

Magnetostructural Correlations in α -VO(HPO₄)·2H₂O: Magnetic Susceptibility and ³¹P Solid-State NMR Study

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Magnetic interactions in α -VO(HPO₄)·2H₂O are reported. The antiferromagnetic interaction between V⁴⁺ centers occurs by spin transfer through the phosphate bridges. Despite the layer structure built from connecting VO₆ chains, the compound behaves magnetically as isolated dimers. Emphasis is made on the role of the local probe (³¹P solid-state NMR) to elucidate the exchange mechanism and eliminate the possible ambiguities derived from observation of the structure only.

In recent years there has been significant interest by solid-state chemists in the V-P-O system, given its catalytic relevance,^{1,2} in particular, oxovanadium(V) α -VOPO₄ and related intercalated phases have been widely studied.³⁻⁷ On the other hand, oxovanadium(IV) phosphates offer a large variety of crystal structures yielding different types of low-dimensional magnetic interactions.⁸ Hence, the magnetic behavior ranges from isolated vanadyl dimers in VO(HPO₄)·¹/₂H₂O,⁹ to regular vanadyl chains in VO(PO₃)₂ and VO(H₂PO₄)₂,^{8,10} and to double chains in (V-O)₂P₂O₇ and VO(HPO₄)·4H₂O.^{11,12}

Recently, other members of the family of hydrogen phosphate hydrates have been isolated, namely, VO(HPO₄)·*n*H₂O with *n* = 1, 2 (α and β), and 3,¹³ the crystal structures of the two forms of the dihydrate have been determined.^{14,15} Although all of these structures are based on linking of VO₆ octahedra and PO₄ tetrahedra, they are actually very different. The magnetic properties differ not only on the type of interactions (dimers, single or double chains) but also on their strength. The observed exchange constants $|J|$, vary from 2K for VO(H₂PO₄)₂ to 43K for VO(HPO₄)·¹/₂H₂O. A classification of the [VO₆]-[PO₄] connections has been proposed which is able to offer a consistent qualitative magnetostructural correlation for the known oxovanadium(IV) phosphates.¹³ This classification is based on the fact that the exchange pathways seem to involve to some extent the [PO₄] tetrahedra. If this is the case, one should expect some difference in the ³¹P NMR spectra, due to the shift created by the presence of a finite spin density at the phosphorus nuclei. In fact, some correlation exists between the shift of the NMR line and the exchange constant.^{13b}

In this article we present the magnetic properties of the dihydrate α -VO(HPO₄)·2H₂O and their interpretation on the basis of an isotropic Heisenberg model. Experimental evidence of the role of [PO₄] groups in the exchange mechanism is also given: the shift observed in the ³¹P NMR line and its thermal variation confirm the presence of a finite spin density at the phosphorus nuclei.

The crystal structure of α -VO(HPO₄)·2H₂O has been recently established.¹⁵ The unit cell is monoclinic, space group *P*2₁/*c* with *a* = 7.621 Å, *b* = 7.439 Å, *c* = 9.493 Å and β = 95.44°. The structure consists of infinite chains

of corner sharing [VO₆] octahedra running along the *b* axis. These chains are linked together by HPO₄ groups which share two oxygen atoms with two adjacent [VO₆] octahedra from the same chain and a third one with an octahedron belonging to an adjacent chain (Figure 1). Vanadyl hydrogen phosphate layers are formed, held together by hydrogen bonding.

Experimental Section

α -VO(HPO₄)·2H₂O was prepared using a method described elsewhere.¹³ A mixture of V₂O₅ and concentrated H₃PO₄ (85%) in acetone-water medium (ratio 6:100) was refluxed at 50 °C during 50 h (under the hood) with a small excess of HI(aq) as reducing agent and proton donor. After cooling, the microcrystalline blue solid is filtered, washed with CCl₄ and acetone, and then dried by suction in air.

Thermal analysis was carried out using a Setaram B70 thermobalance. The observed loss of water corresponds to 2 water molecules/vanadium. A first water molecule, the uncoordinated one, evolves in the temperature range 100-170 °C yielding a monohydrate species through a topotactic process. This monohydrate (*a* = 6.91 (1) Å, *b* = 7.261 (2) Å, *c* = 9.32 (2) Å, and β = 70.91 (3)°; *z* = 4, space group *P*2₁/*c*)^{13b} collapses irreversibly to the hemihydrate at temperatures higher than 230 °C. The final product (*T* > 600 °C) is the oxovanadium(IV) pyrophosphate.^{13c}

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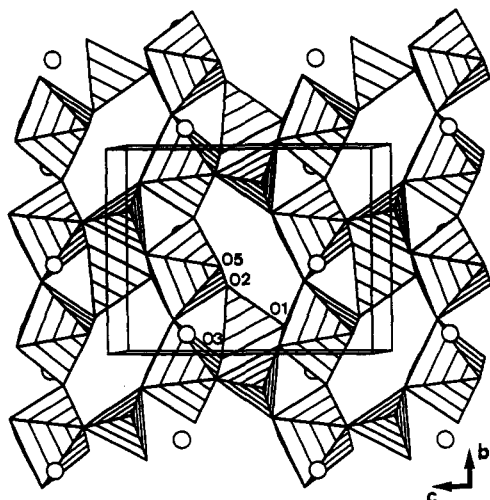


Figure 1. View of α -VO(HPO₄)·2H₂O showing the layer organization (after ref 15).

X-ray powder diffraction pattern was obtained by means of a Siemens Kristalloflex 810 diffractometer using Cu K α radiation. It agrees with the crystal structure of α -VO(HPO₄)·2H₂O determined previously.¹⁵

The IR spectrum, using a KBr pellet, was recorded on a FT IR Perkin-Elmer 1750 spectrophotometer. Room-temperature electronic spectra (diffuse reflectance) were obtained between 8000 and 30 000 cm⁻¹ using a Perkin-Elmer Lambda-9 spectrometer. Both spectra coincide with those reported previously.¹⁶ All experiments, then, characterize this compound unambiguously as α -VO(HPO₄)·2H₂O.

X-band ESR spectra were recorded on a Bruker ER 200D spectrometer equipped with a liquid nitrogen cryostat.

Magnetic measurements were performed at 0.1 T in the temperature range 2–150 K with a SQUID (SHE) magnetometer-susceptometer.

³¹P NMR spectra were recorded at 80.962 MHz on a high-power Bruker MSL 200 spectrometer equipped with a 4.7-T superconducting magnet and using a solid echo sequence with phase cycling. The spectral width was 500 kHz. Variable temperature studies were performed using the gas-flow technique. The temperature was stabilized at ± 1 K during accumulation. The shifts of the lines were referenced to 85% H₃PO₄(aq) measured in the same probe.

Magnetic Susceptibility Studies

The thermal variation of the molar magnetic susceptibility of α -VO(HPO₄)·2H₂O is given in Figure 2. No evidence of long-range magnetic ordering is found down to 2 K. Nevertheless, a broad maximum is observed at 28 K which is ascribed to low-dimensional antiferromagnetic interactions. At higher temperature ($T \geq 60$ K) the susceptibility follows a Curie-Weiss law $X = C/(T - \theta)$, with $C = 0.36$ and $\theta = -12$ K.

The magnetic behavior cannot be unambiguously inferred from the crystallographic structural features, although tridimensional magnetic interactions have to be excluded given the hydrogen-bonded layered topology of the compound as well as the broadness and the temperature of the magnetic susceptibility maximum. A first glance at the connectivity in each layer would suggest 1-D (V–O–V chains along the *c* axis) or 2-D low-dimensional magnetic interactions as responsible for the observed susceptibility data. Moreover, the ESR spectrum clearly shows a half-field signal generally associated with low-dimensional magnetic systems (Figure 3). Indeed, the $\Delta M_s = 2$ transition is not completely forbidden due to dipolar

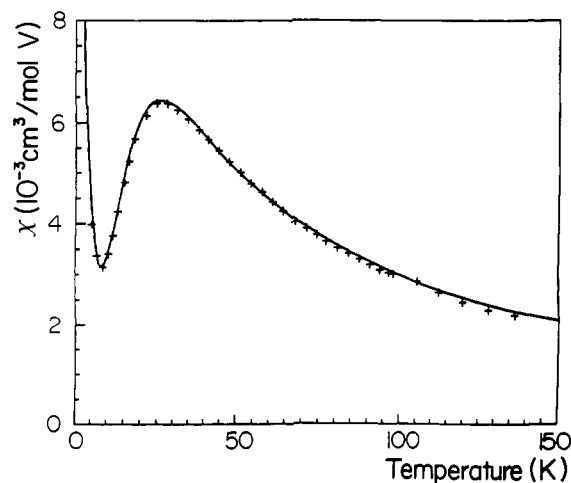


Figure 2. Thermal variation of the molar magnetic susceptibility of α -VO(HPO₄)·2H₂O. The full line represents the calculated curve for dimers (see text).

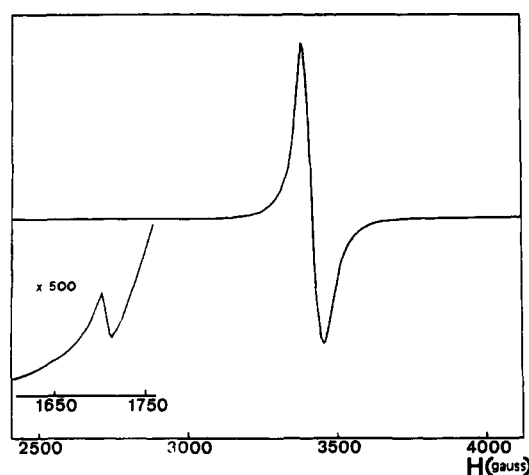


Figure 3. Room-temperature ESR spectrum showing the half-field transition.

coupling. Such a signal is frequently observed in dimers but it can also be observed in chains, for instance, in N(CH₃)₄MnCl₃,^{17,18} and it would theoretically appear in 2-D magnetic systems,¹⁹ for which we are not aware of any example.

Due to the strong distortion of the vanadium environment from octahedral symmetry, the ground state is a well-stabilized orbital singlet, hence the Heisenberg exchange Hamiltonian will be used as a good approximation to describe the magnetic behavior. However, it was not possible to obtain any satisfactory fit with either a 2-D system or an isolated infinite chain of spin 1/2. On the contrary, a good fit is obtained if we assume the existence of dimers antiferromagnetically coupled by an isotropic exchange interaction, $H = -2JS_1S_2$. In this case, the magnetic susceptibility per vanadium atom follows the Bleaney-Bowers equation:

$$X = \frac{Ng^2\beta^2}{kT} \frac{1}{3 + \exp(-2J/kT)}$$

At the lowest temperatures, the susceptibility increases below 7 K instead of dropping to zero as expected. This

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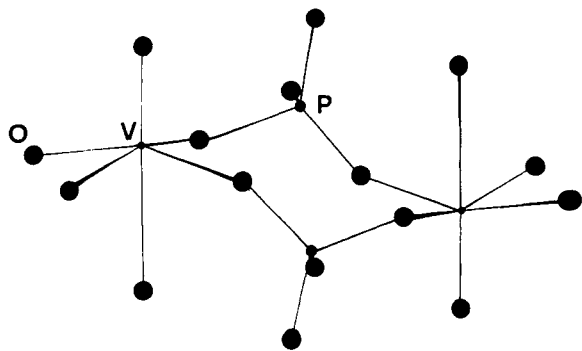


Figure 4. Structural dimeric unit in α -VO(HPO₄)·2H₂O.

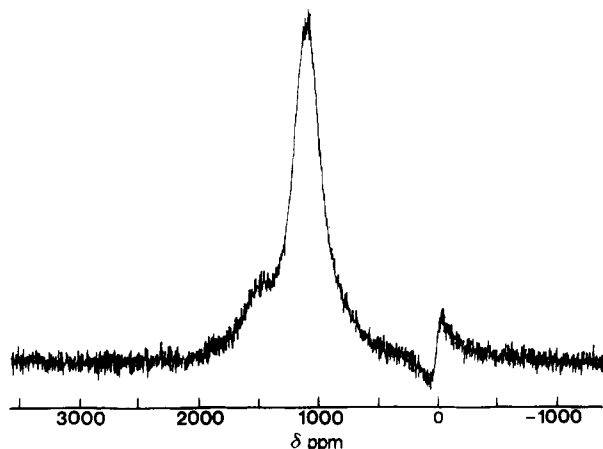


Figure 5. Room-temperature ³¹P solid-state static NMR spectrum for α -VO(HPO₄)·2H₂O.

behavior is usually ascribed to the presence of a small amount of isolated paramagnetic centers, here probably V⁴⁺, the susceptibility of which is assumed to follow Curie's law $X = C/T$. Thus, the magnetic susceptibility becomes

$$X = fX_{\text{imp}} + (1 - f)X_{\text{dim}}$$

where f is the fraction of V⁴⁺ monomers in the sample. A least-squares fitting of the experimental curve, using J and f as adjustable parameters and $g = 1.97$ from ESR measurements, gives very satisfactory results leading to $J/k = -23$ K and $f = 3\%$ (Figure 2).

Hence, both magnetic susceptibility and ESR data indicate that α -VO(HPO₄)·2H₂O consists of isolated antiferromagnetic dimers. Taking into account the whole lattice topology (Figure 1) and by "reductio ad absurdum" arguments, the only structural unit that can be considered as an isolated magnetic dimer is represented in Figure 4: it consists of two VO₆ octahedra cis-bridged through two μ (OO')-phosphate tetrahedra. Any other hypothesis should give rise to extended mono- or bidimensional magnetic lattice. Thus, it appears that the exchange pathway must involve phosphate groups. It is for this reason that a ³¹P NMR study was undertaken. Preliminary results for some hydrogen phosphates at room temperature showed some correlation between the isotropic shift of the phosphorus NMR line and the magnitude of the exchange coupling constant.¹³

³¹P NMR Results

The ³¹P NMR spectrum obtained at room temperature is given in Figure 5. It presents an anisotropic strongly shifted intense line (toward high frequencies) and a very weak quasi-isotropic nearly unshifted one (Figure 6). The intensity of the smaller peak is estimated to be 3–4% that of the main peak, independent of the experimental con-

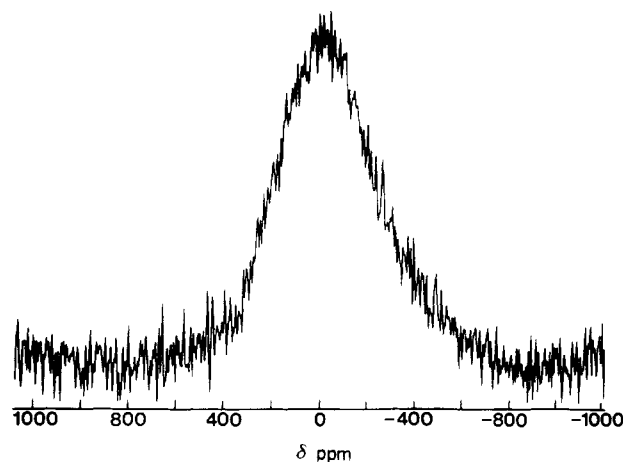


Figure 6. Room-temperature ³¹P solid-state static NMR spectrum for α -VO(HPO₄)·2H₂O. Expansion of the small unshifted line.

ditions and acquisition parameters. Thus, this resonance can be ascribed to the presence of impurities. Its width at half-height (40 kHz) is much too large to come solely from dipole-dipole interaction. (For instance, the width observed in the diamagnetic phosphate KVOOHPO₄ is 5 kHz.) Thus, the extra width is due to nuclear-electron dipolar interactions. Accordingly the impurity must be paramagnetic. The consistency between the percentage of paramagnetic impurity obtained from magnetic susceptibility and from NMR data is remarkable.

The main resonance is due to the dihydrate phosphorus adsorption. The isotropic part of the shift, given by the center of gravity of the line, is $\delta = 1360$ ppm. Such a large paramagnetic shift may be caused by a strong spin-orbit coupling²⁰ and/or a magnetic exchange coupling.²¹ In the case of V⁴⁺ compounds, the only operative mechanism is the last one. The exchange mechanism should involve spin transfer through s and p (and perhaps d) phosphorus orbitals. The spin density in s orbitals is the origin of the isotropic shift while the contribution of the p (d) orbitals manifests itself in the anisotropy of the line which also includes the dipolar contribution from V⁴⁺ centers. Given the low symmetry of the structure and the lack of single crystals, a quantitative determination of the spin densities is feasible only for the s orbitals and is obtained from the thermal evolution of the isotropic shift. The expression commonly used to obtain the Fermi contact term from the isotropic NMR shift is of the form

$$\delta = \frac{g\beta S(S+1)}{3k(T-\Theta)\gamma} A_s$$

This expression is valid for exchange coupled systems following Curie-Weiss law as long as $kT \gg J$.

The different terms have their usual meaning and the hyperfine electron-nucleus coupling constant A_s (in hertz) is proportional to the unpaired electron spin density occupying s orbitals centered at the phosphorus nucleus.

Figure 7 shows the linear variation of the isotropic shift versus $1/(T - \Theta)$. The slope of the line yields $A_s = 22.7 \pm 0.5$ MHz. The A_s value obtained from this fit may be taken with confidence since the experimental error in the NMR line shift does not modify significantly the observed dependence of δ with T^{-1} . Although the same is not true for the value of Θ , it is remarkable that a full fit leads to $\Theta = -18$ K, a value reasonably close to that obtained from

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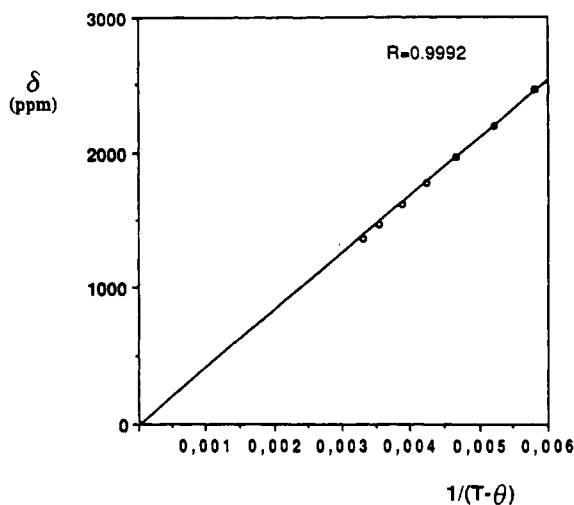


Figure 7. Variation of the isotropic ³¹P NMR shift vs 1/(T - θ).

susceptibility data. Either value of θ yields the plot observed in Figure 7.

For a unit spin density in the phosphorus 3s orbital, the hyperfine coupling constant is 10178 MHz.²² This would imply a spin density of 2.2×10^{-3} unpaired electron/3s phosphorus orbital in α -VO(HPO₄)·2H₂O. However, the electronic states of phosphorus in phosphates are better described by sp³ hybridization. Thus, the presence of 1 electron/sp³ orbital would correspond to a hyperfine coupling constant equal to one-fourth that for the free atom. But, as shown in Figure 4, the bridging through each phosphate group involves two sp³ orbitals, both contributing to the observed A_s value. Hence, the transferred spin density is 4.5×10^{-3} unpaired electron/sp³ orbital involved in the exchange. This value is to be compared to that generally observed in paramagnetic complexes ($\approx 10^{-7}$) in the absence of any observable exchange coupling.²³

In antiferromagnetically coupled systems, the exchange constant depends on the transfer integral *b*, by the relation $J \approx -b^2/U$ (ref 24) (where *U* is the Coulomb integral). Thus, some correlation is expected between the NMR shift due to a finite spin density at the phosphorus nuclei and the *J* value. Preliminary results obtained on the hemihydrate VO(HPO₄)·1/2H₂O allow us to estimate the A_s value to 28.5 MHz for an exchange constant, *J*, of 43 K.^{13b} A systematic ³¹P NMR study in other vanadyl phosphates is in progress.

Conclusions

The involvement of phosphate groups in the spin density transfer between V(IV) ions coupled antiferromagnetically has been established with the help of variable-temperature solid-state ³¹P NMR. The participation of phosphate groups in the magnetic exchange may be considered unusual, although not completely unexpected. It is noteworthy that the superexchange through PO₄³⁻ turns out to be more effective than through oxo bridges involving the long V-O bond. The experimental observation of hyperfine interaction between the ligand nuclear spin and the unpaired electron spin in the magnetic ion constitutes the best evidence that the ligand (phosphate in our case) participates in the magnetic exchange. The role of the bridging ligands

is to provide a common orbital which when suitably admixed with the magnetic d orbitals provides a new pathway of direct interaction between the magnetic centers.

In our case, a good overlap of the magnetic orbitals is provided through the pathway involving the following set of atomic orbitals on the μ (O,O')phosphate dimeric moiety: d_{xy}(V)//p_x(O)//d_{xy}(P)//p_y(O)//d_{xy}(V), using the Ginsberg notation,²⁵ where the symbol // indicates simply a nonzero overlap (in this case a π overlap). The maximum overlap, and so the stronger magnetic interaction, provided by this path is obtained when the VO₆ octahedra from the dimer are situated in such a way that the vanadium d_{xy} orbitals are coplanar and share a lobe axis. This situation is that observed in the intrachain di- μ (O,O')phosphate bridges in (VO)₂P₂O₇ ($J_{\mu(O,O')} = -46$ K).^{13a} Any modification of this optimal topology leads to a significant drop of the overlap and consequently of the magnetic interactions. Thus, the small displacements in the *xy* plane and along the *z* axis observed in the title compound lead to a $J_{\mu(O,O')} = -23$ K. Larger in-plane displacements (as occur in the intrachain di- μ (O,O')phosphate bridges of (VO)₂P₂O₇ or in the *z* axis in VO(HPO₄)·4H₂O) lead to negligible coupling constants. Other distortions, as twisting or rocking of the equatorial planes, present in β -VO(HPO₄)·2H₂O and VO(HPO₄)·0.5H₂O, respectively, lead to exchange pathways through phosphate groups, also ineffective.

Propagation of significant magnetic interaction along a chain of μ -oxo-bridged VO₆ octahedra would imply an important admixture of d_{zz} 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 of the small value of the magnetic interaction ($|J| < 3$ K) observed in compounds as VO(H₂XO₄)₂ (X = P, As).²⁶ Indeed, no exchange pathway involving well-matched phosphate orbitals exists when the octahedra chain has additional μ (O,O')phosphate bridges as occurs in the title compound and in a new member of the A-V-P-O series, Tl₃V₂O₃(VO)(PO₄)₂(HPO₄).²⁷ A layered structure identical with the former is presented by the isostructural oxovanadium(IV) phosphate VOC₆H₅PO₃·H₂O,²⁸ for which a susceptibility maximum is observed around 15 K. A set of magnetically interacting units involved in oxovanadium phosphates and consistent with susceptibility and NMR data has been recently proposed.^{13a}

The V-P-O system gives a wide variety of crystal structures originated on the diversity of ways in which phosphate tetrahedra and oxovanadium octahedra can be interlinked. The prediction and/or interpretation of the magnetic properties on the basis of the structural aspects is difficult. The now evident participation of phosphate groups in the magnetic exchange has been usually neglected in the related literature.^{11,12} The use of a highly sensitive local probe on the bridging atoms, such as ³¹P NMR, combined with magnetic susceptibility techniques seems to be very adequate to eliminate ambiguities about the nature of the active superexchange mechanism.

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