Magnetic Properties of Metal-Intercalated Layered Vanadyl Phosphates

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Received July 27, 1995

Without well-defined structure, any sensible interpretation of magnetic behavior at the molecular level is necessarily speculative. Nowhere is this difficulty more striking than in the field of the host−guest chemistry of layered materials. It is for this reason that we have turned our attention to layered vanadium phosphates. Inorganic magnetic host structures are generated upon the reduction of the V^{V} centers of the native layered $VOPO_4$ compound.[1,2] These redox intercalated compounds are highly crystalline when the negative charge of the reduced layers is neutralized by metal ion guests, and structural data for several cases are available. In a series of benchmark papers Lii et al. have reported the hydrothermal synthesis and X-ray crystal structure determinations for several $M_xVOPO_4\cdot nH_2O$ systems.[3] Of specific interest to this work are the alkali metal compounds $Na_{0.5}VOPO_4\cdot 2H_2O$ and $K_{0.5}VOPO_4\cdot 1.5H_2O$,[4] as well as the alkaline earth metal compound $Sr_{0.5}VOPO_4\cdot 2H_2O$.[5] Systematic magnetic studies of this series, augmented with $Rb_{0.5}VOPO_4\cdot 1.5H_2O$ reported here, have revealed a surprising range of magnetic behaviors varying from ferro- to antiferromagnetism.

Hydrothermal synthesis of the Rb^+-intercalated layered phosphate yields highly crystalline material with the formula $Rb_{0.5}VOPO_4\cdot 1.5H_2O$.[6] We have solved a single-crystal X-ray structure for this compound as well as verifying the Na^+, K^+, and Sr^{2+} syntheses and structures.[7] Figure 1 shows a view looking down on a segment of a layer of $Rb_{0.5}VOPO_4\cdot 1.5H_2O$. As with the other alkali metal systems, the layer is composed of distorted vanadium octahedra and phosphate tetrahedra. Each vanadium octahedron shares its four equatorial oxygen atoms with four different phosphates. The two axial positions are occupied by a vanadyl oxygen and a water molecule. An additional water molecule is proximate to the Rb^+ ion and located so that it can hydrogen-bond to phosphates of different layers. Rb^+, Na^+, and K^+ compounds are isostructural with only subtle differences arising from ion size and the different numbers of waters coordinating the alkali metal cations. Interlayer *d* spacings of 6.57, 6.40, and 6.51 Å are observed for intercalates of the hydrated alkali metal cations, $Na^+\cdot 2H_2O$, $K^+\cdot 1.5H_2O$, and $Rb^+\cdot 1.5H_2O$, respectively. The variations among these numbers are small in light of the ∼1 Å electrostatic compression in the intercalates relative to the *d* spacing of 7.43 Å[8] for the neutral parent $VOPO_4\cdot 2H_2O$ layered compound.

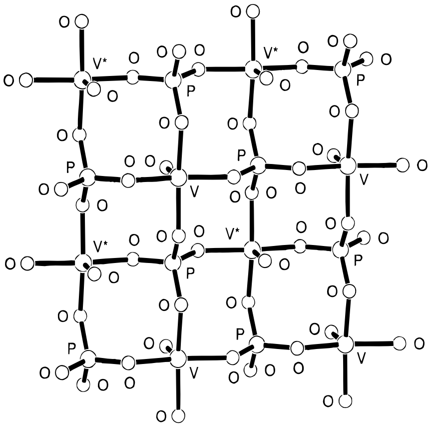

Figure 1. A segment of the layer of $Rb_{0.5}VOPO_4\cdot 1.5H_2O$ that we believe contains the structural elements responsible for magnetic variations for the alkali metal intercalants. The vanadium pseudooctahedral ligand sphere consists of a weakly coordinated water molecule ($d(V-O_{ax}) = 2.35$ Å), the vanadyl oxygen ($d(V-O) = 1.60$ Å), and four equatorial oxygen atoms ($d_{av}(V-O_{eq}) = 1.95$ Å) shared with four different phosphate tetrahedra ($d_{av}(P-O_{eq}) = 1.54$ Å). The two V_4 squares (V_4 and V^*_4) are symmetry related via the inversion center in the middle $V(OPO)_2V$ ring.

Figure 2 shows plots of χT vs T for the three alkali metal intercalated vanadyl phosphates described above.[9] The upturns seen in the data reveal ferromagnetic couplings in the layers. This finding is in contradistinction to earlier magnetic measurements for the Na^+ compound, which was synthesized by the reaction of NaI with $VOPO_4\cdot 2H_2O$ in acetone and characterized by indexing the lattice parameters from powder X-ray diffraction data.[10] Here the magnetic susceptibility was determined over a range of relatively high temperatures ($T = 90-300$ K), and weak antiferromagnetic interactions were assigned on the basis of a small negative Weiss constant.[11] For the hydrothermally synthesized compounds, the values of the Curie constants at high temperatures (0.358, 0.365, and 0.351 for Na^+, K^+, and Rb^+ compounds, respectively) are all close to the spin-only value of ∼0.369 ($g = 1.966$, determined from EPR measurements), which indicates good agreement between our chemical

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(1) Whittingham, M. S.; Jacobson, A. J. *Intercalation Chemistry*; Academic Press: New York, 1982.

(2) (a) Jacobson, A. J.; Johnson, J. W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 412. (b) Jacobson, A. J.; Johnson, J. W.; Brody, J. F.; Scanlon, J. C.; Lewandowski, J. T. *Inorg. Chem.* **1985**, *24*, 1782.

(3) Lii, K. H. *J. Chin. Chem. Soc.* **1992**, *39*, 569.

(4) Wang, S. L.; Kang, H. Y.; Cheng, C. Y.; Lii, K. H. *Inorg. Chem.* **1991**, *30*, 3496.

(5) Kang, H. Y.; Lee, W. C.; Wang, S. L.; Lii, K. H. *Inorg. Chem.* **1992**, *31*, 4743.

(6) Procedures for the hydrothermal synthesis of the alkali and alkaline metal phosphates are well established.[3−5]

(7) A Rigaku diffractometer with Mo Kα radiation ($\lambda = 0.710\,73$ Å) was used to collect data to a maximum of $2\theta = 60°$ from crystals of 0.42 × 0.24 × 0.02 mm dimensions at 293 K. A total of 1623 independent reflections were collected, of which 1498 reflections were considered observed ($I > 2\sigma(I)$) after Lp and absorption correction (correction was based on ψ scans of a few suitable reflections with χ values close to 90°). Crystallographic data are as follows: $H_3Rb_{0.46}O_{6.5}PV$, MW = 227.40, triclinic, space group $P\bar{1}$, $a = 6.2853(12)$ Å, $b = 6.2908(6)$ Å, $c = 6.849(2)$ Å, $\alpha = 89.73(2)°$, $\beta = 107.79(2)°$, $\gamma = 90.147(13)°$, $V = 257.85(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.929$ g cm^{-3}. The structure was solved by using direct methods (SIR-88) and refined by using full-matrix least-squares procedures based on F^2 (SHELXL-93) with R1 = 0.0517 and wR2 = 0.1474. Structure refinement gave a value of $Rb_{0.46}$, but forcing a total value of $Rb_{0.5}$ (two sites) only increased the wR2 factor by 0.0007.

(8) Tietze, H. R. *Aust. J. Chem.* **1981**, *34*, 2035.

(9) Magnetic susceptibilities were determined using a SQUID susceptometer (Quantum Design MPMSR2 susceptometer). To verify the identity of the samples used for susceptibility and for X-ray structural studies, powder patterns computed from the single-crystal data were compared to those measured on a Rigaku Rotaflex RU-200B for the ground crystalline materials.

(10) Siskova, R.; Benes, L.; Zima, V.; Vlcek, M.; Votinsky, J.; Kalousova, J. *Polyhedron* **1993**, *12*, 181.

(11) Our experience shows that the iodide synthesis method can lead to samples with variable magnetic behavior. Specifically, we have observed cases where a Curie−Weiss fit over the same high-temperature range reproduces the negative Weiss constants as found by Siskova et al.[10] However, *positive* Weiss constants are found when susceptibility data are collected down to liquid helium temperatures.

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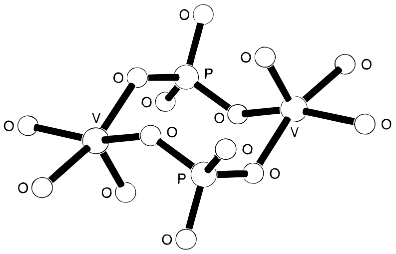
analyses[12] and magnetic measurements. A simple two-dimensional Heisenberg model for a ferromagnetic square planar lattice fits well to each of the sets of magnetic susceptibility data shown,[13] yielding $J/k = +0.61$, $+0.59$, $+0.64$ K, respectively, for the Na^+, K^+, and Rb^+ intercalates.

In the paramagnetic VO_6 centers, the tetragonal vanadium−oxo ligand field gives rise to $b_2(d_{xy})$ and $e(d_{xz},d_{yz})$ lowest levels, with significant destabilization of the latter resulting from a strong metal−oxo π^* interaction.[14] In the mixed-valence alkali metal intercalates, half of the d_{xy} orbitals are occupied by an unpaired electron. No static structural distortion was discerned between V^{IV} and V^{V} centers, and only a single vanadium appears in the asymmetric unit. Neighboring vanadium centers are linked by $V(OPO)_2V$ rings with a "chairlike" arrangement:



Each vanadium center participates in four such rings as seen in Figure 1. In closely related layered vanadium phosphates and phosphonates, Villeneuve et al. have correlated magnetic properties with various structural aspects of the $V(OPO)_2V$ rings that compose the layers.[15] These studies concluded that a parallel arrangement of the basal planes of the $(VO)O_4$ square pyramid was optimal for ferromagnetic coupling. This preference suggests that through-space interactions cannot be dominant, since antiferromagnetic coupling would then be expected between the d_{xy} magnetic orbitals of the V^{IV} centers; thus, superexchange via phosphate bridges is thought to carry the magnetic coupling. Consistent with this analysis, the $(VO)O_4$ basal planes in the rings of the ferrromagnetically coupled Na^+, K^+, and Rb^+ intercalates are parallel by symmetry.

This magneto/structural relationship is maintained for other layered vanadyl systems, but in these cases the layers are composed entirely of V^{IV} centers. The magnetic behavior and exchange constants of the alkali metal intercalates are consonant with results reported for α-$VOSO_4$, a compound whose layers are isostructural with those of the present systems.[13] In this layered compound, the exchange interaction of the d^1 V^{IV} centers composing the layers is also weak and ferromagnetic ($J/k = +1.5$). Conversely, in compounds containing similar $V(OPO)_2V$ subunits with nonzero dihedral angles between the $(VO)O_4$ planes, the materials exhibit antiferromagnetic coupling. For example, a significant antiferromagnetic ordering ($J/k = -4.7$)[15b] accompanies a 6.7° dihedral angle between the vanadyl oxo basal planes in $VO(HPO_4)\cdot 4H_2O$. Is the orientation of the $(VO)O_4$ intralayer subunits a key to the nature of the exchange interaction in these simple layered phosphates? In order to further address this question, we hydrothermally prepared and characterized $Sr_{0.5}VOPO_4\cdot 2H_2O$, as previously reported by Lii.[5] This layered compound is nearly isostructural with the alkali metal $VOPO_4$ intercalates and α-$VOSO_4$, but the $(VO)O_4$ planes of the Sr^{2+} intercalate are canted toward each other by 2.5°. As shown in Figure 2, the layered compound is antiferromagnetic with $J/k = -2.5$. Interestingly, in comparison to the case of $VO(HPO_4)\cdot 4H_2O$, the smaller dihedral angle is also reflected in a smaller antiferromagnetic exchange interaction.

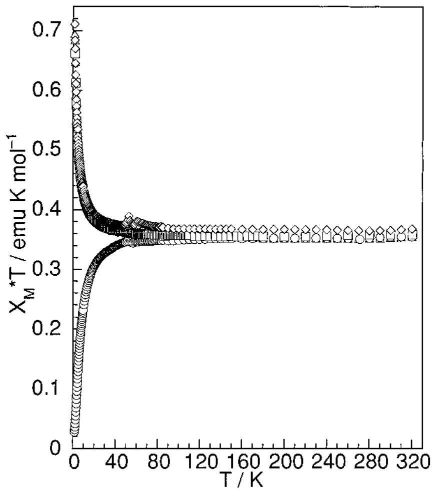


Figure 2. Plot of χT vs T for $Na_{0.5}VOPO_4\cdot 2H_2O$ (□), $K_{0.5}VOPO_4\cdot 1.5H_2O$ (◇), $Rb_{0.5}VOPO_4\cdot 1.5H_2O$ (△), and $Sr_{0.5}VOPO_4\cdot 2H_2O$ (○) showing varying ferro- and antiferromagnetic responses.

Within the data set discussed here, the comparison between the V^{IV}/V^{V} mixed-valence alkali metal intercalates and the all-V^{IV} systems appears to work well. Parallel $(VO)O_4$ basal planes in these vanadyl layered intercalates correlate with ferromagnetic coupling. These systems are complex networks, however, and each V center has eight (five symmetry-distinct) nearest neighbor interactions via OPO bridges, so the observed magnetic behaviors must reflect averages over several similar coupling paths. One simplifying approach is to divide each layer into two square sublattices, related by an inversion that overlays them slightly off-center of staggered. In the lattice segment shown in Figure 1, the groups of four V and four V* atoms define the two sets. Viewed in this way, the problem reduces to two relationships: one intra- and one interlattice. The mixed valency of the alkali metal intercalates adds uncertainties as to the relative locations of paramagnetic centers. If only one of the sublattices is considered to contain V^{IV} paramagnetic centers, then only the intralattice coupling, mediated by all-staggered OPO and gauche $OPOV^{V}OPO$ links, would contribute. Alternatively, electron hopping from V^{IV} to neighboring V^{V} sites might be involved in spin communication, leading to itinerant magnetic behavior. We are actively pursuing transport and reflectivity measurements to address this possibility. Only by such systematic analyses will useful principles relating magnetism to structure emerge.

Acknowledgment. The financial support of National Science Foundation Grant DMR-9311597 and the Center for Fundamental Materials Research at MSU are gratefully acknowledged.

Supporting Information Available: Tables giving crystal data, structure refinement details, atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, anisotropic thermal parameters, and least-squares planes, an ORTEP view of the unique atoms, a packing diagram, and textual details of the synthesis (13 pages). Ordering information is given on any current masthead page.

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(12) Anal. Calcd (found) for $Na_{0.5}VOPO_4\cdot 2H_2O$: Na, 5.48 (5.21); V, 24.32 (24.02); P, 14.79 (15.01) %. Calcd (found) for $K_{0.5}VOPO_4\cdot 1.5H_2O$: K, 9.38 (9.15); V, 24.43 (23.93); P, 14.85 (14.99) %. Calcd (found) for $Rb_{0.5}VOPO_4\cdot 1.5H_2O$: Rb, 18.45 (16.64); V, 22.40 (22.77); P, 13.62 (13.70) %. Calcd. (found) for $Sr_{0.5}VOPO_4\cdot 2H_2O$: Sr, 18.12 (17.96); V, 21.07 (20.96); P, 12.81 (12.78) %. TGA results for all compounds confirmed the assigned water contents. For the Rb^+ compound, χT (SQUID) and g (EPR) values can be used to compute Rb content (assumes susceptibility is due to spin only), giving a value of $Rb_{0.47}$.

(13) Lezama, L.; Villeneuve, G.; Marcos, M. D.; Pizarro, J. L.; Hagenmuller, P.; Rojo, T. *Solid State Commun.* **1989**, *70*, 899.

(14) (a) Gray, H. B.; Ballhausen, C. J. *Inorg. Chem.* **1962**, *1*, 111. (b) Winkler, J. R.; Gray, H. B. *Comments Inorg. Chem.* **1982**, *1*, 256.

(15) (a) Beltrán-Porter, D.; Amorós, P.; Ibáñez, R.; Le Bail, A.; Ferey, G.; Villeneuve, G. *Solid State Ionics* **1989**, *32*, 57. (b) Beltrán-Porter, D.; Beltrán-Porter, A.; Amorós, P.; Ibáñez, R.; Martinez, E.; Le Bail, A.; Ferey, G.; Villeneuve, G. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 131.