

Transition metal derivatives of low oxidation state phosphorus oxoacids: synthetic pathways and structural studies

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A general synthetic approach intended to rationalize the solution preparative chemistry of transition metal phosphites and hypophosphites is presented. As previously shown for other derivatives containing also tetrahedral or pseudotetrahedral oxoanions, the hydrolytic processes affecting the cationic moieties play a determinant role on the very nature of the final solid. In fact, despite the limited number of donor atoms in the anions, the crystal chemistry of these compounds is quite intricate because of both the variety of possible cationic aggregates and the many ways to interconnect them through pseudotetrahedral anionic groups.

1. Introduction

In a previous publication we have reviewed the most recent advances in the chemistry and properties of oxovanadium phosphates [1]. In particular, a specially challenging task from the theoretical point of view has been to establish magnetostructural correlations in a very rich system that includes a variety of derivatives whose magnetic behaviour cannot be explained from their respective structural features only [1-3]. In part, the latter is due to the involvement of phosphate bridges in the spin transfer between metallic centers [2,3].

Following our studies in this field, and looking mainly for new low dimensional systems, it was believed that this last aim might be further favoured by replacing phosphate groups by other related anionic entities, such as phosphite or hypophosphite groups, having a lower connectivity (i.e., a lower number of donor atoms).

The chemistry of low oxidation state phosphorus oxoanions-containing materials is poorly known. The number of published works on the subject is relatively small. They mainly deal with specific preparative and/or structural aspects concerning alkaline, alkaline-earth or lanthanide derivatives [4-7]. The

scarcity of data on transition metal derivatives is remarkable, although some related organophosphonate derivatives have been studied in more detail because of their potential applications [8-11].

The lack of literature data dealing with simple transition metal phosphites and hypophosphites is, very likely, due in part to the synthetic difficulties arising in solution chemistry when, besides the redox and acid-base reactions affecting the anionic species, there are superimposed problems originated from the hydrolytic processes, which the cationic counterparts may undergo. In this sense, we have recently advanced a synthetic approach [12], which by controlling two main variables (pH and metal ion concentration), has allowed us to obtain a wide set of Co, Ni and Zn phosphites showing different structural types, including tunnelled [12,13] and layered [14-16] arrangements. This structural versatility results from the very different arrays which may result from the connection of the variety of possible cationic aggregates through the pseudotetrahedral anionic moieties [17]. In fact, despite the limited connectivity of the anions, the flexibility of the possible bridging modes gives rise to structures ranging from 1-D to 3-D and contributes to offer alternative exchange pathways able to support magnetic interactions between metallic centers.

The present study is firstly intended to systema-

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tize the abovementioned preparative approach, extending it to both other metal ions and phosphorous oxoanions. Thus, a general unifying synthetic scheme is presented from a chemically based argument. On the other hand, the classification of the up-to-now known structures of transition metal phosphites and hypophosphites, using criteria similar to those applied for grouping mineral phosphates, may contribute to rationalize their crystallochemistry.

2. Preparative chemistry

Classically, in order to prepare new oxoanionic derivatives, the attention has been paid mainly to the reactions involving the anionic species. Notwithstanding, when approaching the solution synthesis of transition metal compounds (oxophosphorous derivatives in the present case), the possible complications due to those hydrolytic processes affecting the cationic species cannot be obviated. Our synthetic approach is based on a very simple idea focussed on these hydrolytic processes: the resulting cationic network in the final solid would be essentially controlled by the cationic aggregates present in the mother solution.

The hydrolysis and subsequent condensation of cationic species, which results favoured by high densities of charge on the metal, can occur through nucleophilic substitution or addition reactions, depending on the fact that the preferred coordination of the metal will be or not satisfied in the molecular precursor [18]. Condensation is unlikely from aquocomplexes, $[M(H_2O)_n]^{z+}$, and an effective condensation process would be possible when OH^- groups are present in the coordination sphere of the metal ion. Connectivity and charge balance in the final solid would be provided by OH^- and/or other (when present) coordinating anions. In practice, for a given cation, the pH is the main variable determining the presence of coordinated hydroxo groups, while the metal ion concentration regulates the metal ion to hydroxo-ligand ratio [19]. It can consequently be stated that the condensation degree of the cationic aggregates in the mother solution may be modulated by adjusting both these main variables, i.e. pH and metal ion concentration (C_M).

These hydrolytic processes may be substantially

altered by the presence in solution of another ions able to coordinate the metal cations [18–20], as occurs in the case of phosphorous oxoanions. The resulting molecular precursors usually have a chemical activity towards hydrolytic and condensation reactions very different from that expected for the aquocations only. In fact, the ability of these polydentate ligands to connect the – formally – preexisting cationic entities would imply the possibility of forming polymeric species.

Hypophosphorous acid is a rather strong monoprotic acid ($pK = 1.1$). The only derived species with coordinating capability is $H_2PO_2^-$. Phosphorous acid is diprotic ($pK_1 = 1.3$, $pK_2 = 6.7$), with $H_2PO_3^-$ and HPO_3^{2-} as conjugated bases. The basic strength of these three anions, which ranges between those of OH^- and H_2O , varies in the sense $HPO_3^{2-} \gg H_2PO_3^- \approx H_2PO_2^-$, what is related to their respective net charge and the number of donor oxygen atoms. The stability of the derived complexes follows this same strength order [21]. Schematized in fig. 1 are some of the different bridging modes in which these anions may be involved.

From these possible coordination modes, and taking into account the very nature of the cationic species in the starting solution (which depends on pH and C_M), some reasonable proposals about how the cationic coordination polyhedra should be in the final solid (i.e., correlations between the synthetic conditions and the nature of the final solid) can be advanced. These predictions have been summarized in table 1, where they are compared to the experimental findings. Labels in table 1 correspond to the polyhedra schematized in fig. 2. Listed in table 1 also are the known experimental conditions under which phosphite and hypophosphite compounds have been isolated.

Octahedral hexahydrated aquocations are usually the most stable species in moderately concentrated aqueous solutions of 3d metals at low pH values. The formation of oxophosphorous derivatives might be thought of as resulting from the competition between coordinated water molecules and the respective anionic ligands present in the solution. Dealing with di- or tri-valent metal ions, and given the relatively low basicity of the anions (which implies that the lone pairs on the oxygen atoms are in highly electronegative orbitals), the formation of strongly co-

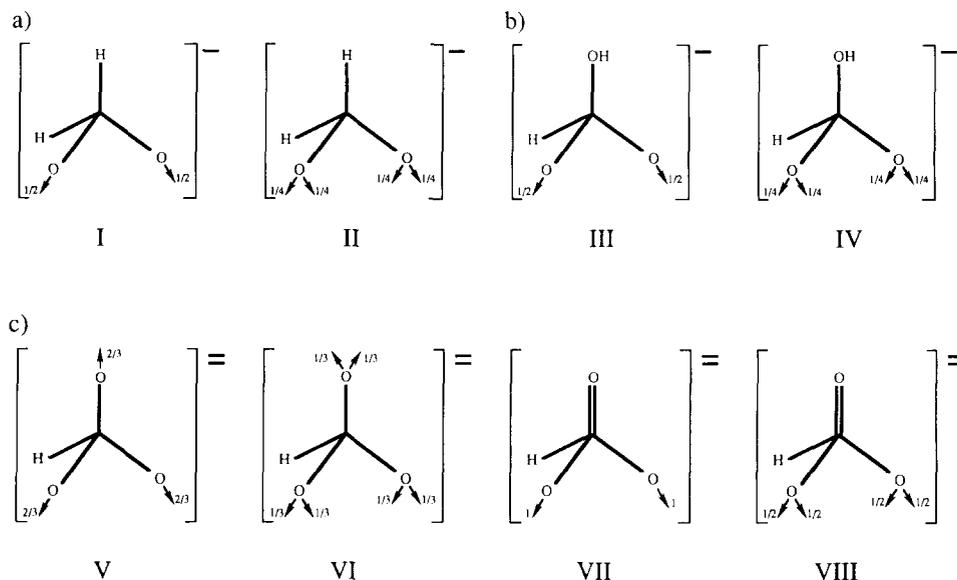


Fig. 1. A schematic representation of some coordination modes in which oxophosphorous anions may be involved: (a) hypophosphite, H_2PO_2^- ; (b) hydrogenphosphite, H_2PO_3^- ; (c) phosphite, HPO_3^{2-} . For each anion only the extreme situations (corresponding to symmetric charge transfer from oxygen donor atoms) have been displayed, but intermediate modes are also possible. It is assumed that the net anionic charge is equally distributed among the coordinating oxygen atoms.

valent M to O (ligand) bonds seems unlikely, what in turn would result in the formation of definite P to O double bonds in the oxophosphorous ligand. The metal to oxophosphorous ligand interactions would predominantly be electrostatic, and it may be assumed that the net anionic charge is symmetrically distributed among all the oxygen donor atoms. Accordingly, to predict the most probable coordination environment of the cations in the resulting solid, we postulate that, in the formally progressive coordinated water molecules substitution: (1) the entering anions would supply the cation with the maximum charge fraction carried by one oxygen donor atom, and (2) to avoid possible competition for the metal orbitals, further incoming of ligands will preferably result in cis-substituted arrangements. Both the number of substituting oxophosphorous ligands and their respective coordination (bridging) modes will be then determined by the derivative stoichiometry.

For divalent transition metal ions, charge compensation requires ligand to metal ratios equal to 2 (H_2PO_2^- , H_2PO_3^-) or 1 (HPO_3^{2-}). According to fig. 1, maximum direct charge transfer from each donor atom would imply four oxygen atoms in the case of

hypophosphite (coordination mode I) and hydrogenphosphite (c. m. III) ligands, and two (c. m. VII) or three (c. m. V) oxygen atoms for phosphite ligands. Thus, it might be expected that hypophosphites and hydrogenphosphites of 3d M(II) ions crystallize in acid media with two water molecules in the cation coordination sphere (i.e., B mode in fig. 2a). In the case of phosphite derivatives, trihydrated (O, fig. 2b) or tetrahydrated (N, fig. 2b) metal coordination environments would be expected. On the contrary, dealing with trivalent transition metal cations, anhydrous products are predicted for hypophosphite and hydrogenphosphite materials (J), whereas trihydrated (P for c. m. VII) or monohydrated (U for c. m. V) polyhedra are expected in the case of the phosphite anion. Except for this last case (which implies dimeric cationic entities formed by octahedra corner sharing – the $\text{PO}_{1/3}$ unit –, i.e. the presence of μ -oxo M–O–M bridges), in all the above compounds the cationic octahedra would not share structural elements, and only μ -(O, O')-ligand bridges would connect the metallic centres throughout the lattice.

As indicated in table 1, although there are no

Table 1
Synthetic conditions, predicted and found metal environments and crystallochemical classification of transition metal phosphites and hypophosphites.

Compound	Starting reagents	P/M ratio	[P] ^{a)} (pH)	Medium	T (°C)	M env ^{c)}		Type	Category	Ref.
						P	F			
Fe(H ₂ PO ₂) ₂ ·6H ₂ O	FeSO ₄ + Ba(H ₂ PO ₂) ₂ →			water	v.e. ^{a)}	A	A			[27]
M(H ₂ PO ₂) ₂ ·6H ₂ O	M(OH) ₂ + H ₃ PO ₂ →			water	v.e. ^{a)}	A	A(Ni)			[29]
M = Co(II), Ni(II)	MSO ₄ + Ba(H ₂ PO ₂) ₂ →			water	<20	A				[25]
Zn(H ₂ PO ₂) ₂ ·6H ₂ O	ZnSO ₄ + Ba(H ₂ PO ₂) ₂ →			solid	50–60	B				[29]
Ni(H ₂ PO ₂) ₂ ·2H ₂ O	Ni(H ₂ PO ₂) ₂ ·6H ₂ O + Q →			water		B				[28]
Co(H ₂ PO ₂) ₂ ·2H ₂ O	CoCl ₂ + NH ₄ H ₂ PO ₂ →			water		B				[23]
Mn(H ₂ PO ₂) ₂ ·3H ₂ O	MnSO ₄ + Ba(H ₂ PO ₂) ₂ →			water		B				[23]
Mn(H ₂ PO ₂) ₂ ·3H ₂ O	Mn(H ₂ PO ₂) ₂ ·3H ₂ O + P ₂ O ₅ →			water	T _{room}	G	G	I	trans-VO(O _T) ₄ O _w	[37,54]
VO(H ₂ PO ₂) ₂ ·H ₂ O	V ₂ O ₅ + H ₃ PO ₂ →	7/3	2.7	water	T _{room}					
	VOSO ₄ + H ₃ PO ₂ →	7/3	1.7	water	T _{room}					
	VO(OH) ₂ + H ₃ PO ₂ →	7/3		water	T _{room}					
α-Mn(H ₂ PO ₂) ₂ ·H ₂ O	MnSO ₄ + Ba(H ₂ PO ₂) ₂ →	1/1	0.7	acetone		C	C	II	M ₂ O ₁₀	[31]
β-Mn(H ₂ PO ₂) ₂ ·H ₂ O	(unknown)					C	K+L			[22]
α-Zn(H ₂ PO ₂) ₂ ·H ₂ O	ZnSO ₄ + Ba(H ₂ PO ₂) ₂ →			water	20	C	C	II	M ₂ O ₁₀	[22]
M(H ₂ PO ₂) ₂ M = Zn, Co	MSO ₄ + Ba(H ₂ PO ₂) ₂ →			water	50	E	F	V	trans ⁻¹ [MO ₄]	[25]
Me = Fe	FeSO ₄ + Ba(H ₂ PO ₂) ₂ →			acetone		E	F			[35]
Cu(H ₂ PO ₂) ₂	Cu(acetate) + acid →			ethanol	0	I or H				[35]
	Cu(NO ₃) + NaH ₂ PO ₂ →			glycine	0					[16]
MCl(H ₂ PO ₂) ₂	MCl ₂ ·6H ₂ O + H ₃ PO ₂ →	1/1	5	water	T _{room}	D	D	V	trans ⁻¹ [M ₂ O ₆ Cl ₃]	[36]
M = Co, Ni										
Cd(H ₂ PO ₃) ₂ ·H ₂ O	CdHPO ₃ + H ₃ PO ₃ →			water		C	C	II	M ₂ O ₁₀	[32]
Zn(H ₂ PO ₃) ₂ ·3H ₂ O	ZnCl ₂ + H ₃ PO ₃ →	5/2	5	water		B or C	E	V	cis ⁻¹ [MO ₄]	[33]
Zn(H ₂ PO ₃) ₂ ·1/3H ₂ O	ZnO + H ₃ PO ₃ →	3/1	conc	water	50	E	E	V	cis ⁻¹ [MO ₄]	[34]
Fe(H ₂ PO ₃) ₃	Fe ₂ O ₃ + H ₃ PO ₃ →	4/1	conc	water		J	J	I	M[O _T] ₆	[27]
Cu(H ₂ PO ₃) ₂	CuO + H ₃ PO ₃ →	3/1	0.9	water		I or H	H	II	M ₂ O ₁₀	[40]
MnH ₃ P ₂ O ₆ ·2H ₂ O	Mn ₂ O ₃ ·nH ₂ O + H ₃ PO ₃ →	5/1	conc	water		M	M	I	cis-M(O _T) ₄ (O ₂) ₂	[41]

continued on next page

Table 1 (continued)

Compound	Starting reagents	P/M ratio	[P] ^{a)} (pH)	Medium	T (°C)	M env ^{c)}		Type	Category	Ref.
						P	F			
Ni(HPO ₃) ₂ ·6H ₂ O	NiCO ₃ +H ₃ PO ₃ →			water		A or O				[27]
Ni(HPO ₃) ₂ ·3H ₂ O	Ni(HPO ₃) ₂ ·6H ₂ O dehyd./H ₂ SO ₄ →			water		O				[27]
M(HPO ₃) ₂ ·2H ₂ O	CuCl ₂ ·6H ₂ O+ H ₃ PO ₃ →	3/2		water		R	R	IV	trans ¹ _∞ [MO ₅]	[38]
M=Cu, Cr	MnSO ₄ +NaHPO ₃			water		Q				[39]
Mn(HPO ₃) ₂ ·2H ₂ O	MnSO ₄ +NaHPO ₃	1/1	0.2	water	180	S	S	V	cis ¹ _∞ [M ₂ O ₈]	[23]
M(HPO ₃) ₂ ·H ₂ O	MCl ₂ ·6H ₂ O+ H ₃ PO ₃ →		(#3)	water	HT	T	T			[14]
M=Co, Ni	M(HPO ₃) ₂ ·H ₂ O		1.0	water	180	W	W			[16]
M ₁₁ (HPO ₃) ₈ (OH) ₆	MCl ₂ ·6H ₂ O+KOH +K ₂ HPO ₃ →	8/11		water	HT	V	V	II	M ₂ O ₉	[12]
M=Zn, Co, Ni	Fe ₂ O ₃ +H ₃ PO ₃ →	3/2	0.7	water	HT	V	V			[13]
Fe ₂ (HPO ₃) ₃										[55]

a) Concentration of the pseudo tetrahedral specie. b) Vacuum evaporation. c) Metallic environment, P=predicted, F=found.

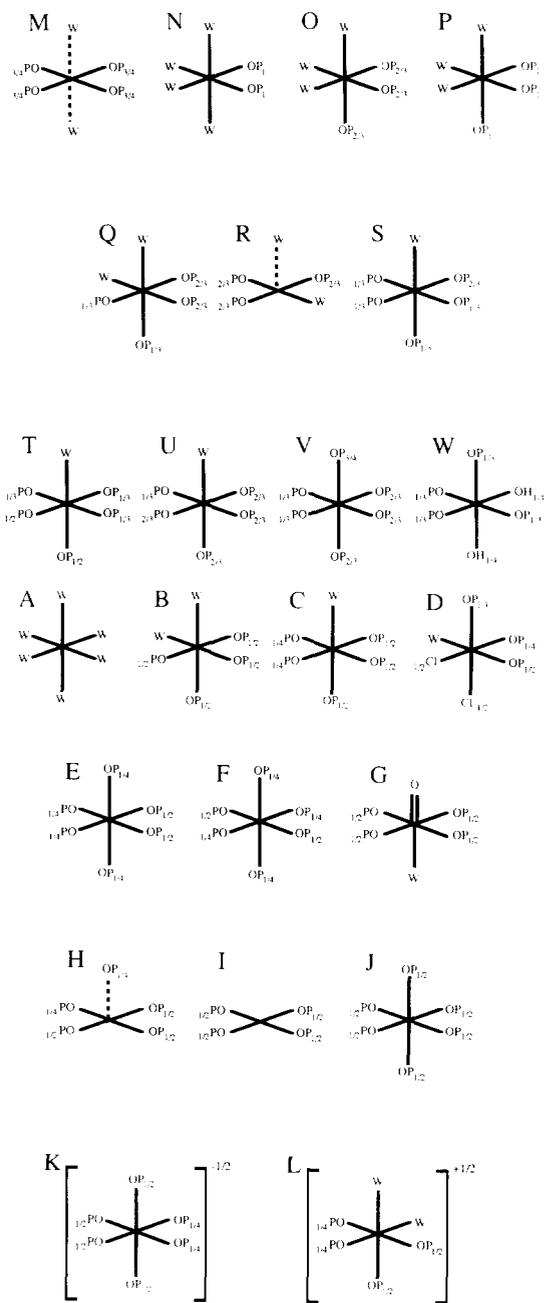


Fig. 2. The main types of cationic polyhedra found in oxophosphorous derivatives. W=coordinated water; OP_{1/2}=μ-(O, O) bridges from hypophosphite or hydrogenphosphite anions; OP_{1/4}=μ-(O) bridges from hypophosphite or hydrogenphosphite anions; OP_{2/3}=μ-(O,O) bridges from tridentate phosphite anion; OP_{1/3}=μ|| (O) bridges from tridentate phosphite anion; OP₁=μ-(O,O) bridges from bidentate phosphite anion; OP_{1/2}=μ-(O) bridges from bidentate phosphite anion.

structural data, it may be expected to find the type-B polyhedra for Mn in the case of $\text{Mn}(\text{H}_2\text{PO}_2)_2 \cdot n\text{H}_2\text{O}$, $n=2$ and 3 [22,23]. The fact that the third water molecule of the trihydrate be easily lost in the presence of P_2O_5 to give the dihydrate suggests that it is a lattice water molecule, and, consequently, that the Mn coordination polyhedra are equivalent in both hydrates. Also, derivatives such as $\text{Mn}(\text{H}_2\text{PO}_2)_2 \cdot \text{L}$ (L=bipy, ophen) [24] and $\text{M}(\text{H}_2\text{PO}_2)_2(\text{py})_2$ (M=Co(II) and Zn(II)) [25], which can be obtained in the presence of high concentrations of the neutral organic amines, would fit in well with the above hypothesis, with a bidentate L ligand or two monodentate pyridine groups replacing water molecules in the metal coordination sphere. On the other hand, the predicted J octahedra have been actually found in the anhydrous Fe(III) hydrogenphosphite, $\text{Fe}(\text{H}_2\text{PO}_3)_3$ [26].

Higher hydrates only have been described for some M(II) hypophosphite compounds $\{\text{M}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$, M=Fe [27], Co [28], Ni [29] and Zn [25] $\}$, and also in the case of $\text{Ni}(\text{HPO}_3) \cdot 6\text{H}_2\text{O}$ [29]. Among these, the crystal structure only has been determined for $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$ [27], and it contains isolated $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ regular octahedra. As mentioned above, H_2PO_2^- is the weakest basic ligand among the ones considered here, and gives rise to the least stable complexes. This results in the need for using more concentrated solutions to crystallize hypophosphites than those from which the analogous phosphites are isolated. It is not surprising that in diluted aqueous solutions the advance of the anation reaction becomes limited (this allowing the isolation of the hexahydrated cationic species). Notwithstanding, the solid hexahydrates may easily lose four water molecules (i.e. it is enough to heat at 50–60°C in the Ni case) to give the respective dihydrate [28,29], in accordance with our prediction.

The fact that $\text{Ni}(\text{HPO}_3) \cdot 6\text{H}_2\text{O}$ be the only known hexahydrate M(II) phosphite might be related to the well-known inertness of d^8 Ni(II) ions towards ligand substitution [30]. The crystal structure of $\text{Ni}(\text{H}_2\text{PO}_3) \cdot 6\text{H}_2\text{O}$ has not been determined. In contrast to the already discussed $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$ instance, HPO_3^{2-} ligand originates in the most stable complexes within the anion series we are dealing with. Although the Ni^{2+} inertness always would favour highly hydrated cationic environments, it seems now

unlikely that anation reaction also be stopped at the hexahydrated $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ isolated ions, and a part of the water molecules might be lattice water molecules. Whatever the result be in $\text{Ni}(\text{HPO}_3) \cdot 6\text{H}_2\text{O}$, it easily loses three water molecules (in the presence of H_2SO_4 [29]) to give the trihydrated species. Once again, this fact fits well with our prediction of trihydrated (N) metal coordination environments for phosphites of divalent ions.

As shown in table 1, however, the isolation of solids having hydration degrees lower than those initially predicted is possible. This is a consequence of varying the experimental conditions to which the initial predictions were referred: low pH, low C_M (room temperature, atmospheric pressure).

From a formal point of view, elimination of water molecules from the metal coordination sphere requires the incoming of more oxygen atoms from the oxophosphorous anions. To maintain the cationic charge balanced, any increase in the number of coordinated donor oxygen atoms must imply a lowering in the effective charge transferred from some of these oxygen atoms. The latter, in turn, implies that these oxygen atoms would be shared by two metallic centers, i.e. they would be involved in μ -O bridges (which means that the cationic octahedra would share structural elements). For example, going from B to C involves the replacement a water molecule (W) by an O atom in the coordination sphere of a M^{2+} ion. To maintain the electroneutrality, two of the ligands must adopt in C coordination modes II or IV (fig. 1) instead of I or III (in B; fig. 1).

In practice, coordinated water elimination may be accomplished in different ways. Indeed, as shown in table 1, by increasing the crystallization temperature and/or limiting the presence of water in the reaction medium, monohydrated hypophosphites have been obtained for Mn(II) [22,31] and Zn(II) [22], and anhydrous hypophosphites for Fe(II) [25], Co(II) [25] and Zn(II) [22,25]. Predictions on the metal coordination polyhedra listed in table 1 have been made on the basis of the expected consequences of progressive water molecules replacement in an idealized dihydrate. The case of $\text{Mn}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$ deserves a short comment. Two polymorphs, α and β , are known, the α variety being isostructural to $\text{Zn}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$. The experimentally found C polyhedron in the α polymorph (which, as illustrated

above, imply dimeric cationic entities) nicely agrees with that expected from elimination of a water molecule (and subsequent condensation) of each type B octahedron in the dihydrate. However, the β variety contains some more complex coordination metal polyhedra. The experimentally found dimeric cationic entities might be thought of as resulting from a dehydration process in which two water molecules were eliminated from one B octahedron (to give the type K polyhedron), and the subsequent condensation would occur through two $\text{PO}_{1/4}$ units of another octahedron (L) which retains its water molecules.

On the other hand, given the competitiveness between H_2PO_3^- and the more basic HPO_3^{2-} ligands, hydrogenphosphite derivatives have to be obtained in the presence of high anion concentrations and at very low pH values. The increased P/M ratio and the required restriction of the presence of water in the reaction medium would explain the isolation of monohydrated (Cd(II) [32]; C) or anhydrous (Zn(II) [33,34]; E) phases instead of the idealized dihydrated ones. (In fact, no hydrogenphosphite dihydrate derivative has been reported until now; water molecules in the formula of the Zn(II) derivatives are not coordinated but interstitial, which would explain their lability.)

Similarly, the use of hydrothermal treatments favours the obtention of low hydrated materials. In this way, the synthesis of M(II) monohydrated phosphites has been described for Co(II) [14] and Ni(II) [16]. The resulting metal coordination polyhedra, T, cannot be predicted with our simple model, and imply a very intricate network of phosphite bridges.

A nice example of the influence of the procedural variables on the nature of the resulting solid is provided by the preparation of the highly condensed materials of the dumortierite family, $\text{M}_{11}(\text{HPO}_3)_8(\text{OH})_6$, $\text{M}=\text{Co}, \text{Ni}, \text{Zn}$ [11,12]. As indicated above, the phosphites $\text{MHPO}_3 \cdot \text{H}_2\text{O}$ ($\text{M}=\text{Co}, \text{Ni}$) were prepared using soft hydrothermal treatments ($\text{pH}=3$, moderate pressure, $T=180^\circ\text{C}$). The same experimental procedure, but adjusting the pH to 5–6 and using higher concentrations of the respective metallic ion (C_M), yields materials characterized by the presence of cationic aggregates in which four metal atoms are connected to one OH^- group. The resulting chains may be thought of as built

up from dimeric, $\text{M}_2(\text{OH})^{3+}$, or tetrameric, $\text{M}_4(\text{OH})_4^{4+}$, entities, which are the principal products of hydrolysis in these conditions of pH and C_M [19]. To deepen a little more in this aspect, we have schematically shown in fig. 3 the results obtained by varying the pH in two series of solutions containing different concentrations of cobalt ions (series A: $C_M=0.34 \text{ M}$; series B: $C_M=0.50 \text{ M}$). In the case of the less concentrated series A, the only detected phase up to $\text{pH}=5$ is $\text{CoHPO}_3 \cdot \text{H}_2\text{O}$. In the pH range from 5 to 8 the isolated solids are mixtures of $\text{CoHPO}_3 \cdot \text{H}_2\text{O}$ and the highly condensed $\text{M}_{11}(\text{HPO}_3)_8(\text{OH})_6$ phase. The latter material is obtained pure when the pH is adjusted to values ranging from 8 to 10. In contrast, when starting from the more concentrated series B the stability range of $\text{M}_{11}(\text{HPO}_3)_8(\text{OH})_6$ becomes expanded towards lower pH values in approximately 1 pH unity. In both cases, pH values higher than 10 lead to the precipitation of cobalt hydroxide.

Besides these effects due to modifications of the procedural variables, two other factors may lead to results different from our initially simple predictions, namely the presence in the starting solution of other additional species and the specific characteristics of a given metal ion. Several examples may illustrate the first case. Indeed, the isolation of hypophosphites of the most acid cations is very difficult because of the reductor character of the anion. In the case of copper (II), however, a successful synthesis of $\text{Cu}(\text{H}_2\text{PO}_2)_2$ has been possible in the presence of glycine [35]. Glycine is able to coordinate copper ions, lowering their acidity. The subsequent glycine replacement by hypophosphite allowed the isolation of the anhydrous derivative. Another example is the

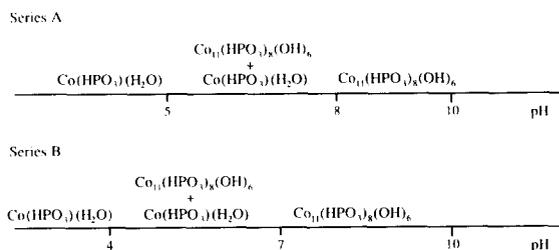


Fig. 3. Stability ranges for $\text{Co}(\text{HPO}_3)(\text{H}_2\text{O})$ and $\text{Co}_{11}(\text{HPO}_3)_8(\text{OH})_6$. Series A: $C_M=0.34 \text{ M}$; Series B: $C_M=0.50 \text{ M}$.

synthesis of mixed chlorine-hypophosphite compounds. Even though the stability of hypophosphite complexes is higher than that of the chlorine complexes, the basic strength of both anions is not very different. In the presence of high Cl^- concentrations, it is possible to partially replace H_2PO_2^- ligands in the cationic coordination sphere. D polyhedra present in $\text{MCl}(\text{H}_2\text{PO}_2)(\text{H}_2\text{O})$ $\{\text{M} = \text{Ni}(\text{II})$ [16] and $\text{Co}(\text{II})$ [36] $\}$ may be thought of as derived from $\text{MCl}(\text{H}_2\text{O})_5$ molecular precursors.

On the other hand, peculiarities of the cations can result in coordination polyhedra very different from those so far discussed. This is the case of the highly anisotropic oxovanadium VO^{2+} ion. Its characteristic vanadium oxygen double bond may hardly be substituted. Moreover, the usually long V–O distance, trans to the double bond in the vanadium environment, is inadequate for effective ligand charge transfer. The result is the presence of its typical 4+1+1 coordination mode (G) in $\text{VO}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$ [37]. Active Jahn–Teller cations also give rise to specific geometries. The usual occurrence of four short equatorial distances and two long axial ones determines the occupational preference of the oxophosphorous ligands towards the equatorial sites. Hence, it is reasonable that $\text{Cu}(\text{II})$ [38] and $\text{Cr}(\text{II})$ [39] yield phosphite dihydrates, $\text{M}(\text{HPO}_3) \cdot 2\text{H}_2\text{O}$, having M type coordination pseudooctahedra. Although it might equally be expected that $\text{Cu}(\text{II})$ hydrogenphosphite would have a dihydrated 4+2 coordination mode (I type), it seems to be the lower basicity of the ligand what favours the experimentally found anhydrous derivative (4+1+1, H type) [40]. Taking into account the $\text{Mn}(\text{III})$ Jahn–Teller activity, the M type polyhedra found in $\text{Mn}(\text{H}_3\text{P}_2\text{O}_6) \cdot 2\text{H}_2\text{O}$ is as expected [41].

In this context, it deserves to stress the difficulties arising when approaching the synthesis of $\text{Zn}_{11}(\text{HPO}_3)_8(\text{OH})_6$. The well-known tendency of Zn to adopt tetrahedral environments, both in solution [42] and in solid state [43], obligated us to maintain the temperature of the solution close to 0°C in order to favour the formation of octahedral species [12]. Once again, the validity of the idea guiding our synthetic approach (i.e., the nature of the structural network in the resulting solid is controlled by the cationic aggregates present in the mother solution) finds support in the need for alteration of the

procedural variables in order to get the Zn analogous of the Co and Ni hydroxiphosphites.

There are several additional examples of phosphite derivatives illustrating this Zn tendency towards four coordination. Thus, contrary to Co and Ni, the simple phosphite is pentahydrated, $\text{Zn}_2(\text{HPO}_3)_2 \cdot 5\text{H}_2\text{O}$, and includes both octahedrally and tetrahedrally coordinated Zn atoms [33]. A similar situation occurs in the phosphites of formula $\text{Zn}_3\text{A}_2(\text{HPO}_3)_4$ ($\text{A} = \text{Na}, \text{K}, \text{Ba}$) [33] and $\text{ZnA}(\text{HPO}_3)_2 \cdot 2\text{H}_2\text{O}$ ($\text{A} = \text{Ca}, \text{Sr}$) [44], as well as in some related organophosphonates such as $\text{Zn}(\text{BuPhPO}_2)_2$ [45]. The simultaneous presence of ZnO_6 octahedra and ZnO_4 tetrahedra in the solid lattice also has precedents in the phosphates chemistry, as exemplified by the hopeite mineral, $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ [46], and the mixed sodium salt $\text{NaZn}_2\text{P}_3\text{O}_{10} \cdot 9\text{H}_2\text{O}$ [47].

3. Crystal chemistry

The extraordinary structural versatility found in the field of mineral phosphates was nicely put in order by Moore [17,48–50] on the basis of two main criteria, namely the topology of the cationic aggregates present in the structure and the connectivity pattern established among them through phosphate bridges. More recently, Hawthorne [51] has extended this structural scheme to mineral sulfates, vanadates, arsenates and silicates. According to them, it becomes possible to recognize up to eight great structural categories among these derivatives. A summary of the main structural motives guiding this classification is shown in table 2.

Contributing to the already mentioned structural

Table 2
Structural motives guiding the mineralogical classification proposed by Hawthorne.

Category I	Isolated octahedra
Category II	Finite clusters of octahedra
Category III	Face sharing trimeric entities
Category IV	Infinite chains of corner sharing octahedra
Category V	Infinite chains of edge sharing octahedra
Category VI	Layered structures
Category VII	Close-packing structures
Category VIII	Glaserite type structures

diversity of the transition metal, phosphites and hypophosphites are factors due to the cationic species that, logically, would fit in well within the Moore and Hawthorne scheme. Dealing with the anionic counterparts, however, the availability of a different number of oxygen donor atoms (two for H_2PO_2^- and H_2PO_3^- , three for HPO_3^{2-}) implies a new variable with regard to the more symmetric tetrahedral species. It was this lowering of the anions symmetry and coordinating ability (when compared to PO_4^{3-}) what initially prompted us to approach the study of these systems in our search for low dimensional materials.

As far as possible, we have adapted the above criteria trying to progress in the rationalization of the crystallochemistry of the little compounds. The derivatives whose structure has been determined can be arranged as shown in table 1.

The category I is based on the presence of isolated $[\text{MO}_6]$ octahedra in the lattice. The connection among them occurs through oxo bridges from H_2PO_2^- or H_2PO_3^- groups, the contribution from hydrogen bonding being also possible. As might be expected, this structural type encompasses many of the solids obtained in acid media. Attending to the relative arrangement and the chemical nature of the oxygen atoms (i.e. to their belonging to H_2O ligands (O_w) or anionic species (O_T)), the $[\text{MO}_6]$ octahedra might initially adopt one of ten different configurations. Thus, in the case of $\text{Fe}(\text{H}_2\text{PO}_3)_3$ [24] all six oxygen atoms of each isolated $[\text{FeO}_6]$ octahedron belong to different dihydrogenphosphite groups, i.e. they can be represented as $\text{M}(\text{O}_T)_6$, whereas in the $\text{MNa}(\text{H}_2\text{PO}_3)_3 \cdot \text{H}_2\text{O}$ ($\text{M}=\text{Co}, \text{Mn}$) solids [52,53] the cationic polyhedra are of the type $\text{M}(\text{O}_T)_5(\text{O}_w)$, with the five O_T atoms coming from three different H_2PO_3^- groups. In the manganese salt $\text{MnH}_3\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ [40] both hydration water molecules are cis-coordinated to metallic atoms, defining cis- $\text{Mn}(\text{O}_T)_4(\text{O}_w)_2$ pseudooctahedra. Within this category, we finally find $\text{VO}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$ [54]. In this case, one of the oxygen atoms (trans to the hydration water molecule) in the vanadium environment is actually an oxo terminal ligand, a possibility that was not considered in the Moore scheme. By analogy, the vanadium polyhedra may be represented as trans- $\text{VO}(\text{O}_T)_4(\text{O}_w)$, belonging the four O_T atoms to four H_2PO_2^- anions.

Compounds in category II also have been isolated

in acid media but in the presence of relatively high C_M . They contain simple dimeric entities resulting from edge or face sharing between two cationic octahedra. The sharing of one edge leads to $[\text{M}_2\text{O}_{10}]$ units, which are the structural motives found in $\text{Cd}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$ [39], $\text{Cu}(\text{H}_2\text{PO}_3)_2$ [31], $\beta\text{-Mn}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$ and $\alpha\text{-M}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$, $\text{M}=\text{Zn}, \text{Mn}$ [22,30] (fig. 4a). On the other hand, face sharing gives the $[\text{M}_2\text{O}_9]$ aggregates found in $\text{Fe}_2(\text{HPO}_3)_3$ [55] (fig. 4b). The dimeric $[\text{M}_2\text{O}_{10}]$ units of all the hydrated compounds include two terminal oxygen atoms belonging to water molecules.

Whereas there is no oxophosphorous derivative whose structure may be related to the so-called category III (table 1) known, there are several examples of chained materials that can be classified in category IV, a structural type widely represented among phosphates. It is characterized by the presence of chains of axially condensed metallic octahedra (i.e., each octahedron shares two opposite corners – occupied by OH^- groups – with two other adjacent ones), and the structures displaying this framework are usually referred to as 7 Å structures, given that this is the typical repetitive MOM distance. Phosphates in this class usually appear as pseudolayered compounds, as a consequence of the interconnection of these chains through tetrahedral $[\text{PO}_4]$ groups. Among the materials we are dealing with, this type of chains, ${}_{\infty}^1[\text{MO}_5]$, has been observed in the isostructural $\text{M}(\text{HPO}_3) \cdot 2\text{H}_2\text{O}$, $\text{M}=\text{Cu}, \text{Cr}$ [37,38], solids (see fig. 5a). Each $[\text{MO}_6]$ octahedron shares two water molecules occupying trans sites, the equatorial plane being defined by three oxygen atoms from HPO_3^{2-} different ligands and another one from a water molecule.

In the category V are included the structures involving either chains of octahedra condensed through edges (defining cis- or trans- ${}_{\infty}^1[\text{MO}_4]$ entities) or mixed chains containing both edge and corner shared octahedra. The first is the case of the isostructural $\text{M}(\text{H}_2\text{PO}_2)_2$, $\text{M}=\text{Fe}, \text{Co}, \text{Zn}$ [22,28], compounds, whose structure can be described as built up from trans- ${}_{\infty}^1[\text{MO}_4]$ aggregates having an edge shared between each pair of adjacent octahedra (see fig. 5b). The hydrogenphosphites of formulation $\text{Zn}(\text{H}_2\text{PO}_3)_2 \cdot n\text{H}_2\text{O}$ ($n=1/3, 3$) [32,33] show an identical bonding network and can be only differentiated by the number of water molecules located

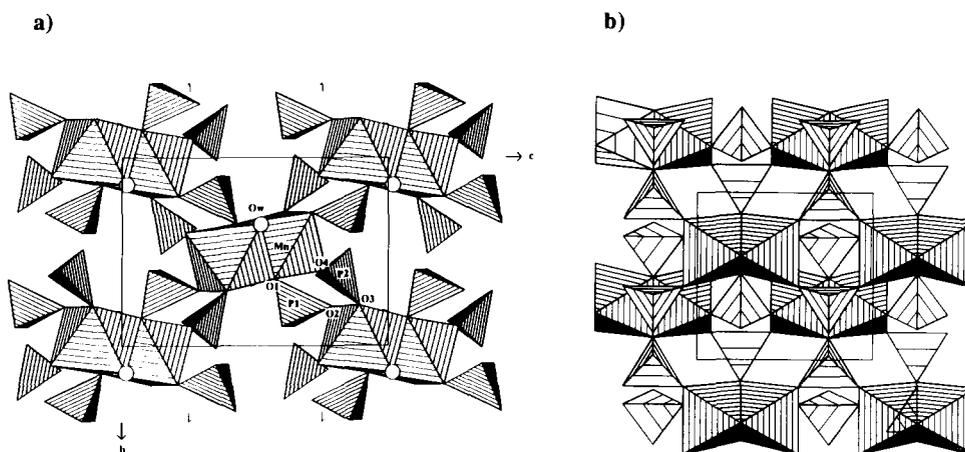


Fig. 4. (a) Projection along the (100) direction of the crystal structure of α -Mn(H₂PO₂)₂·(H₂O). Octahedra edge sharing gives dimeric [M₂O₁₀] units; (b) polyhedral representation of the Fe₂(HPO₃)₃ structure showing the dimeric [M₂O₉] units resulting from octahedra face sharing.

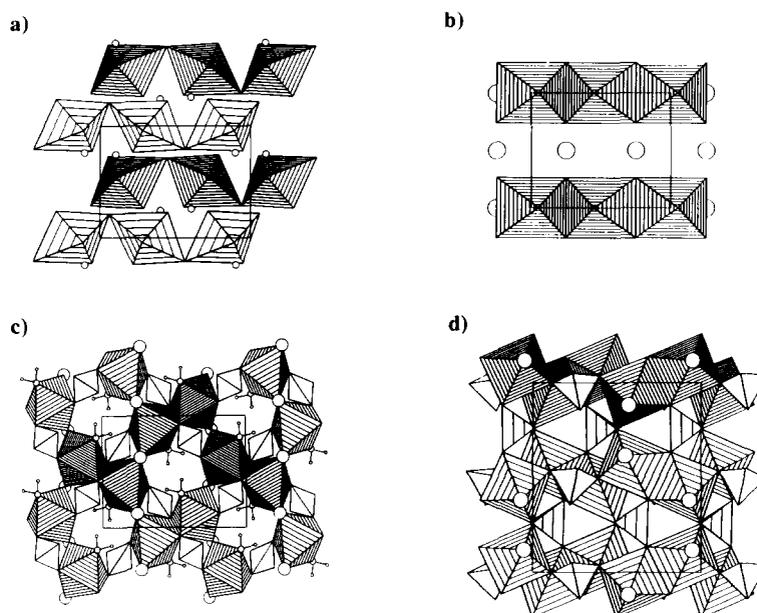


Fig. 5. (a) Characteristic $\frac{1}{\infty}$ [MO₅] chains of the 7 Å type observed in M(HPO₃·2H₂O) (M=Cu(II) and Cr(II)); (b) trans- $\frac{1}{\infty}$ [MO₄] chains in M(H₂PO₂)₂ [M=Fe(II), Co(II) and Zn(II)]; (c) crystal structure of MCl(H₂PO₂)·(H₂O) [M=Co(II) and Ni(II)] projected along (010). Chlorine bridging atoms are represented by the biggest circles; (d) packing of cis- $\frac{1}{\infty}$ [M₂O₈] chains found in M(HPO₃)·H₂O [M=Co(II) and Ni(II)].

in their hexagonal channels. The packing of octahedra in these hydrates can be considered as constituted by cis- $\frac{1}{\infty}$ [MO₄] chains. On the other hand, mixed chains appear in the structure of the related

chlorohypophosphites MCl(H₂PO₂)·H₂O, M=Co, Ni [16,35]. Their structure can be alternatively described as constituted by cis- $\frac{1}{\infty}$ [M₂O₆Cl₃] chains running along the (001) direction or by trans-

$\frac{1}{\infty}[\text{M}_2\text{O}_6\text{Cl}_3]$ chains along the (101) direction. The chlorine atoms act also as bridges among these mixed chains, which may equally be thought of as formed by (edge fused) dimers that share corners between them (fig. 5c). Lastly, the structure of the monohydrogenphosphites $\text{M}(\text{HPO}_3) \cdot \text{H}_2\text{O}$, $\text{M} = \text{Co}, \text{Ni}$ (fig. 5d), can be described on the basis of infinite $\text{cis-}\frac{1}{\infty}[\text{M}_2\text{O}_8]$ [14,35] chains running along the (100) direction and interlinked through oxygen atoms from HPO_3^{2-} groups.

The cobalt (or nickel) chlorohypophosphite and hydrated monohydrogenphosphite derivatives might have equally been classified in the VI category (i.e., layered structures), given that the packing of the abovementioned chains originates sheets piled up along the *a* or *b* directions for the chlorohypophosphite and phosphite compound, respectively. Actually, within this type were included many-layered mineral phosphates showing a variable condensation of the cationic polyhedra in their structures. According to Nriagu and Moore [17], the complexity of the aggregates of cationic polyhedra increases steadily as the pH and the metal ion concentration do, in such a manner that a certain progressive sequence can be established. Notwithstanding, the highly condensed phases of formula $\text{M}_{11}(\text{HPO}_3)_8(\text{OH})_6$, $\text{M} = \text{Co}, \text{Ni}, \text{Zn}$ [12,13], which are characterized by a complicated network of double chains of octahedra of the type $\frac{1}{\infty}[\text{M}_4\text{O}_{12}]$ which propagate along the (001) direction, see fig. 6, may hardly be classified under the Moore and Hawthorne's criteria.

Although the above considerations may be useful for the rationalization of the observations related to the cationic direct connectivity, they are in some way oversimplifying because we have relegated in the discussion the structural role played by the pseudotetrahedral species. This lack would make ambiguous our classification in some cases with regard to the very structural dimensionality of the lattice. Moreover, as suggested above, the understanding of the magnetic properties of the title compounds would not be possible without the consideration of the involvement of the anionic bridges in the exchange pathways between the metallic atoms. In fact, besides simple oxo (from H_2O or OH^- ligands) bridges, the phosphite and hypophosphite structures may display two basic bridging modes implying the

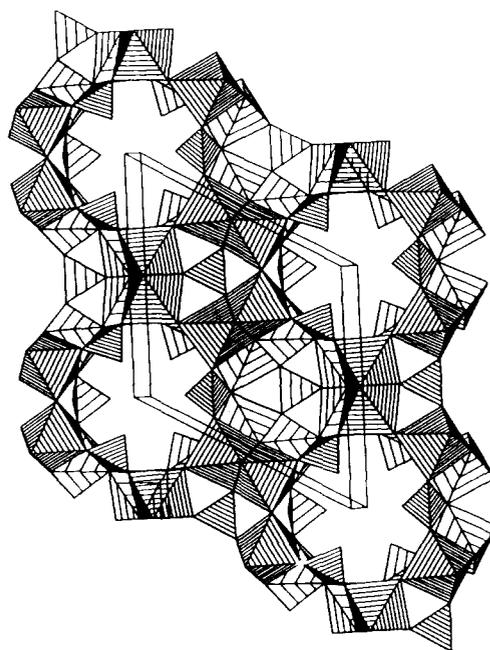


Fig. 6. View down *c* direction of the $\text{M}_{11}(\text{HPO}_3)_8(\text{OH})_6$ crystal structure.

oxoanions, namely $\mu-(\text{O})\text{H}_2\text{PO}_2^-$ or $\mu-(\text{O})\text{H}_n\text{PO}_3^{(3-n)-}$ and $\mu-(\text{O},\text{O}')\text{H}_2\text{PO}_2^-$ or $\mu-(\text{O},\text{O}')\text{H}_n\text{PO}_3^{(3-n)-}$.

As long as the formation of $\mu-(\text{O})$ bridges imply the sharing of an oxygen atom (regardless of its chemical nature) between different cationic polyhedra, they are absent in the solids of category I. However, the latter can present double $\mu-(\text{O},\text{O}')$ bridges connecting either two transition metal atoms, such as occurs in $\text{VO}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$ [54], $\text{Fe}(\text{H}_2\text{PO}_3)_3$ [24] and $\text{MnH}_3\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ [40], or one transition metal atom and one alkaline atom, as in $\text{MNa}(\text{H}_2\text{PO}_3)_3 \cdot \text{H}_2\text{O}$, $\text{M} = \text{Co}, \text{Mn}$ [52,53].

The phosphites displaying structures containing chains of the 7 Å type, $\text{M}(\text{HPO}_3) \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Cu}, \text{Cr}$) [37,38], exhibit both $\mu-(\text{O})$ and $\mu-(\text{O},\text{O}')$ bridges, but the first ones correspond to the hydration water molecules. On the contrary, the pseudotetrahedral anionic species may be involved in both bridging modes, $\mu(\text{O})$ and $\mu-(\text{O},\text{O}')$, in the case of the derivatives prepared in moderate acidic media with structures involving cationic condensations ranging from dimeric units up to chained or layered

entities. On the other hand, the role of chlorine atoms in the reported chlorohypophosphites is similar to that played by OH^- groups in the more condensed phases obtained in basic media, with the M-Cl-M bridges contributing to enhance the connectivity.

The role of these bridges may result determinant in order to establish the true structural dimensionality of the considered materials. In fact, as indicated above, although the initial idea prompting our investigation on these compounds was to favour the lowering of the structural dimensionality by going from PO_4^{3-} to HPO_3^{2-} , H_2PO_3^- and H_2PO_2^- , the result in practice is that a given anion, such as H_2PO_2^- , can give rise to structures ranging from monodimensionals, i.e. $\text{VO}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$, to tridimensionals, i.e. $\alpha\text{-M}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Mn}, \text{Zn}$).

In the structure of $\text{VO}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$ [54] (fig. 7), which we have described as built up from iso-

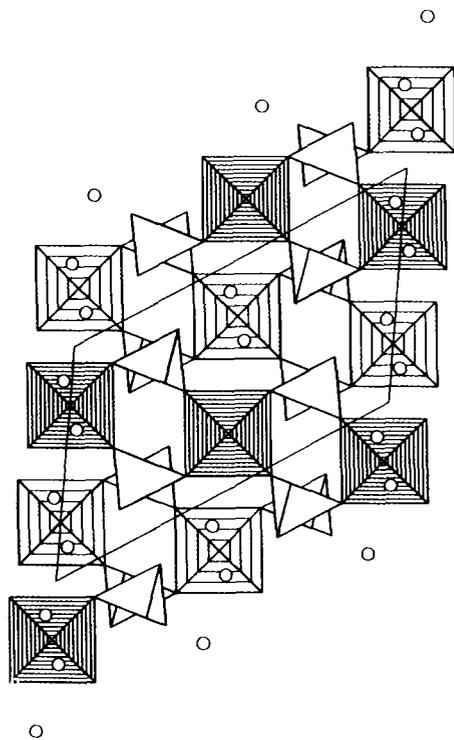


Fig. 7. Projection of the atomic arrangement of $\text{VO}(\text{H}_2\text{PO}_2)_2 \cdot (\text{H}_2\text{O})$ along b direction.

olated octahedra, both the presence of $\text{di-}\mu\text{-(O,O')}$ bridges and the characteristic anisotropy of the oxovanadium cation cooperate to yield a truly 1-D system (i.e., the coupling of the isolated octahedra through the $\text{di-}\mu\text{-}$ bridges originates chains that propagate along the (101) direction). The only connection among these chains is due to an hydrogen bonding network involving the water molecules trans to the short V-O double bonds and the apical oxygen atoms from octahedra of adjacent chains. The weakness of this link among chains becomes manifest from the temperature dependence of their relative arrangement, which affect appreciably to the cell parameter values.

This same $\text{di-}\mu\text{-(O,O')}$ H_2PO_2^- bridge type gives rise to 3D lattices in the case of the $\alpha\text{-M}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Zn}, \text{Mn}$) solids. The difference lies in the fact that the $\text{di-}\mu\text{-}$ bridges are now connecting dimeric $[\text{M}_2\text{O}_{10}]$ units laying in the ac and ab planes, what results in a tridimensional bonding framework. A similar situation occurs in the case of $\beta\text{-Mn}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$ [22].

4. Concluding remarks

Starting from very simple hypotheses, it has been possible to make reasonably successful proposals about the metal coordination polyhedra in the solids. Furthermore, it seems possible to predict the way in which the connectivity would vary as consequence of changes in the experimental conditions. Thus, cationic condensation is favoured by increasing pH values, whereas an increase of C_M (for a given P/M ratio) induces condensation by water removal and $\mu\text{-O}$ -ligand bridges formation. The latter also is facilitated by increasing the experimental pressure and temperature. In short, it is possible to predict rather accurately the metal coordination polyhedron, and subsequently the connectivity through the solid, in any oxophosphorous derivative starting from the only knowledge of its stoichiometric composition.

From the rationalization of the transition metal oxophosphorous derivatives preparative chemistry, it can reasonably be expected that new compounds will be fully characterized in a next future. The latter, in turn, would help to progress in the understanding of the intricate nature of the magnetos-

structural correlations involving more or less symmetrical diamagnetic anions, and further developments in this field would become possible.

As occurred for phosphate derivatives, the structural diversity of oxophosphorous derivatives makes particularly interesting to search for correlations leading to guidelines for the rationalization of their magnetic properties. Although this aim is complicated at this moment because of the systematic absence of data in the literature, we have recently approached the study of the magnetic behaviour of several materials in these families [14,15]. From the previous results on oxovanadium phosphates [1-3], it seems reasonable to assume that the magnetic properties of transition metal phosphites and hypophosphites will be highly dependent on the possible involvement of the phosphorus d orbitals in the propagation of magnetic interactions. Both ferro and antiferromagnetic interactions have been observed in those derivatives whose magnetic behaviour we have investigated. Initially, it may be expected that the activity of μ -(O) bridges in the transmission of exchange interactions be more relevant than that of the μ -(O,O') ones. However, this activity will depend to a great extent on their topology as well as on their relative orientation with regard to the spin density containing orbitals of the metallic atoms. Although the implication of the HPO_3^{2-} or H_2PO_2^- groups in the propagation of the exchange interactions seems very likely, the complexity of the structural networks of these materials makes currently impossible to discuss accurately about the activity of one or another bridge in the exchange pathways, and a systematic comparative study of the magnetic properties of other transition metal derivatives is needed to gain insight in the understanding of the magnetic interactions occurring in these materials.

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References

- [1] D. Beltrán, A. Beltrán, P. Amorós, R. Ibáñez, E. Martínez, A. Le Bail, G. Ferey and G. Villeneuve, *Eur. J. Solid State Inorg. Chem.* 28 (1991) 131.
- [2] G. Villeneuve, K.S. Shu, P. Amorós, N. Casañ and D. Beltrán, *Chem. Mater.* 4 (1992) 108.
- [3] P. Amorós, A. Beltrán and D. Beltrán, *J. Alloys Compounds* 188 (1992) 123.
- [4] R.G. Hazell, A.C. Hazell and B. Kratochvill, *Acta Cryst. B38* (1982) 1267.
- [5] M. Loukili, J. Durand, L. Cot and M. Rafiq, *Acta Cryst. C44* (1988) 6.
- [6] J. Durand, M. Loukili, N. Tijani, M. Rafiq and L. Cot, *Eur. J. Solid State Inorg. Chem.* 25 (1988) 297.
- [7] J. Loub and B. Kratochvill, *Chem. Listy* 81 (1987) 337.
- [8] G. Huan, A.J. Jacobson, J.W. Johnson and D.P. Goshorn, *Chem. Mater* 4 (1992) 661.
- [9] Y. Zhang and A. Clearfield, *Inorg. Chem.* 31 (1992) 2821.
- [10] A. Clearfield, in *Design of New Materials*, eds. A. Clearfield and L. Cocke (Plenum Press, New York, 1986).
- [11] M.B. Dines and P. Digiacomo, *Inorg. Chem.* 20 (1981) 92.
- [12] M.D. Marcos, P. Amorós, R. Martínez-Mañez, A. Beltrán and J.P. Attfield, *Chem. Mater.* 5 (1993) 121.
- [13] M.D. Marcos, P. Amorós and A. Le Bail, *J. Solid State Chem.*, to be published.
- [14] F. Sapiña, P. Gómez, M.D. Marcos, P. Amorós, R. Ibáñez, D. Beltrán, R. Navarro, C. Rillo and F. Lera, *Eur. J. Solid State Inorg. Chem.* 26 (1989) 603.
- [15] M.D. Marcos, P. Gómez, P. Amorós, F. Sapiña, D. Beltrán, R. Navarro, C. Rillo and F. Lera, *J. Appl. Phys.* 67 (1990) 5998.
- [16] M.D. Marcos, P. Amorós, R. Martínez-Mañez, A. Beltrán and J.P. Attfield, *Inorg. Chem.*, to be published.
- [17] J.O. Nriagu and P.B. Moore, *Phosphate Minerals* (Springer, Berlin, 1984).
- [18] J. Livage, M. Henry and C. Sanchez, *Prog. Solid State Chem.* 18 (1988) 259.
- [19] C.F. Baes Jr. and R.E. Mesmer, *The Hydrolysis of Cations* (Wiley, New York, 1976).
- [20] C.J. Brinker and J.W. Sherer, *Sol-Gel Science. The Physics and Chemistry of Sol-Gel Processing* (Academic Press, Oxford, 1990).
- [21] N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements* (Pergamon Press, Oxford 1985).
- [22] T.J.R. Weakley, *Acta Cryst. B25* (1979) 42.
- [23] *Gmelin Handbook of Inorganic Chemistry, Vol. Mn (C9)* 8th Ed. (Springer, Berlin, 1983).
- [24] J. Sala, R. Kergoat and J. Guerschais, *C. R. Acad. Sci. (Paris)* 274 (1972) 595.
- [25] G. Brun and M. Dumail, *C. R. Acad. Sci. (Paris)* 272 (1971) 1866.
- [26] M. Sghygar, J. Durand, L. Cot and M. Rafiq, *Acta Cryst. C47* (1991) 8.
- [27] *Gmelin Handbook of Inorganic Chemistry, Vol. Fe (59B)* (Springer, Berlin, 1932).

- [28] Gmelin Handbook of Inorganic Chemistry, Vol. Co (58A) (Springer, Berlin, 1961).
- [29] Gmelin Handbook of Inorganic Chemistry, Vol. Ni (57B) (Springer, Berlin, 1966).
- [30] K.F. Purcell, J.C. Kotz, *Inorganic Chemistry* (W.B. Saunders Co., Philadelphia, 1977), Chap. 13.
- [31] M.D. Marcos, P. Amorós, F. Sapina and D. Beltrán, *J. Alloys Compounds* 188 (1992) 133.
- [32] M. Sghyar, J. Durand, L. Cot and M. Rafiq, *Acta Cryst. C* 46 (1990) 1378.
- [33] C.Y. Ortiz, P.J. Squattrito, M. Shieh and A. Clearfield, *Inorg. Chem.* 28 (1989) 2608.
- [34] J. Durand, L. Cot, M. Sghyar and M. Rafik, *Acta Cryst. C* 48 (1992) 1171.
- [35] J.I. Michailow, O.I. Lomowski, A.B. Brosalin and W.W. Boldirew, *Z. Anorg. Allg. Chem.* 463 (1980) 199.
- [36] M.D. Marcos, R. Ibáñez, P. Amorós and A. Le Bail, *Acta Cryst. C* 47 (1991) 1152.
- [37] E.J. Baran, S.B. Etcheverri and E. Diemann, *Polyhedron* 4 (1985) 1711.
- [38] M. Hanlovic, *Acta Cryst. B* 25 (1969) 227.
- [39] B. Jiri, B. Kratochvil and I. Cisarova, *Collect. Czech. Chem. Commun.* 52 (1987) 1742.
- [40] J. Loub, J. Podlahova and J. Jecny, *Acta Cryst. B* 34 (1978) 32.
- [41] I. Cisarova, C. Novak, V. Petricek, B. Kratochvil and J. Loub, *Acta Cryst. B* 38 (1982) 1687.
- [42] L.G. Sillen and A.E. Martell, *Stability Constants of Metal Ion Complexes* (Alden Press, Oxford, 1971).
- [43] K. Iijima, F. Marumo and H. Takei, *Acta Cryst. B* 38 (1982) 1112.
- [44] M. Shieh, K.J. Martin, P.J. Squattrito and A. Clearfield, *Inorg. Chem.* 29 (1990) 958.
- [45] F. Giordano, L. Randaccio and A. Ripamonti, *Acta Cryst. B* 25 (1969) 1057.
- [46] A. Whitaker, *Acta Cryst. B* 31 (1975) 2026.
- [47] M.T. Averbuch-Pouchot and J.C. Guitel, *Acta Cryst. B* 33 (1977) 1427.
- [48] P.B. Moore, *Neues Jahrb. Mineral. Monatsh.* H1 (1970) 39.
- [49] P.B. Moore, *Neues Jahrb. Mineral. Monatsh.* H4 (1970) 163.
- [50] P.B. Moore, *Proc. 2nd Intern. Congress on Phosphorous Compounds*, April 21–25, Boston (1980).
- [51] F.C. Hawthorne, *Am. Miner.* 70 (1985) 455.
- [52] R. Chmelikova, J. Loub and V. Petricek, *Acta Cryst. C* 42 (1986) 1281.
- [53] B. Kratochvil, J. Podlahova, S. Habibpur, V. Petricek and K. Maly, *Acta Cryst. B* 38 (1982) 2436.
- [54] M.D. Marcos, P. Amorós and A. Le Bail, unpublished results.
- [55] M. Sghyar, J. Durand, L. Cot and M. Rafiq, *Acta Cryst. C* 47 (1991) 2515.