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Structural Relationships of the $MM'O_4.nH_2O$ Hydrates. I. The Monohydrates $MM'O_4.H_2O$

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Abstract

In the framework of a systematic study of the hydrates $MM'O_4.nH_2O$ (M: an element possessing an octahedral environment of O atoms, M': an element possessing a tetrahedral environment) a classification has developed which not only allows the various compounds to be placed in their structural groups, but also allows the prediction of the possible theoretical structural types. The study of the possible combinations of octahedra and tetrahedra for the monohydrates $MM'O_4.H_2O$ has allowed eight different structural classes to be foreseen.

Introduction

A literature study of the hydrates $MM'O_4.H_2O$ shows that structural relationships can be found between them. In order to specify the relationships which seem to exist in such a large family of hydrated compounds, we were forced to restrict our study. As in these structures known fragments or molecular entities can be recognized, it would appear logical to consider first these geometric entities: octahedra and tetrahedra.

(i) The first coordination sphere of element M is octahedral and that of M' is tetrahedral. (ii) Moreover all the octahedra are considered identical and thus so are all the tetrahedra. (iii) With respect to the formulation $MM'O_4.H_2O$, the number of octahedra is equal to that of tetrahedra. (iv) The O atoms octahedrally placed around the element M are either from the tetrahedra or from the water molecules; in this way, all the O atoms coordinated to element M are bonded either directly or through hydrogen bonds to M'. (v) The O—O distances in the $M'O_4$ tetrahedra are to be considered shorter than the O—O distances in the MO_6 octahedra, in agreement with the ratio of the volumes of the two polyhedra.

Taking into account these principles, the expected structures of hydrated compounds are based upon the geometric study of the packing of octahedra and tetrahedra. As all the polyhedra of the same type are identical, it follows that only isolated octahedra, groups of two octahedra, or finally infinite groups of octahedra can exist. The bonds between octahedra, if they exist, can be formed by vertex, edge or face sharing.

In order to give a detailed and precise description of the packing, we have adopted the following notation.

The general formula of the hydrated compounds $MM'O_4.H_2O$ can be condensed into $MM'O_{4+n}H_{2n}$, and to differentiate between the O atoms (X) supplied by the tetrahedra and those (Y) from the water molecules, the formula can be written as: $MM'X_pY_qH_{2q}$.

As H atoms do not intervene in the combination of the polyhedra, they are omitted in the synoptic formula which can be written as:

$$\left[M[X]_{n_i/p_i}[Y]_{n_j/p_j}M'[X]_{n_k/p_k}\right]^{\infty s}$$

with $\sum n_i + n_j = 6$; $\sum n_k = 4$; $\sum (n_i/p_i + n_j/p_j + n_k/p_k) = 4 + n$; where $p =$ the number of polyhedra having X or Y in common; and $s =$ the dimensionality of the packing.

Derivation and characteristics of the monohydrate packing

For the monohydrates $MM'O_4.H_2O$ ($MM'X_4Y$), the systematic study of the packing of octahedra and tetrahedra leads to only eight possible structures among which six correspond to a three-dimensional network and the two others to a two-dimensional network. In Table 1 we enumerate the types of bonds formed in the octahedra and the tetrahedra and their ideal symmetry groups. Using models corresponding to each type of packing, we are able to predict the theoretical crystallographic parameters. All the known monohydrate structures are classified in the structural types derived from this study.

Structural type 1: $(MYX_{2/3}X_{3/2}M'X_{1/3}X_{3/2})^{\infty 3}$

This type of packing is obtained by joining two octahedra together by an edge. These groups of octahedra are joined together by tetrahedra (Fig. 1*a*)

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Table 1. *Types of bonds formed in the octahedra and the tetrahedra and their ideal symmetry groups*

Type number	Synoptic formula	Number of MX or MY bonds/ symmetry of octahedron	Number of $M'X$ bonds/ symmetry of tetrahedron	Theoretical crystallographic relationships	Known compounds ($MM'O_4.1H_2O$) and space groups	References
1	$(MYX_{2/3}X_{3/2}M'X_{1/3}X_{3/2})^{\infty 3}$	3 (2 + 3 + 1) $C_s\,(m)$	2 (1 + 3) $C_{3v}\,(3m)$	Monoclinic system $a = 2(O{-}O)_O + (O{-}O)_T$ $b = 2(O{-}O)_O + \sqrt{3}(O{-}O)_T$ $c = 2(M{-}O)_O + \tfrac{8}{3}(M'{-}O)_T$ Translation symmetry elements		
2	$(MY_{2/2}X_{4/2}M'X_{4/2})^{\infty 3}$	2 (4 + 2) $D_{4h}\,(4/mmm)$	1 (4) $T_d\,(\bar{4}3m)$	Pseudo tetragonal system $a = b = (O{-}O)_T + 2(M{-}O)_O$ $c = 2(M{-}O)_O$		
3	$(MY_{2/2}X_{4/2}M'X_{4/2})^{\infty 3}$	2 (4 + 2) $D_{4h}\,(4/mmm)$	1 (4) $T_d\,(\bar{4}3m)$	Monoclinic system $a = 2(M{-}O)_O + (O{-}O)_T$ $b = 2(M{-}O)_O + \sqrt{2}(O{-}O)_T$ $c = 2\sqrt{2(M{-}O)_O^2 + 2p(M{-}O)_O^2\sqrt{1-p2/4}}\,^*$ $\cos\beta = -\dfrac{c}{2a}$ Translation symmetry elements	MSO_4 (M = Co, Zn, Fe, Ni, Mg, Mn); $C2/c$ $MSeO_4$ (M= Ni, Co, Zn, Mn); $C2/c$ $MgSO_4$; $C2/c$ $CuSO_4$; $P\bar{1}$ $CdSO_4$; $P2_1/c$ $CdSeO_4.HgSeO_4$; $P2_1/c$ $NaClO_4$; $C2/c$ $NaHSO_4$; Cc $CaCrO_4$; $Pbca$	(1) (1) (2) (3) (4) (5), (12) (6) (7) (8)
4	$(MYX_{4/3}X_{1/2}M'X_{2/3}X_{1/2}X)^{\infty 3}$	3 (4 + 1 + 1) $C_{4v}\,(4mm)$	3 (2 + 1 + 1) $C_s\,(m)$	Orthorhombic system $a = (O{-}O)_O + (O{-}O)_T$ $b = 2(M{-}O)_O + \sqrt{2}(O{-}O)_T$ $c = 2(O{-}O)_O$ Translation symmetry elements	$HgSO_4$; $Pmcn$	(9) (10)
5	$(MY_{2/2}X_{2/3}X_{2/2}M'X_{1/3}X_{2/2}X)^{\infty 3}$	3 (2 + 2 + 2) $C_{2v}\,(mm)$	3 (2 + 1 + 1) $C_s\,(m)$	Orthorhombic system $a = (O{-}O)_O + (O{-}O)_T$ $b = 2(M{-}O)_O + \sqrt{2}(O{-}O)_T$ $c = 2(O{-}O)_T + \dfrac{4(M{-}O)_O}{3}\left[\sqrt{3-p^2} - p\sqrt{2}\right]^*$	NaH_2PO_4; $Pna2_1$	(11)
6	$(MY_{2/2}X_{4/3}M'X_{2/3}X_2)^{\infty 3}$	2 (4 + 2) $C_{2v}\,(mm)$	2 (2 + 2) $C_s\,(m)$	Monoclinic system $a - c = \sqrt{3}(O{-}O)_O + \sqrt{3}(O{-}O)_T$ $b = \dfrac{4}{\sqrt{3}}(M{-}O)_O$		
7	$(MY_{2/2}X_{4/3}M'X_{2/3}X_2)^{\infty 2}$	2 (4 + 2) $C_{2v}\,(mm)$	2 (2 + 2) $C_s\,(m)$	$a = \sqrt{3}(O{-}O)_O + \sqrt{3}(O{-}O)_T$ $b = \dfrac{4}{\sqrt{3}}(M{-}O)_O$		
8	$(MY_{2/2}X_{4/3}M'X_{2/3}X_2)^{\infty 2}$	2 (4 + 2) $D_{4h}\,(4/mmm)$	2 (2 + 2) $C_s\,(m)$	$a = (O{-}O)_O + (O{-}O)_T$ $b = \dfrac{4}{\sqrt{3}}(M{-}O)_O$		

References: (1) Oswald (1965); (2) Bregeault, Herpin, Manoli & Pannetier (1970); (3) Coing-Boyat & Le Fur (1966); (4) Bregeault & Herpin (1970); (5) Herpin & Bregeault (1968); (6) Berglund, Thomas & Tellgren (1975, 1976); (7) Grimvall (1971); (8) Bars *et al.* (1977); (9) Bonefacio (1961); (11) Templeton *et al.* (1964); (10) Catti & Ferraris (1976); (12) Stålhandske (1978).

$$^*p = \frac{(O{-}O)_T}{(O{-}O)_O}.$$

having one vertex shared by two octahedra and the other three vertices shared with a single octahedron. The packing, in the **c** direction, is formed by displacing the layers (Fig. 1*b*) with respect to one another. This allows us to predict the existence of translational symmetry. The water molecule is not shared and occupies a vertex of the octahedra in the **c** direction. For a pair of octahedra sharing an edge the water molecules are *trans* to one another. This alternance in the **c** direction of water molecules and O atoms creates cavities in the packing.

Structural type 2: $(MY_{2/2}X_{4/2}M'X_{4/2})^{\infty 3}$

In this case we find chains of octahedra which are linked together by a vertex, the linking atom being an oxygen of a water molecule. These chains are linked together by tetrahedra of which all the vertices are shared (Fig. 2). The resulting structure is three dimensional and very compact which reduces the possibility of the formation of hydrogen bonds; moreover the water molecules are imbricated with the octahedra.

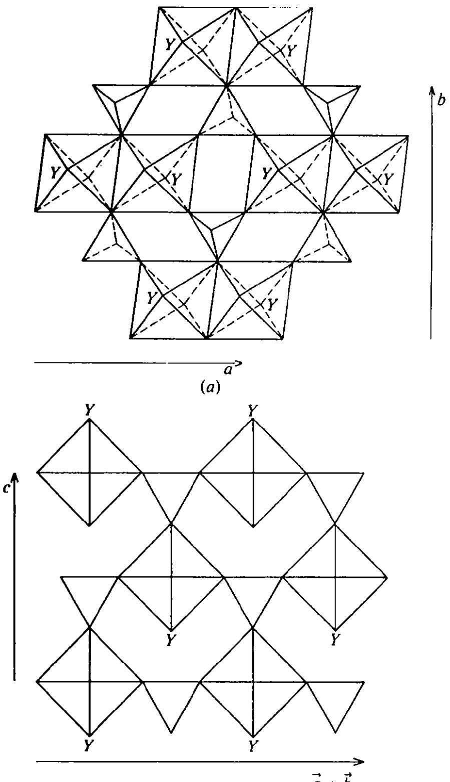

Fig. 1. (a) Structural type 1 in the (001) plane. (b) Structural type 1 in the $(1\bar{1}0)$ plane.

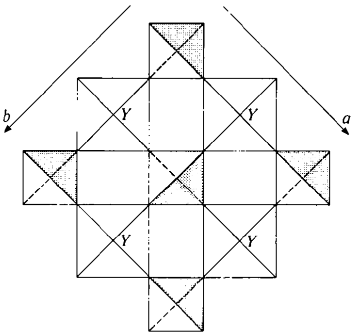

Fig. 2. Structural type 2.

Structural type 3: $(MY_{2/2}X_{4/2}M'X_{4/2})^{\infty 3}$

The chains of octahedra are identical to those in the preceding structural type; however, each $M'X_4$ group is bonded to four different octahedra of which two belong to the same chain (Fig. 3). This disposition of the polyhedra causes a twisting of the chain due to the fact that the M—M distances are greater than the O—O distances of the tetrahedra. In this case a displacement of the chains with respect to one another is observed which implies the presence of translational symmetry elements. Because of the twisting in the chains the water molecules are not so tightly packed and hence they might be able to form hydrogen bonds between the chains and therefore consolidate the assembly.

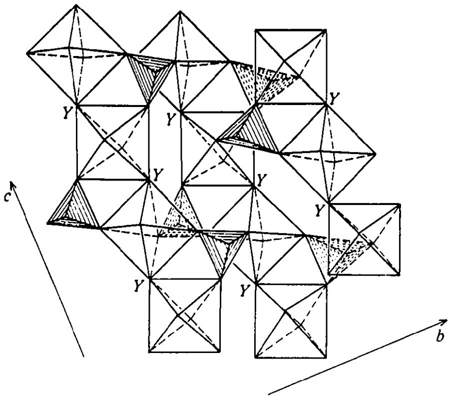

Fig. 3. Structural type 3.

In this group a series of sulphates and selenates are found and are grouped together in Table 1. All the compounds crystallize in the monoclinic system (except for $CuSO_4.H_2O$) with a glide plane of type c. The distortion observed for $CuSO_4.H_2O$ is caused uniquely by the nature of the element Cu. The theoretical crystallographic parameters calculated, as an example, for $CoSO_4.H_2O$ are the following: $a = 6{\cdot}62$, $b = 7{\cdot}65$, $c = 7{\cdot}79$ Å, $\beta = 126{\cdot}04°$, which are comparable to the observed parameters: $a = 6{\cdot}598$, $b = 7{\cdot}570$, $c = 7{\cdot}621$ Å, $\beta = 118{\cdot}41°$ (Oswald, 1965). The differences are due to the irregularities of the polyhedra and to the packing which can deviate from the ideal to facilitate the formation of hydrogen bonds.

Following the nature of the cations M and M' or more precisely the relationship between their effective ionic radii (Shannon, 1976), the chains of octahedra are more or less distorted as summarized in Table 2. It is important to note that the size of the cation M is the governing factor for the straightness of the chains.

In this group we have placed a particular hydrate: $CaCrO_4.H_2O$ (Bars, Le Marouille & Grandjean, 1977); the coordination number of 8 for the Ca ion does not correspond to our initial criteria; however, in considering only $(O—O)_{\text{octahedral}} > (O—O)_{\text{tetrahedral}}$ we can define the coordinaton of the Ca ion as 6 + 2 and hence $CaCrO_4.H_2O$ enters perfectly into this type.

Structural type 4: $(MYX_{4/3}X_{1/2}M'X_{2/3}X_{1/2}X)^{\infty 3}$

This time the octahedra are linked together by a common edge, in which water molecules do not intervene. The chains are joined together by the tetrahedra which are orientated alternatively up and down for reasons of packing (Fig. 4). The layers obtained are packed together in such a way that a vertex of a tetrahedron coincides with a free vertex of an octahedron of the next layer and conserves the water–oxygen alternance, resulting from a displacement of the layers with respect to one another.

Table 2. *Ratio of ionic radii of M/M'*

Ionic radii of M / Ionic radii of M'	Co^{2+} 0·65	Zn^{2+} 0·74	Fe^{2+} 0·61	Ni^{2+} 0·69	Mg^{2+} 0·72	Mn^{2+} 0·67	Cu^{2+} 0·73	Cd^{2+} 0·95	Na^+ 1·02	Hg^{2+} 1·02
S^{6+} 0·12	5·42	6·17	5·08	5·75	6·00	5·58	6·08	7·92	8·50	
Cl^{7+} 0·08									12·75	
Se^{6+} 0·28								3·39		3·64
	Straight chain							Distorted chain		

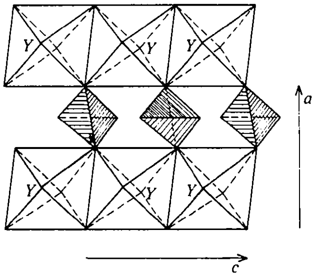

Fig. 4. Structural type 4.

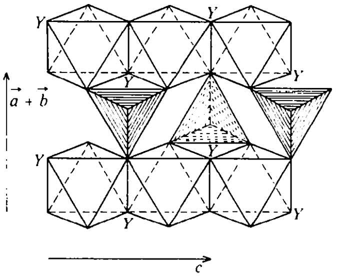

Fig. 5. Structural type 5.

The monohydrate $HgSO_4.H_2O$ corresponds to this type of packing and shows a large deformation of the polyhedra as predicted from their ideal symmetry. The orthorhombic system *Pmcn* confirms our forecasts as well as the theoretical parameters: a = 5·77, b = 8·21, c = 7·89 Å, which are comparable to the observed values: a = 5·416, b = 8·964, c = 7·874 Å (Templeton, Templeton & Zalkin, 1964).

Structural type 5: $(MY_{2/2}X_{2/3}X_{2/2}M'X_{1/3}X_{2/2}X)^{\infty 3}$

The chains of octahedra are identical to those in type 4 except that the common edge is formed by an O atom from a water molecule and an O atom from the $M'X_4$ tetrahedra (Fig. 5). Each tetrahedron bridges the vertices of two neighbouring octahedra of the same chain and causes a twisting of the chain; a third vertex of the tetrahedron is shared by the neighbouring chain, the fourth is free.

$NaH_2PO_4.H_2O$ represents this type of packing but the existence of a free vertex for the tetrahedra gives a certain degree of freedom to the $M'X_4$ motif which explains the differences between the observed and theoretical parameters: a = 7·616, b = 7·899, c = 7·382 Å (Catti & Ferraris, 1976), and: a = 6·02, b = 8·48, c = 6·86 Å respectively.

Structural type 6: $(MY_{2/2}X_{4/3}M'X_{2/3}X_2)^{\infty 3}$

The octahedra are linked together by a common face forming chains of high density. The water molecules are situated *cis* to one another on one of the shared faces of the octahedron (Fig. 6). So large tunnels can be seen running along **b** which cause a certain fragility of the linking. This structural type has a monoclinic symmetry with a β angle of 120°. At the present time no known structure enters this structural type.

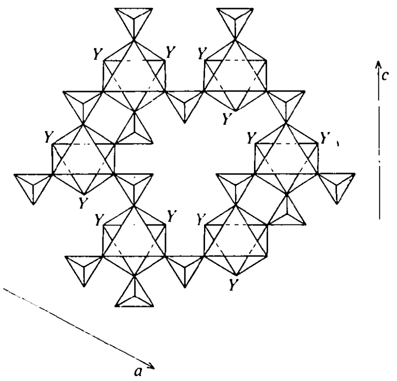

Fig. 6. Structural type 6.

Structural type 7: $(MY_{2/2}X_{4/3}M'X_{2/3}X_2)^{\infty 2}$

The arrangement of the octahedra is identical to that of type 6 except for the position of the water molecules which are situated *cis* to one another but on two different shared faces of the octahedra (Fig. 7). This gives a two-dimensional structure linked together by hydrogen bonds. Two of the three parameters can be predicted, the third depends on the hydrogen bonds.

Structural type 8: $(MY_{2/2}X_{4/3}M'X_{2/3}X_2)^{\infty 2}$

Again we have the same arrangement for the octahedra as in type 7 except for the position of the

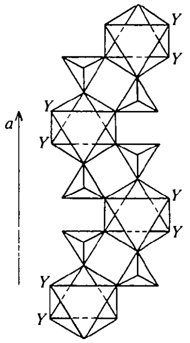

Fig. 7. Structural type 7.

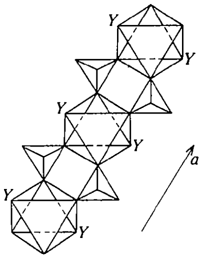

Fig. 8. Structural type 8.

water molecules which are now situated *trans* to one another and hence cause another two-dimensional structure (Fig. 8).

Conclusion

The derivation of these eight possible structural types for the monohydrates $MM'O_4.H_2O$ includes all the possible packings of octahedra and tetrahedra. Our work shows that it is now possible to predict theoretical crystallographic-parameter relationships and the existence of translational symmetry elements in the crystallographic unit cell for each structural type. The monohydrates $MM'O_4.H_2O$ crystallize in only three-dimensional or two-dimensional networks. Moreover, if as a base the double criteria of a packing as compact as possible (still allowing the formation of hydrogen bonds) and the highest possible symmetry for each polyhedra are taken, structural types 3, 4 and 5 are particularly stable and include all the known structures. This derivation shows for the first time crystallographic similarities between monohydrated sulphate, selenate, chromate or chlorate compounds.

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