

Structural Relationships of the $MM'O_4 \cdot nH_2O$ Hydrates. II. The Dihydrates $MM'O_4 \cdot 2H_2O$

BY O. BARS, J. Y. LE MAROUILLE AND D. GRANDJEAN

Laboratoire de Chimie du Solide et Inorganique Moléculaire, Associé au CNRS, LA n° 254, UER 'SPM',
Campus de Beaulieu, 35042 Rennes CEDEX, France

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Abstract

The extension of the systematic study carried out for the monohydrates to the dihydrates $MM'O_4 \cdot 2H_2O$ has allowed the prediction of nine different structural classes, involving one-, two- and three-dimensional networks. In the dihydrate structures the two water molecules can lie on vertices which are *trans* or *cis* to one another, so leading to a greater number of associations of these polyhedra. The chain structures here present a new class which was not obtained for the monohydrates.

Introduction

In part I (Bars, Le Marouille & Grandjean, 1981), we have presented all possible types of packing for the monohydrates $MM'O_4 \cdot H_2O$, specifying the existence of some translational symmetry elements and theoretical unit-cell parameters. Monohydrate structures found in the literature were classified and agreed with our work. A similar study for the dihydrates $MM'O_4 \cdot 2H_2O$ has allowed us to obtain nine different types of packing, and all our results are summarized in Table 1.

Structural type 1: $(MY_2X_{4/2}M'X_{4/2})^{\infty 3}$

The octahedra, formed by four O atoms (X) belonging to the tetrahedra and two O atoms (Y) coming from water molecules, are isolated in this case. The atoms Y are *cis* to one another and hence the symmetry of the octahedra is C_{2v} ; the placing of the two types of polyhedra leads in the first instance to the formation of planes; the tetrahedra A and B (Fig. 1) can have the same orientation, *i.e.* their vertices either up or down, or an alternance of their vertices. These two possibilities lead to two different crystallographic parameters a , related by a factor of 2.

The orientation of the tetrahedra A and B imposes the orientation of the tetrahedra C and D in order to realize a three-dimensional structure.

The synoptic formula $(MY_2X_{4/2}M'X_{4/2})^{\infty 3}$ shows that the four vertices of a tetrahedron are shared. To

realize this, it is necessary to place an identical plane on either side of the plane obtained in Fig. 1 in such a manner that the fourth vertices of the tetrahedra A , B , C , D are shared by the octahedra. In this way it leads to a shear of these planes and so there must appear translational symmetry elements. A series of phosphates and arsenates correspond to this group, some of them having two allotropic forms which correspond to the alternance of the tetrahedra. This is the case for $AlPO_4 \cdot 2H_2O$ for which there are two varieties, one orthorhombic (Kniep, Mootz & Vegas, 1977) and the other monoclinic (Kniep & Mootz, 1973). In both cases, translational symmetry elements are found as predicted by our study. The examination of the synoptic formula $(MY_2X_{4/2}M'X_{4/2})^{\infty 3}$ implies a high order of regularity for the polyhedra because around the cation M two types of bonds are observed: $M-X$ and $M-Y$, whereas around the cation M' only a single type is observed: $M'-X$. The distances observed in $AlPO_4 \cdot 2H_2O$ correspond exactly to these constraints. Only slight distortions of the polyhedra are observed.

Structural type 2: $(MY_2X_{4/2}M'X_{4/2})^{\infty 2}$

The second possible environment around atom M is obtained by placing the atoms Y *trans* to one another, so leading to a D_{4h} symmetry. The arrangement of the octahedra and tetrahedra is identical to the preceding

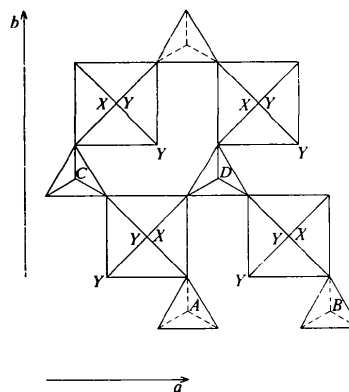


Fig. 1. Structural type 1.

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 ·2H ₂ O) and space groups	References
1	(MY ₂ X _{4/2} M'X _{4/2}) ^{∞3}	2 (4 + 2) C _{2v} (mm)	1 (4) T _d (43m)	Orthorhombic system a ₁ = (O-O) _o + (O-O) _r a ₂ = 2a ₁ b ₁ = 2(O-O) _o + √3(O-O) _r b ₂ = b ₁ c ₁ = 2(M-O) _o + 3(M'-O) _r c ₂ = c ₁ Translation symmetry elements	InPO ₄ , TIPO ₄ , TIASO ₄ ; Pbca InAsO ₄ , FePO ₄ , AlAsO ₄ ; Pbca FeAsO ₄ ; Pbca AlPO ₄ ; Pbca AlAsO ₄ ; Pbca GaPO ₄ , GaAsO ₄ ; Pbca CdSeO ₄ , MnSeO ₄ ; Pbca AlPO ₄ ; P2 ₁ /n FePO ₄ ; P2 ₁ /n	(1) (2) (3) (4) (5) (6) (7) (8) (9) (10)
2	(MY ₂ X _{4/2} M'X _{4/2}) ^{∞2}	2 (4 + 2) D _{4h} (4/mmm)	1 (4) T _d (43m)	a = 2(M-O) _o + (O-O) _r b = 2(M-O) _o + (O-O) _r		
3a	(MY ₂ X _{2/3} X _{2/3} M'X _{1/3} X _{2/3} X) ^{∞2}	3 (2 + 2 + 2) C _{2v} (mm)	3 (1 + 1 + 2) C _s (m)	a = 2(O-O) _o + (O-O) _r b = 2(M-O) _o + √3(O-O) _r	ZnMoO ₄ ; P2 ₁	(11)
b				a = 2(M-O) _o + (O-O) _r b = $\frac{\sqrt{3}}{2}$ (O-O) _o + $\frac{\sqrt{3}}{2}$ (O-O) _r	MgMoO ₄ ; P2 ₁	(12)
4	(MY _{2/2} YX _{3/2} M'X _{3/2} X) ^{∞3}	3 (3 + 2 + 1) C _{2v} (mm)	2 (3 + 1) C _{3v} (3m)	Orthorhombic system a = 4(M-O) _o + 2(O-O) _r b = 2(M-O) _o + √3(O-O) _r c = 4(M-O) _o	NaH ₂ PO ₄ ; P2 ₁ 2 ₁ 2 ₁	(13)
5	(MY _{2/2} YX _{3/2} M'X _{3/2} X) ^{∞2}	3 (3 + 2 + 1) C _{2v} (mm)	2 (3 + 1) C _{3v} (3m)	a = 2(M-O) _o + √3(O-O) _r b = 2√2(M-O) _o ² + 2p(M-O) _o ² √(1 - p ² /4) *		
6	(MY _{4/2} X _{2/2} M'X _{2/2} X) ^{∞2}	2 (4 + 2) D _{4h} (4/mmm)	2 (2 + 2) C _s (m)	a = 2(O-O) _o b = 2(M-O) _o + (O-O) _r		
7	(MY ₂ X _{4/3} M'X _{2/3} X) ^{∞2}	2 (4 + 2) D _{4h} (4/mmm)	2 (2 + 2) C _s (m)	a = 2(O-O) _o	CaSO ₄ ; I2/a	(14)
				b = (O-O) _o + (O-O) _r	CaSeO ₄ ; A2/n	(15)
					CaHAsO ₄ ; Ia	(16)
					CaHPO ₄ ; Ia	(17)
					CaPO ₃ F; Pī	(18) (19) (20)
8	(MY _{2/2} YX _{3/3} X _{1/2} M'X _{1/3} X _{1/2} X) ^{∞3}	4 (2 + 2 + 1 + 1) C _{2v} (mm)	3 (2 + 1 + 1) C _s (m)	Orthorhombic system a = (O-O) _o + $\frac{2\sqrt{3}}{3}$ (O-O) _r b = 2(M-O) _o + 3(M'-O) _r c = 2(O-O) _o Translation symmetry elements		
9	(MY _{4/2} X _{2/3} M'X _{1/3} X) ^{∞1}	2 (4 + 2) D _{4h} (4/mmm) or C _{2v} (mm)	2 (3 + 1) C _{3v} (3m)	c = $\frac{4}{\sqrt{3}}$ (M-O) _o	NaNH ₄ CrO ₄ ; P2 ₁ 2 ₁ 2 ₁	(21)
					NaNH ₄ SO ₄ ; P2 ₁ 2 ₁ 2 ₁	(22)
					NaNH ₄ SeO ₄ ; P2 ₁ 2 ₁ 2 ₁	(23)
					NaNH ₄ SeO ₄ ferroelectric; P2 ₁	(24)

References: (1) Mooney-Slater (1961); (2) Tarte & Paques-Ledent (1968); (3) Kitahama, Kiriyama & Baba (1975); (4) Hawthorne (1976); (5) Kniep *et al.* (1977); (6) Klieber & Weiner (1958); (7) Paques-Ledent & Tarte (1968); (8) Kokkoros (1938); (9) Kneip & Mootz (1973); (10) McConnel (1940); (11) Le Marouille *et al.* (1980); (12) Meullemestre & Penigault (1975); (13) Bartl *et al.* (1976); (14) Cole & Lancucki (1974); (15) Atoji & Rundle (1958); (16) Simon, Pierrot & Kern (1963); (17) Ferraris (1969); (18) Beevers (1958); (19) Jones & Smith (1962); (20) Perloff (1972); (21) Khan & Baur (1972); (22) Corazza, Sabelli & Giuseppetti (1967); (23) Krouglik, Simonov & Iouzvak (1973); (24) Krouglik (1976).

$$* p = \frac{(O-O)_r}{(O-O)_o}$$

case but gives rise to a two-dimensional structure (MY₂X_{4/2}M'X_{4/2})^{∞2} (Fig. 2). In order that hydrogen bonds can be formed between the planes to stabilize the structure, it is necessary to move the planes with

respect to one another giving rise to crystallographic translational symmetry elements. No structures of this type are yet known and so no comparison can be made with our theoretical parameters.

Structural type 3: $(MY_2X_{2/3}X_{2/2}M'X_{1/3}X_{2/2}X)^{\infty 2}$

If two octahedra have an edge in common the synoptic formula becomes $(MY_2X_{2/3}X_{2/2}M'X_{1/3}X_{2/2}X)^{\infty 2}$ when the water molecules do not form the common edge. These water molecules can be either *trans* or *cis* to one another. In the first case, a layer structure is obtained as represented in Fig. 3(a), the layers being held together by strong hydrogen bonds since the fourth vertex of the tetrahedron is not shared.

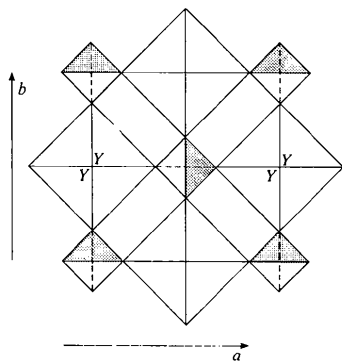


Fig. 2. Structural type 2.

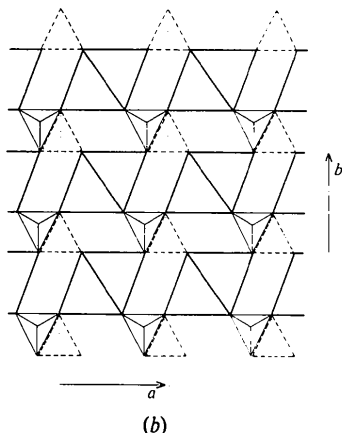
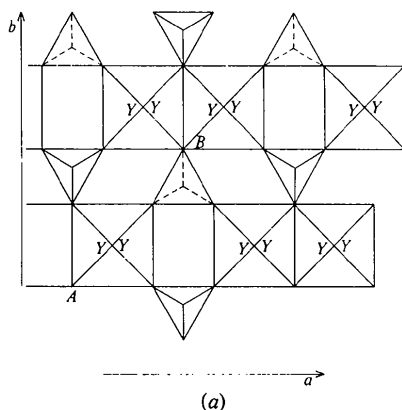


Fig. 3. Structural type 3.

In the second case, a layer structure is again obtained; Fig. 3(b) shows the double octahedra along the view axis. The dotted and full-line tetrahedra are at different heights.

$ZnMoO_4 \cdot 2H_2O$ and $MgMoO_4 \cdot 2H_2O$ belong to the first type. The theoretical parameters of the layer calculated for $ZnMoO_4 \cdot 2H_2O$: $a = 8.80$, $b = 10.91$ Å, are similar to those observed: $a = 8.546$, $b = 10.263$ Å (Le Marouille, Bars & Grandjean, 1980).

The similarity of the size of the tetrahedron MoO_4 and the octahedron ZnO_6 makes it impossible to form a compact packing of type 1.

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

The octahedra are linked together by a common vertex and form infinite chains in the *c* direction. The octahedra have three water molecules two of which are at the shared vertices of the octahedra, which hence has the symmetry C_{2v} . The *ab* plane is represented in Fig. 4. In order to avoid crowding due to the tetrahedra, the next plane will show the fourth vertex of the tetrahedra in the opposite direction. The tetrahedron *A* forms the links between the octahedra 1, 2 and 3 in the first plane, and 1, 2 and 4 in the next plane. The unit cell will be trirectangular, but there will be quite large holes which can be filled by other ions or atoms.

No compound corresponds exactly to this model; however, it is possible to include $NaH_2PO_4 \cdot 2H_2O$ (Bartl, Catti & Ferraris, 1976) in this group, where the chains of octahedra are obtained by linking the polyhedra by the contiguous vertices. This creates an important torsion in the chains and increases the cohesion of the structure.

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

In the previous case, each tetrahedron shared three vertices with three octahedra belonging to three different chains. It is possible to imagine that the tetrahedron $M'X_4$ is linked to two consecutive octa-

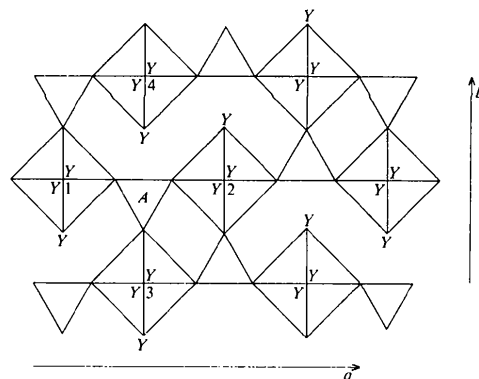


Fig. 4. Structural type 4.

hedra in the same chain (Fig. 5). This arrangement necessitates a twisting of the chain which depends on the relative size of the two types of polyhedra. Between two parallel chains *A*, can be placed a chain *B* at such a height that the apices *X* from the chains *A* coincide with the vertices of the octahedra of the *B* chains in order to form a two-dimensional network. The vertices of the octahedra of the same chain will be alternately *Y* and *X*.

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

This time the chains are obtained by edge-sharing octahedra. This edge is formed by the water molecules which will therefore all be shared by the octahedra as shown by the synoptic formula $(MY_{4/2}X_{2/2}M'X_{2/2}X_2)^{\infty 2}$ and will give rise to a D_{4h} symmetry in the octahedra.

Each tetrahedron is a bridge between two chains of octahedra so as to form a two-dimensional structure (Fig. 6). For steric reasons, the tetrahedra are arranged head-to-tail with respect to one another.

Structural type 7: $(MY_2X_{4/3}M'X_{2/3}X_2)^{\infty 2}$

Again the octahedra share a common edge but this time the common edge consists of O atoms from the $M'X_4$ tetrahedra and not water molecules (Fig. 7).

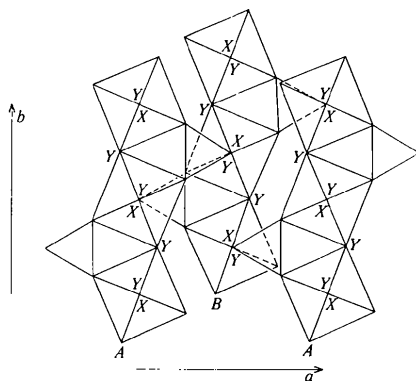


Fig. 5. Structural type 5.

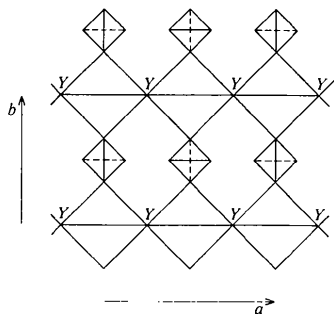


Fig. 6. Structural type 6.

Several particular compounds have been placed in this type (Table 1).

The Ca salts do not correspond to our original criteria as the Ca ion has a coordination number of either 7 or 8. As for the case of calcium chromate monohydrate (Bars, Le Marouille & Grandjean, 1977) it is necessary to change the coordination number of the Ca ion to either 6 + 1 or 6 + 2 by eliminating the longest Ca—O distances, or by eliminating the shortest O—O distances following the original criterion: $(O-O)_{\text{octahedral}} > (O-O)_{\text{tetrahedral}}$. With this second possibility the calcium hydrate can be classified in this structural type 7.

Structural type 8: $(MY_{2/2}YX_{2/3}X_{1/2}M'X_{1/3}X_{1/2}X_2)^{\infty 3}$

The chains of octahedra are still formed by the octahedra sharing a common edge formed by *X* and *Y* atoms, so the symmetry of an octahedron becomes C_{2v} .

In order to realize such a structure it is necessary that, in a given chain, the orientation of the octahedra is alternating (Fig. 8); i.e. the vertex *A* of one octahedron is an O atom and the vertex of the two adjacent octahedra will be water molecules. A three-dimensional structure is obtained by displacing the chains with respect to one another and implies the presence of translational symmetry elements in a trirectangular unit cell.

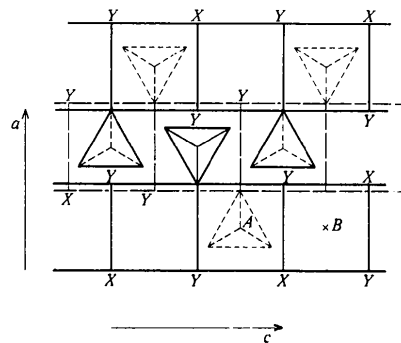


Fig. 7. Structural type 7.

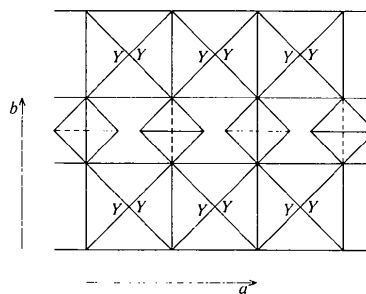


Fig. 8. Structural type 8.

Structural type 9: $(MY_{4/2}X_{2/3}M'X_{1/3}X_3)^{\infty 1}$

The octahedra share a common face, and can have either the symmetry D_{4h} (Fig. 9a) or C_{2v} (Fig. 9b and c). In the latter case, the O atoms in the octahedra are *cis* to one another and either can be in the shared face (Fig. 9b) or belong to two different faces (Fig. 9c). A relatively unstable structure can be obtained in all three cases, because the chains are held together only by hydrogen bonds. It is possible to increase the stability of the structure by placing other elements in the holes of this structure as is the case for $NaNH_4SO_4 \cdot 2H_2O$, $NaNH_4SeO_4 \cdot 2H_2O$ and $NaNH_4CrO_4 \cdot 2H_2O$ (Table 1) where the symmetry of the octahedra is D_{4h} .

Conclusion

All the $MM'O_4 \cdot 2H_2O$ hydrates whose structures are known, of which there are quite a few, can be classified into one of our structural types. For these hydrates,

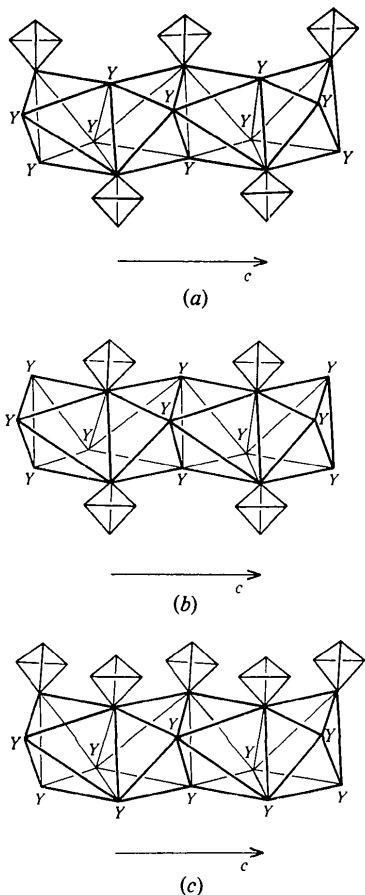


Fig. 9. Structural type 9.

chain structures are observed which do not exist for the monohydrates, and very few three-dimensional structures are possible. However, some phosphates and arsenates have a three-dimensional structure. The hydrogen bonds become more numerous due to the fact that there are two water molecules and they have the important role of assuring the stability of the structures.

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