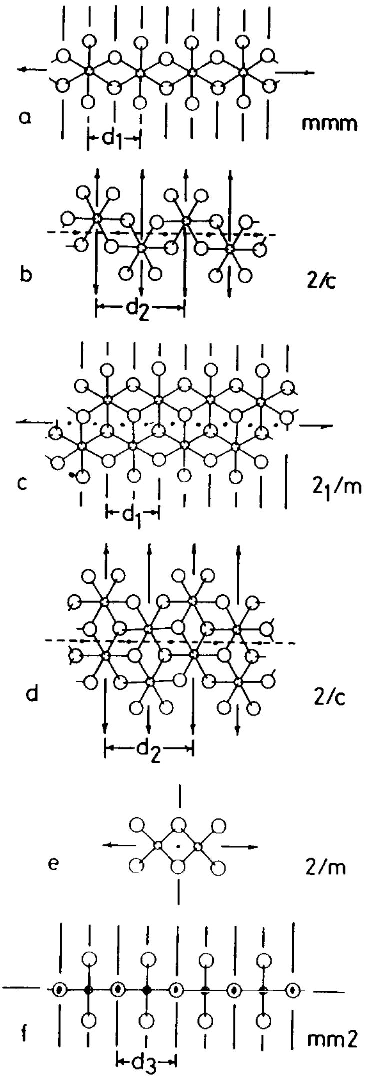

FIG. 3. Six possible types of polyanions containing only halide ligands. The conventions are the same as in Fig. 2. (a) single straight octahedral chains, (b) single staggered octahedral chains, (c) double straight octahedral chains, (d) double staggered octahedral chains, (e) edge sharing tetrahedral dimer, (f) corner sharing tetrahedral chain. Symmetry elements of the polyanion are shown as are the repeat distances along the chain polyanions. The chain shown in (a) has two further mirror planes that lie at 45° to the plane of the figure.

that form the structures of $CdCl_2$ and $CdBr_2$. Structure G would be expected for Zn salts where 4-coordination is the norm. Here either an edge sharing dimer (Fig. 3e) or a corner-sharing chain (Fig. 3f) are possible.

In addition to the structures listed above one can envisage a number of structures that involve only partial elimination of water. Only two of these are observed:

H. 1:2:8 + 4 = $[Me(H_2O)_6]^{2+}$ $[Me_2'X_6(H_2O)_2]^{2-} \cdot 4H_2O$ containing the polyanion shown in Fig. 4a and four interstitial water molecules.

I. 1:4:8 + 2 = $[Me(H_2O)_6]^{2+}$ $[Me_4X_{10}(H_2O)_2]^{2-} \cdot 2H_2O$ containing the polyanion shown in Fig. 4b and two interstitial water molecules.

Although these structures are consistent with the assumptions made in this paper, only when the spatial arrangements of the complex ions are considered does it become clear that these are the only two partially hydrated polyanions that are expected. The justification for this assignment is presented in the following paper (*23*) but, for completeness, the structures are listed here.

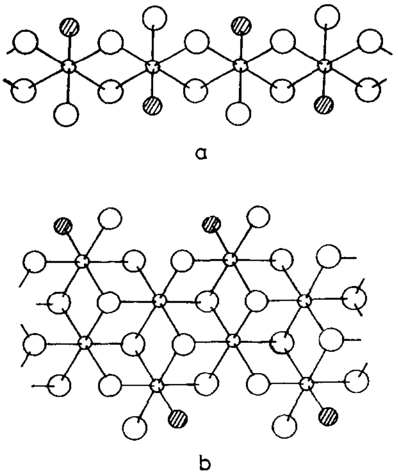

FIG. 4. Two observed types of infinite polyanions containing some water ligands found in (a) $[Mg(H_2O)_6][Cd_2Cl_6(H_2O)_2] \cdot 4H_2O$, (b) $[Ni(H_2O)_6][Cd_4Cl_{10}(H_2O)_2] \cdot 2H_2O$. The conventions are the same as those in Fig. 2.

3c. Chemical Structures with Polymerized Cations

These will occur for Me^{2+} ions that are weak Lewis acids, i.e., have coordination numbers greater than 6 (e.g., Ca^{2+}). Since an independent $Me(H_2O)_8^{2+}$ cation will form hydrogen bonds that are too weak to bond to the anions (see Fig. 1), the higher coordination number is achieved by polymerization. As long as the cation charge remains +2, the hydrogen bonds of the correct strength will only be formed if the complex has 12 hydrogen atoms (i.e., 6 water molecules) per *Me*. A coordination number greater than 6 around Ca^{2+} can be achieved with only 6 water molecules by allowing some of them to bridge between two Ca atoms or, since the Lewis acid strength of 8 coordinate Ca^{2+} is only 0.25 v.u. (Fig. 1), by allowing direct bonding between Ca and the halogen ligands of the anion. Both these mechanisms increase the coordination of Ca without changing the stoichiometry of the double salt. Such salts can therefore be classified as derivatives (indicated by an asterisk) of Types A to I above with the proviso that the cations will be involved in some form of bridging (covalent) bonding to *Me*, *Me'*, or both. An example of the way in which such bridging occurs is illustrated by the sequence of A and A* structures $[Mg(H_2O)_6]_2[CdCl_6]$, $[Ca(H_2O)_6]_2[CdBr_6]$, and $[Ca(H_2O)_6]_2[CdCl_6]$ shown in Fig. 5.

The formation of further direct bonds between Ca and *X* with the elimination of water, accounts for the occurrence of the 1:1:5 structure derived from the 1:1:6 structure D*.

3d. Interstitial Water

Strong bonding in these materials is found within the complex ions. The bonds between the complexes are mostly hydrogen bonds of strength 0.17 v.u. Interstitial water molecules which can both accept and donate two hydrogen bonds of the same strength, 0.17 v.u., are therefore easily included in

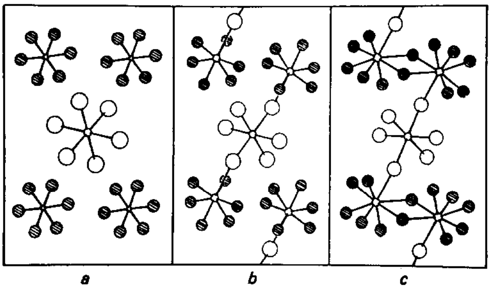

FIG. 5. Three successive stages in the polymerization of the cation (*24*) (a) $[Mg(H_2O)_6]_2[CdCl_6]$ discrete cations; (b) $[Ca(H_2O)_6]_2[CdBr_6]$ polymerization with the anion to form a molecular complex; (c) $[Ca(H_2O)_6]_2[CdCl_6]$ polymerization with the anion and other cations. The conventions are the same as those in Fig. 2.

the structures and do not play any role in the valence matching between anion and cation. They only function to fill what would otherwise be a void in the structure and their presence can only be predicted when the crystal structures are explicitly considered. In the following paper (*23*) we show why they are more likely to be found in crystals containing polymeric anions (Types E to I).

4. Comparison of the Predictions with the Double Salts Found in Particular Systems

The predicted chemical structures (A–I) all include the $Me(H_2O)_6^{2+}$ cation as well as the anions shown schematically in Figs. 2 to 4. The known examples of double chlorides and bromides that exist in equilibrium with saturated aqueous solutions are given in Table I. The structures of some of these solids are known and the remainder have been predicted (*3–7*) to be of the type shown.

Table 1 shows that when Me'^{2+} is Mn^{2+}, Fe^{2+}, Co^{2+} (ions which have borderline hard/soft behavior) anions occur with mixed water molecule and halide environment around Me'^{2+} (structures B and C, Figs. 2c and 2d). When Me'^{2+} becomes definitely soft, e.g., Cd^{2+} or Zn^{2+}, polymerized complex anions are found (structures F and G, Fig. 3c–3f, and structures H and I, Fig. 4a–4b). No examples of the E structure (Figs. 3a–3b) are known.

Double salts with Zn^{2+} are the only ones reported in which Me'^{2+} is 4-coordinated (structures D and G, Fig. 2e and 3e–3f). The simple salt $ZnBr_2 \cdot 2H_2O$ is included in Table I because it also possesses the double-salt structure G (*39*). Almost all the Ca salts show polymerized cation derivatives of the A, B, and F structures although the nature of the polymerization varies from structure to structure. The simple salt, β-$CaCl_2 \cdot 4H_2O$ also has the double-salt A* structure shown in Fig. 5c.

Finally, there are a few double-salt compositions that are observed (although rarely) in the equilibrium ternary systems studied but that do not belong to the predicted Types A–I. These have the compositions 2 : 1 : 12.67, 1 : 1 : 7, 1 : 1 : 5, and 1 : 1 : 4. The structure of $2NiBr_2 \cdot CdBr_2 \cdot 12.67H_2O$ (*44*), the only representative of 2 : 1 : 12.67, is identical to A but with an interstitial water molecule with occupancy 0.67 located in a cavity between the isolated $Ni(H_2O)_6^{2+}$ ions. Its composition should be written as 2 : 1 : 12 + 0.67. The structure of the only 1 : 1 : 7 compound, $MgBr_2 \cdot ZnBr_2 \cdot 7H_2O$ (*45*), is likewise derived from the structure D by the addition of an interstitial water molecule (1 : 1 : 6 + 1). Two 1 : 1 : 5 double salts have been reported in equilibrium systems; $MgCl_2 \cdot ZnCl_2 \cdot 5H_2O$ and $CaCl_2 \cdot ZnCl_2 \cdot 5H_2O$, but their structures are not known. A recent X-ray study of the 1 : 1 : 5 Mg salt suggests that it is probably the hexahydrate (*25*). We obtained crystals of $CaBr_2 \cdot ZnBr_2 \cdot 5H_2O$ (*46*) under nonequilibrium conditions (strong dehydration) and showed that it has a structure derived from D with the elimination of water and the inclusion of bridging Br atoms in the coordination sphere of Ca. $CaCl_2 \cdot ZnCl_2 \cdot 5H_2O$ is probably constructed in a similar way.

The structure of the only 1 : 1 : 4 com-

TABLE I

A LIST OF THE DOUBLE SALTS OF DIVALENT METAL HALIDES KNOWN TO EXIST IN EQUILIBRIUM WITH THEIR SATURATED SOLUTIONS AT ROOM TEMPERATURE

2:1:12 Structure A (Fig. 2a)		Structure A* (Fig. 5b, 5c)	
$2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$ (*26, 27*)	$R\bar{3}$	$2CaBr_2 \cdot CdBr_2 \cdot 12H_2O$ (*24*)	$C2/c$
$2MgBr_2 \cdot CaBr_2 \cdot 12H_2O$†		$2CaCl_2 \cdot CdCl_2 \cdot 12H_2O$ (*32*)	$P2_1/c$
$2MgCl_2 \cdot CdCl_2 \cdot 12H_2O$ (*28*)	$P31c$	$2CaCl_2 \cdot CaCl_2 \cdot 12H_2O$ (= β-$CaCl_2 \cdot 4H_2O$) (*33*)	$P2_1/c$
$2MgBr_2 \cdot CdBr_2 \cdot 12H_2O$ (*29*)	$R\bar{3}$		
$2MgCl_2 \cdot MnCl_2 \cdot 12H_2O$ (*30*)	$P3$		
$2NiCl_2 \cdot CdCl_2 \cdot 12H_2O$ (*31*)	$P3$		
$2CoCl_2 \cdot CdCl_2 \cdot 12H_2O$†			
1:1:8 Structure B (Fig. 2c)		Structure B*	
$MgCl_2 \cdot MnCl_2 \cdot 8H_2O$†		$CaCl_2 \cdot MnCl_2 \cdot 8H_2O$†	
$MgCl_2 \cdot FeCl_2 \cdot 8H_2O$†		$CaBr_2 \cdot MnBr_2 \cdot 8H_2O$ (*34*)	$C2/m$
$MgCl_2 \cdot CoCl_2 \cdot 8H_2O$†		$CaBr_2 \cdot ZnBr_2 \cdot 8H_2O$†	
		$CaBr_2 \cdot CdBr_2 \cdot 8H_2O$†	
1:2:12 Structure C (Fig. 2d)			
$MgCl_2 \cdot 2MnCl_2 \cdot 12H_2O$†			
$MgBr_2 \cdot 2MnBr_2 \cdot 12H_2O$ (*35*)	$C2/m$		
1:1:6 Structure D (Fig. 2e)			
$CoCl_2 \cdot ZnCl_2 \cdot 6H_2O$†			
$FeCl_2 \cdot ZnCl_2 \cdot 6H_2O$†			
$MnBr_2 \cdot ZnBr_2 \cdot 6H_2O$ (*36*)	$Pbam$		
$MgBr_2 \cdot CoBr_2 \cdot 6H_2O$†			
$MgCl_2 \cdot ZnCl_2 \cdot 6H_2O$ (*22*)	$P\bar{1}$		
1:2:6 Structure F (Fig. 3c–3d)		Structure F*	
$NiCl_2 \cdot 2CdCl_2 \cdot 6H_2O$†		$CaCl_2 \cdot 2CdCl_2 \cdot 6H_2O$ (*37*)	$P\bar{1}$
$CoCl_2 \cdot 2CdCl_2 \cdot 6H_2O$†		$CaBr_2 \cdot 2CdBr_2 \cdot 6H_2O$† (See footnote 2)	
1:2:6 Structure G (Fig. 2e)			
$MgBr_2 \cdot 2ZnBr_2 \cdot 6H_2O$ (*38*)	$Immm$		
$ZnBr_2 \cdot 2ZnBr_2 \cdot 6H_2O$ (= $ZnBr_2 \cdot 2H_2O$) (*39*)	$Immm$		
$CaBr_2 \cdot 2ZnBr_2 \cdot 6H_2O$ (*40*)	$C2/m$		
1:2:12 = (1:2:8 +4) Structure H (Fig. 4a)			
$MgCl_2 \cdot 2CdCl_2 \cdot 12H_2O$ (*41*)	$Fdd2$		
$NiCl_2 \cdot 2CdCl_2 \cdot 12H_2O$ (*42*)	$Fdd2$		
$CoCl_2 \cdot 2CdCl_2 \cdot 12H_2O$†			
$FeCl_2 \cdot 2CdCl_2 \cdot 12H_2O$†			
$MnCl_2 \cdot 2CdCl_2 \cdot 12H_2O$†			

TABLE I—*Continued*

1 : 4 : 10 (= 1 : 4 : 8 + 2) Structure I (Fig. 4b)	
$NiCl_2 \cdot 4CdCl_2 \cdot 10H_2O$ (*43*)	$P2_1/c$
$CoCl_2 \cdot 4CdCl_2 \cdot 10H_2O$†	
$MnCl_2 \cdot 4CdCl_2 \cdot 10H_2O$†	
$MnBr_2 \cdot 4CdBr_2 \cdot 10H_2O$†	
2 : 1 : 12.67 (=2 : 1 : 12 + 0.67) Structure (A + interstitial water)	
$2NiBr_2 \cdot CdBr_2 \cdot 12.67H_2O$ (*44*)	$R\bar{3}$
1 : 1 : 7 (= 1 : 1 : 6 + 1) Structure (D + Interstitial water)	
$MgBr_2 \cdot ZnBr_2 \cdot 7H_2O$ (*45*)	$P2_1/n$
1 : 1 : 4 Structure (E with the elimination of 2 waters)	
$CuCl_2 \cdot CdCl_2 \cdot 4H_2O$†	
1 : 1 : 5 Structure (D* with the elimination of 1 water)	
$MgCl_2 \cdot ZnCla_2 \cdot 5H_2O$†	(This may be $MgCl_2 \cdot ZnCl_2 \cdot 6H_2O$—see text and (*25*))
$CaCl_2 \cdot ZnCl_2 \cdot 5H_2O$† (*46*)	
$CaBr_2 \cdot ZnBr_2 \cdot 5H_2O$	$P\bar{1}$ (Not an equilibrium phase)

Note. For references to the equilibrium ternary phase diagrams see (*1*) and (*6*). Structures designated with * are derived from the corresponding unstarred structure by the sharing of ligands by the Ca atoms. Where the crystal structures are known, the reference and space group are shown. Structures marked † have not been determined but are predicted (*3–7*) to be of the type shown.

pound, $CuCl_2 \cdot CdCl_2 \cdot 4H_2O$, is expected to be derived from E with elimination of two H_2O molecules from the environment of Cu and sharing of two Cl^- ions between Cd and Cu. The Lewis acid strength of the Cu^{2+} ion (0.33 v.u.) should preclude such bonds but the normal environment of Cu^{2+}consists of four strong and two weak bonds, the latter having the right strength (0.14 v.u.) for forming direct Cu–halide bonds.

The above discussion shows that the chemical structures of 39 of the 43 compounds considered here can be directly predicted on the basis of a few simple assumptions. The remaining four compounds, while not directly predicted from these assumptions, nevertheless have chemical structures that are simply related to those that are predicted by the addition of interstitial water or the elimination of a coordinated water molecule and the formation of halide bridges.

5. Prediction of the Structure of the Saturated Solutions

The primary difference between the compositions of the solids described above and the saturated solutions is that, at room temperature, the solutions contain on average about four additional water molecules per metal atom, a number that is not sufficient to give each complex ion a complete second coordination sphere. The difference in the physical properties of the two phases lies in the lability of the hydrogen bonds (strength = 0.17 v.u.) formed by the interstitial water molecules. From Assumption 6 we would expect the stronger bonds within the complexes to remain intact as the solid changes to liquid so that the coordination spheres around the metal atoms will be similar in both phases. While the solid is constrained to the simple structures implied by Assumption 2, this constraint is not present in the liquid and a variety of species of the form $Me'X_{n-m}(H_2O)_m^{-n+m+2}$ are expected, with the species found in the equilibrium solid being dominant at any given composition. As in the solids, m will, in general, decrease with the softness of Me', a conclusion supported by the experimental studies reviewed by Magini *et al.* (*47*).

In compounds where the solid contains discrete complex ions (structures A–D) the additional water molecules will be interstitial and merely serve as the lubricant that allows the ions to diffuse, but the situation will be different for compounds containing polyanions since the polymers must, at least in part, be broken up in solution, resulting in ions such as $Me'X_4(H_2O)_2^{2-}$ and $Me'X_3(H_2O)_3^-$ (Fig. 2c–2d). EXAFS and DAS studies (*48, 49*) show that in almost saturated solutions of $ZnBr_2$ (8 M at room temperature) the $Zn_2Br_6^{2-}$ dimer, found in the equilibrium solid $ZnBr_2 \cdot 2H_2O$ (*39*), is broken down into $ZnBr_3(H_2O)^-$.

In cases where the solids contain polymerized cations (Ca salts) the arguments given in Section 3.3 suggest that in solution, if the Ca coordinates more than six water molecules some of them will also act as hydrogen bond acceptors. In saturated solutions, the Ca atom is more likely to be coordinated by six water molecules with its coordination sphere completed by halogen atoms from the anions to form molecular species such as the monomers $[(H_2O)_6Ca \cdot Br \cdot CdBr_4 \cdot Br \cdot Ca(H_2O)_6]$ found in $2CaBr_2 \cdot CdBr_2 \cdot 12H_2O$ (*24*), $[(H_2O)_6Ca \cdot (H_2O)Br \cdot MnBr_3(H_2O)]$ found in $CaBr_2 \cdot MnBr_2 \cdot 8H_2O$ (*34*), or the dimers $[(H_2O)_5Ca \cdot Br_2 \cdot ZnBr_2]_2$ found in $CaBr_2 \cdot ZnBr_2 \cdot 5H_2O$ (*46*). The additional water molecules will all be interstitial. The bonds formed by Ca will be relatively weak (~0.25 v.u.) so that the Ca coordination sphere in solution is likely to be somewhat labile. The coordination of Ca by only six water molecules is consistent with previous observations (*47*).

Acknowledgments

We thank the Natural Science and Engineering Research Council of Canada for funding.

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