

# Superexchange pathways in oxovanadium(IV) phosphates

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## Abstract

Oxovanadium(IV) phosphates show a diversity of magnetic behaviours that cannot be deduced from their respective structural features only. In part, this is due to the involvement of phosphate bridges in the spin transfer between V(IV) centres, and  $^{31}\text{P}$  solid state nuclear magnetic resonance becomes a key tool in determining the exchange mechanisms. The magnetic properties of a wide set of vanadium(IV) containing derivatives can be explained by realizing that a good overlap of the magnetic orbitals may be achieved through paths involving phosphorus d orbitals.

## 1. Introduction

Knowledge of the chemistry of the V–P–O system has been significantly improved in recent years because of the interest shown by solid-state chemists in its catalytic relevance [1]. This system shows a very rich crystallochemistry that, in turn, results in a seemingly very involved magnetochemistry [1, 2]. Both the accessibility of several oxidation states and the ability of vanadium and phosphate polyhedra to form a diversity of frameworks lie behind the versatile solid-state chemistry.

Vanadium(IV) containing materials are characterized by the occurrence of vanadyl groups, formally  $\text{VO}^{2+}$ . In most of them, the environment of vanadium atoms is constituted by oxygen atoms. While the oxygen atoms are usually arranged at the corners of octahedra, distorted octahedra or square pyramids, the very short vanadium to oxygen distance (*ca.* 1.5–1.6 Å) in the vanadyl cation, typical of a V=O double bond, implies a strong anisotropy in the vanadium bonding network [3]. Moreover, the diversity of ways in which oxygen atoms of  $(\text{VO}_6)$  or  $(\text{VO}_5)$  polyhedra may be shared results in a great variety of condensed entities (dimers, regular chains, double chains, ...) [1]. In addition, very different arrays are possible from protonation and condensation of  $(\text{PO}_4)$  units (to give  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{P}_2\text{O}_7^{4-}$ ,  $\text{P}_2\text{O}_6^{2-}$ , ...) [1, 4, 5], and the presence of alkali [6] or transition metal [7] cations gives rise to a wide range of structural types including caged [8], tunnelled [9] or layered [10] arrangements.

Such a diversity of patterns really involves a variety of bridging modes between vanadium atoms able to support magnetic interactions in oxovanadium(IV) derivatives [1, 2, 11]. In this situation, the discovery of magnetostructural correlations is a challenging task from the theoretical point of view. To date, the partici-

pation of phosphate groups in the magnetic exchange has usually been neglected in the related literature [12]. Nevertheless, it has been claimed that superexchange might occur through highly symmetrical diamagnetic anions in molecular derivatives [13], and in oxovanadium(IV) hydrogenphosphate hydrates, the involvement of phosphate groups in the spin density transfer between antiferromagnetically coupled vanadium ions has recently been established with the help of a variable temperature solid-state  $^{31}\text{P}$  nuclear magnetic resonance (NMR) [14].

Based on the thermal variation of susceptibility, electron paramagnetic resonance (EPR) and  $^{31}\text{P}$  NMR experiments and semiquantitative calculations, we present here a series of consistent sets of magnetic orbitals able to explain the diversity of experimental magnetic behaviours and the magnitude of the superexchange interactions in a great number of oxovanadium(IV) phosphates.

## 2. Results and discussion

The experimental data on which the following discussion is based come mainly from our previous work in this field. The more significant results in the present context are summarized in Table 1. Procedural and other experimental details can be found in the references included in the last column.

### 2.1. $^{31}\text{P}$ nuclear magnetic resonance results

The involvement of phosphate groups in the spin transfer between vanadium atoms in oxovanadium(IV) phosphates was suggested in a previous work as the way to overcome the seeming contradictions resulting from the comparison between their structural features

TABLE 1. Magnetic parameters, NMR shift and magnetic active pathway for  $\text{VO}(\text{H}_x\text{PO}_4)_x \cdot y\text{H}_2\text{O}$ ,  $\text{VO}(\text{H}_2\text{AsO}_4)_2$  and  $(\text{VO})_2\text{P}_2\text{O}_7$ 

Solid	Best fit model <sup>a</sup>	$-J(\text{K})$	RSE		NMR $^{31}\text{P}$ $\delta$ shift <sup>c</sup> (ppm)	Reference
			$g$	$\Delta ms = 2$		
$x = 1, y = 0.5$	HD	43.0	1.966	yes	1736	2
$x = 1, y = 2(\beta)$	HLMC	5.0	1.965	no	607–946	2, 10
$x = 1, y = 2(\alpha)$	HD	23.0	1.965	yes	1360	2, 14
$x = 1, y = 4$	HLMC	4.7	1.961	yes	190–334	2, 11
$x = 2, y = 0$	HLMC	2.0	1.968	no	<10	2
$\text{VO}(\text{H}_2\text{AsO}_4)_2$	HLMC	3.0	1.967	no	—	2, 15
$(\text{VO})_2\text{P}_2\text{O}_7$	HAMC ( $\alpha = 0.7$ )	65.7	1.960	yes <sup>(b)</sup>	2000–2500	2

<sup>a</sup>Hamiltonians used to model the experimental magnetic behaviour: HD  $H = -2JS_1 \cdot S_2$  (isotropic Heisenberg dimer), HLMC  $H = -2J\sum_i(S_i \cdot S_{i+1})$  (Heisenberg linear magnetic chain), HAMC  $H = -2J_1\sum_i(S_{2i} \cdot S_{2i+1} + \alpha S_{2i} \cdot S_{2i-1})$  (Heisenberg alternating magnetic chain).

<sup>b</sup>Weak signal detected at  $T < 15$  K.

<sup>c</sup>The shifts of the lines were referenced to 85%  $\text{H}_3\text{PO}_4(\text{aq})$  measured using the same probe.

and the respective modelizations required to reproduce the experimental magnetic behaviours ( $\chi$  vs. T) [2]. It was suggested that experimental evidence supporting this hypothesis (*i.e.* showing that phosphorus atoms support spin density) might be provided using  $^{31}\text{P}$  solid-state NMR as a local probe.

In fact, it has recently been possible to elucidate unambiguously the participation of  $(\text{HPO}_4)$  units in the exchange mechanism in the cases of  $\alpha$ - $\text{VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$  and  $\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$ . Thus, a temperature variable  $^{31}\text{P}$  NMR study yields, respectively, spin densities of  $2.2 \times 10^{-3}$  and  $3.2 \times 10^{-3}$  unpaired electrons per phosphorus nucleus [14]. These are, however, simple cases within the reported oxovanadium(IV) phosphates. In both of them, there is only one phosphorus crystallographic atom type [16, 17] and, moreover, the antiferromagnetic coupling between vanadium atoms is relatively strong. Another simple case is that of  $\text{VO}(\text{H}_2\text{PO}_4)_2$ . The absence of a shift in the NMR line (Table 1) agrees with what might be expected *a priori*: the superexchange through oxo bridges is more effective than through phosphate groups.

The interpretation of  $^{31}\text{P}$  NMR results for the remaining solids (Table 1) is not as straightforward. The presence of more than one structural type of phosphorus atom [10, 18] leads to complex spectra displaying several slightly shifted signals. In addition, their thermal variations do not offer significant additional information because of the weakness of the magnetic coupling (except for  $(\text{VO})_2\text{P}_2\text{O}_7$ ). In any case, we observe both that the  $^{31}\text{P}$  NMR signals appear shifted from the diamagnetic standard and that a correlation exists between the shifts of the NMR lines and the exchange constants. Both factors clearly indicate the presence of a finite spin density at the phosphorus nuclei and, consequently, the participation of their orbitals in the exchange pathways.

## 2.2. Exchange pathways

Given the implication of the phosphate groups in the magnetic interaction mechanism, we may now wonder about its nature, *i.e.* about the possible magnetic orbitals which would involve contributions from phosphate molecular orbitals.

Figure 1 represents an idealized projection showing the relevant fragment of the crystal structure of oxovanadium(IV) pyrophosphate,  $(\text{VO})_2\text{P}_2\text{O}_7$ . This scheme includes a set of structural motifs which *a priori* might act as a support of magnetic interactions. Thus, aside from the  $\mu$ -oxo-bridges which connect vanadium atoms of adjacent layers along the (001) direction, in  $(\text{VO})_2\text{P}_2\text{O}_7$  we find  $\mu$ -(O)phosphate (V1–V2) and two topologically different types of  $\mu$ -(O,O')phosphate (V3–V4, V1–V3) vanadium to vanadium bridges. In fact, obviating their possible distortions, these are the three classes of bridging modes which can be found in oxovanadium(IV) phosphates (see Table 2).

The highest possible local symmetry around phosphorus atoms in all these solids is  $C_{3v}$ . Given that the spin density of vanadium atoms is mainly localized in  $d_{xy}$  orbitals [3], the only phosphorus or oxygen atomic orbitals (AO) which might be involved in the exchange pathways are those able to hold electronic density in the  $xy$  plane, that is to say the  $d_{xy}$ ,  $d_{x^2-y^2}$  and  $p_x, p_y$

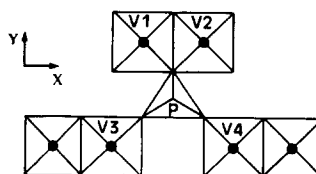


Fig. 1. Fragment of the crystal structure of  $(\text{VO})_2\text{P}_2\text{O}_7$  projected in the  $xy$  plane. This idealized scheme shows  $\mu$ -(O,O') and  $\mu$ -(O) phosphate bridges (see text).

TABLE 2. Magnetic pathways for  $\text{VO}(\text{H}_x\text{PO}_4)_x \cdot y\text{H}_2\text{O}$ ,  $\text{VO}(\text{H}_2\text{AsO}_4)_2$  and  $(\text{VO})_2\text{P}_2\text{O}_7$ 

Solid	Active magnetic pathway
$\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$	$\mu\text{-(O)HPO}_4$
$\beta\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$	$\text{di-}\mu\text{-(O,O')HPO}_4$
$\alpha\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$	$\text{di-}\mu\text{-(O,O')HPO}_4$
$\text{VO}(\text{HPO}_4) \cdot 4\text{H}_2\text{O}$	$\text{di-}\mu\text{-(O,O')HPO}_4$
$\text{VO}(\text{H}_2\text{PO}_4)_2$	$\mu\text{-(oxo)}$
$\text{VO}(\text{H}_2\text{AsO}_4)_2$	$\mu\text{-(oxo)}$
$(\text{VO})_2\text{P}_2\text{O}_7$	$\mu\text{-(O)PO}_4$ and $\text{di-}\mu\text{-(O,O')PO}_4$

phosphorous AO pairs and the symmetry adapted linear combinations (SALC) of p AO coming from the three equivalent oxygen atoms. Taking these considerations into account, good overlaps of the magnetic orbitals are provided through the paths schematized in Fig. 2.

Thus, plotted in Fig. 2(a) are the AO involved in the exchange pathway connecting V1–V2 atoms (Fig. 1) in the dimeric moiety through  $\mu\text{-(O)}$ phosphate bridges. This AO set is defined by  $d_{xy}(\text{V})//p(\text{O})//d_{x^2-y^2}(\text{P})//p(\text{O})//d_{xy}(\text{V})$  where, using the Ginsberg notation [19],

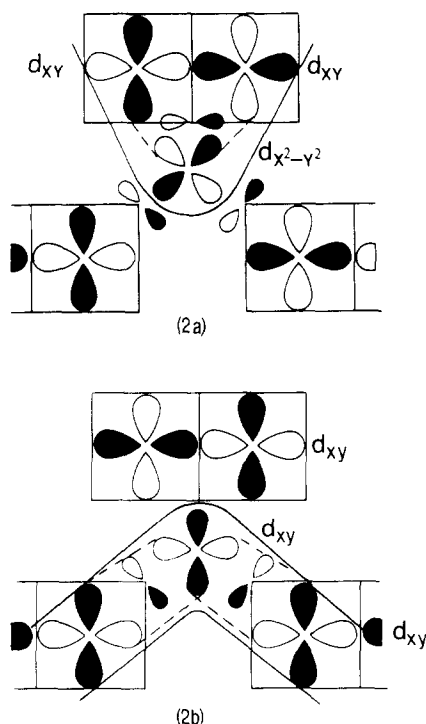


Fig. 2. (a) AO set (projected in the  $xy$  plane) involved in the exchange pathway connecting V1 and V2 atoms through  $\mu\text{-(O)}$ phosphate bridges. (b) AO set in the case of V3–V4 interaction through  $\mu\text{-(O,O')}$ phosphate bridges. It can be noted that V1–V3 and V1–V4 interactions are unfavourable. Dotted lines indicate overlap regions. Solid lines represent nodal zones.

the symbol // indicates non-zero overlap. In the case of the V3–V4 interactions (Fig. 1), the AO set providing an active path through  $\mu\text{-(O,O')}$ phosphate bridges is  $d_{xy}(\text{V})//p(\text{O})//d_{xy}(\text{V})//p(\text{O})//d_{xy}(\text{V})$  (Fig. 2(b)). In both cases, the nature of phosphate HOMO orbitals and the symmetry of the arrangements indicate that non-zero overlap is due to  $\pi$  interactions.

The maximum  $\pi$  overlap resulting from the above AO set, and consequently the strongest magnetic interactions, is obtained when the  $\text{VO}_6$  octahedra in the respective dimeric moieties (V1–V2, V3–V4, V1–V3) are arranged in such a way that vanadium  $d_{xy}$  orbitals are coplanar and share a lobe axis. This situation is actually observed in the intrachain  $\text{di-}\mu\text{-(O,O')}$ phosphate (V3–V4) and  $\text{di-}\mu\text{-(O,O')}$ phosphate (V1–V2) bridges ( $J(\text{V3-V4}) = -46$  K and  $J(\text{V1-V2}) = -65.7$  K [2]) in the case of  $(\text{VO})_2\text{P}_2\text{O}_7$ . Any modification of this optimal topology will reduce the overlap and, accordingly, will result in weaker magnetic interactions. In fact, the magnetic interaction through  $\mu\text{-(O,O')}$ phosphate interchain bridges (V1–V3) in  $(\text{VO})_2\text{P}_2\text{O}_7$  leads to a negligible coupling constant because of the in-plane displacement of the respective  $\text{VO}_6$  octahedra.

Similar considerations allow us to propose as active exchange pathways in oxovanadium(IV) hydrogen-phosphates those listed in Table 2. Thus, the nature of the bridging modes in  $\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$  is the same as that in the above case [2]. However, the fact that the equatorial “ $xy$ ” planes of the edge sharing  $\text{VO}_6$  octahedra (V1–V2) define a  $60^\circ$  dihedral angle [16] leads to a poorer overlap of the magnetic orbitals through the  $\mu\text{-(O)}$ phosphate bridges and makes ineffective both the inter (V1–V3) and intrachain (V3–V4)  $\text{di-}\mu\text{-(O,O')}$ phosphate bridges.

The only phosphato bridges present in the structures of  $\alpha\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$ ,  $\beta\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$  and  $\text{VO}(\text{HPO}_4) \cdot 4\text{H}_2\text{O}$  belong to the  $\mu\text{-(O,O')}$  type [2]. Dealing with these last materials, the fact that the only case in which  $\text{VO}_6$  octahedra are adequately arranged is that of  $\alpha\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$  becomes evident from the magnitude of the magnetic interactions (Table 1). Actually, whereas the topology of the  $\mu\text{-(O,O')}$ phosphate bridges in  $\alpha\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$  [17] is close to that found in  $(\text{VO})_2\text{P}_2\text{O}_7$  (V3–V4), the relative displacement of  $\text{VO}_6$  octahedra along the  $z$  axis in the case of  $\text{VO}(\text{HPO}_4) \cdot 4\text{H}_2\text{O}$  [18] and the twisting of the  $\text{VO}_6$  equatorial planes in that of  $\beta\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$  [10] yield less effective exchange pathways through phosphate groups.

Finally, in the isostructural dihydrogen derivatives  $(\text{VO}(\text{H}_2\text{PO}_4)_2$  and  $\text{VO}(\text{H}_2\text{AsO}_4)_2$ ), magnetic interactions through  $\mu\text{-(O,O')H}_2\text{AO}_4$  ( $A \equiv \text{P, As}$ ) bridges (the only non-oxo bridges present in the structure [15]) can be neglected because of the highly mismatched

disposition of the  $d_{xy}$  spin density containing vanadium AO (similar to V1–V4 shown in Fig. 1). It must be stressed that, contrary to *a priori* expectations [12], the superexchange through  $\text{PO}_4$  groups turns out to be more effective than through simple oxo bridges. In fact, the magnetic activity of  $\mu$ -oxo bridges only becomes apparent in the absence of a suitable path involving  $\text{PO}_4$  groups. In any case, propagation of significant magnetic interaction along a chain of  $\mu$ -oxo bridged  $\text{VO}_6$  octahedra would imply an important admixture of  $d_{xz}$  and  $d_{yz}$  orbitals in the ground state that nevertheless is very small given the strong tetragonal field in oxovanadium(IV) compounds. This is the reason for the small value of the magnetic interaction ( $J < 3$  K) observed in the  $\text{VO}(\text{H}_2\text{AO}_4)_2$  diacid derivatives.

Otherwise, all the above agrees with preliminary results based on simplified extended Huckel calculations. In fact, overlap between magnetic orbitals on vanadium atoms only is achieved when 3d P AO are included in EH calculations.

### 3. Concluding remarks

The reliability of the present approach is supported not only by its ability to interpret the bewildering magnetic behaviour of the oxovanadium(IV) hydrogen-phosphates but also by its ability to rationalize the magnetic properties of a more wide and diverse set of oxovanadium(IV) containing phosphates. Thus, as shown in Table 3, the bridging modes that we suggest as active exchange pathways (according to the above discussion) explain the experimental magnetic behaviour in all cases for which susceptibility data have been reported in the literature. We have also included in Table 3 estimates of the magnitude of the magnetic interactions for phosphates whose structures are known but for which susceptibility measurements are not available. These predictions are based on the nature of the exchange pathways which, in the light of the structural features, would be active according to our considerations. The substantiation of these “prophecies”,

TABLE 3. Exchange pathways in other oxovanadium(IV) phosphates

Compound	V(IV) octahedra array	Magnitude of magnetic interactions	Suggested active bridge <sup>c</sup>	Reference
$\text{K}_2(\text{VO})_3(\text{HPO}_4)_4$	chains	weak (1D) <sup>b</sup>	$\mu(\text{oxo})$ $\mu-(\text{O},\text{O}')\text{PO}_4^{(\text{w})}$	8
$\text{Rb}_2\text{V}_3\text{P}_4\text{O}_{17}$	chains	weak (1D) <sup>b</sup>	$\mu(\text{oxo})$ $\mu-(\text{O},\text{O}')\text{P}_2\text{O}_7^{(\text{w})}$	20
$(\text{VO})_2[\text{CH}_2(\text{PO}_3)_2] \cdot 4\text{H}_2\text{O}$	isolated	weak (isolated)	$\mu-(\text{O},\text{O}')\text{RPO}_3^{(\text{w})}$	21
$\text{VO}_6\text{H}_5\text{PO}_3 \cdot \text{H}_2\text{O}$	chains	strong (dimers) <sup>b</sup>	$\text{di-}\mu(\text{O},\text{O}')\text{RPO}_3^{(\text{s})}$	22
$\text{Ti}_3\text{V}_2\text{O}_3(\text{VO})(\text{PO}_4)_2(\text{HPO}_4)$	chains	weak (1D) <sup>b</sup>	$\mu-(\text{oxo})$ $\text{di-}\mu-(\text{O},\text{O}')\text{PO}_4^{(\text{w})}$	23
$\text{RbV}_3\text{P}_4\text{O}_{17+x}$	chains	weak (1D) <sup>b</sup>	$\mu-(\text{oxo})$ $\mu-(\text{O},\text{O}')\text{P}_2\text{O}_7^{(\text{w})}$	24
$\text{K}_2\text{VOP}_2\text{O}_7$	chains	weak <sup>a</sup> (2D) <sup>b</sup>	$\mu-(\text{O},\text{O}')\text{P}_2\text{O}_7^{(\text{w})}$ $\mu-(\text{O},\text{O}')\text{PO}_4^{(\text{m})}$	25
$\text{A}_2\text{VOP}_2\text{O}_7$ (A $\equiv$ Rb, Cs)	chains	weak <sup>a</sup> (2D) <sup>b</sup>	$\mu-(\text{O},\text{O}')\text{P}_2\text{O}_7^{(\text{w})}$ $\mu-(\text{O},\text{O}')\text{PO}_4^{(\text{m})}$	26
$\text{Zn}_2\text{VO}(\text{PO}_4)_2$	chains	weak <sup>a</sup> (1D) <sup>b</sup>	$\mu-(\text{oxo})$ $\mu-(\text{O},\text{O}')\text{PO}_4^{(\text{w})}$	7
$\text{A}_2(\text{VO})_3(\text{P}_2\text{O}_7)_2$ (A $\equiv$ K, Rb, Cs)	chains	weak <sup>a</sup> (1D) <sup>b</sup>	$\mu-(\text{oxo})$ $\mu-(\text{O},\text{O}')\text{P}_2\text{O}_7^{(\text{w})}$	9
$\text{LiVOPO}_4$	chains	weak <sup>a</sup> (1D) <sup>b</sup>	$\mu-(\text{oxo})$ $\mu-(\text{O},\text{O}')\text{PO}_4^{(\text{w})}$	27
$\text{K}_2(\text{VO})_2\text{P}_3\text{O}_9(\text{OH})_3 \cdot 1.125\text{H}_2\text{O}$	isolated	medium <sup>a</sup> (1D) <sup>b</sup>	$\text{di-}\mu-(\text{O},\text{O}')\text{PO}_4^{(\text{m})}$	6
$\text{KVPO}_5$	chains	weak <sup>a</sup>	$\mu-(\text{oxo})$ $\mu-(\text{O},\text{O}')\text{PO}_4^{(\text{w})}$	28
$\beta\text{-K}_2\text{V}_3\text{P}_4\text{O}_{17}$	chains	strong <sup>a</sup> (1D) <sup>b</sup>	$\mu-(\text{O})\text{P}_2\text{O}_7^{(\text{s})}$ $\mu-(\text{O},\text{O}')\text{P}_2\text{O}_7^{(\text{w})}$	29

<sup>a</sup>Magnetic data not reported in the literature, estimations based on the model discussed in this work.

<sup>b</sup>Suggested magnetic dimensionality.

<sup>c</sup>When phosphate bridges are involved, the superscripts indicate that their topology is (s) favourable, (m) medium and (w) unfavourable.

through future experimental evidence, would constitute a definitive justification of the present approach.

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