

Magnetic Properties of $M(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($M = \text{Co(II)}, \text{Ni(II)}$), Layered Compounds Containing Distinct Magnetic Linear Trimers

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A magnetic study has been carried out on the transition metal intercalated vanadyl phosphates $M(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($M = \text{Co}^{2+}, \text{Ni}^{2+}$), which contain linear trimers of $\text{V}=\text{O}-\text{M}-\text{O}=\text{V}$ between the layers. Ferromagnetic interactions have been found to be mediated through these linear trimers. © 1998 Academic Press

INTRODUCTION

Layered vanadyl phosphate, $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, is well known for its catalytic activity (1). The presence of readily reducible V(V) ions in this compound allows for the intercalation of a number of metal ions with the parent layered structure maintained (2). Based on the kind of guest cations, such intercalates which share the stoichiometry $M(\text{VOPO}_4)_2 \cdot n\text{H}_2\text{O}$ can be classified into two types: (i) monovalent metal intercalates, e.g., $M(\text{VOPO}_4)_2 \cdot n\text{H}_2\text{O}$ ($M = \text{Na}, \text{K}, \text{Rb}; n = 3, 4$) (3,4), where V^{5+} is partially reduced to V^{4+} , resulting in mixed-valence compounds; (ii) divalent metal intercalates, e.g., $M(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($M = \text{Ca}, \text{Sr}, \text{Pb}, \text{Ni}, \text{Co}, \text{Cu}$) (5–7), where V^{5+} is fully reduced to V^{4+} . The divalent transition metal intercalates are principally of interest because of their strong tendencies toward coordination. Therefore, in $M(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($M = \text{Ni}, \text{Co}$) (5,6), the neighboring layers of VOPO_4 are revealed to be linked by the second metal ions whereas in $\text{Cu}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ (7), each Cu atom is connected to one layer.

Recently, Papoutsakis *et al.* (4) reported an investigation on the magnetic properties of $\text{Na}^+, \text{K}^+, \text{Rb}^+, \text{and Sr}^{2+}$ compounds. Conclusions were drawn that the bulk ferromagnetic or antiferromagnetic interactions in these compounds correlate with the orientation of the $(\text{VO})\text{O}_4$ intralayer subunits. The through-space interlayer interactions, on the other hand, cannot be dominant since the

spaces are filled with alkaline metal or alkaline-earth metal ions in addition to water molecules. With the introduction of a transition metal ion as a guest cation, the magnetic properties would be significantly modified. When the cation is Ni^{2+} or Co^{2+} , the adjacent VOPO_4 layers are fused to each other through direct coordination of Ni^{2+} (or Co^{2+}) with two trans vanadyl oxygens. The remaining equatorial positions of the second metal are occupied by four water oxygens (see Fig. 1). Consequently, a linear $\text{V}=\text{O}-\text{M}-\text{O}=\text{V}$ trimer forms between the layers, which provides an interesting through-space magnetic exchange pathway. This pathway is actually much more efficient than that of the intralayer interaction. A description of the magnetic behaviors of both Co^{2+} and Ni^{2+} compounds is presented in this paper. To the best of our knowledge, they are the first examples that deal with the magnetic behavior of linear $\text{V}=\text{O}-\text{M}-\text{O}=\text{V}$ ($M = \text{Ni}, \text{Co}$) trimers.

EXPERIMENTAL

Both compounds were hydrothermally synthesized in a 23-mL Teflon-lined pressure vessel. For $\text{Ni}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$, a mixture with a 2.35:1.0:3.3:8.0:10.9:10.1:1902, of $\text{KVO}_3 : \text{V} : \text{CH}_3\text{PO}(\text{OH})_2 : \text{H}_3\text{PO}_4 : (\text{CH}_3)_2\text{NH} : \text{NiCl}_2 : \text{H}_2\text{O}$ molar ratio was heated at 200°C for 4 days according to Haushalter *et al.* (8). The X-ray powder pattern of the bulk product indicates that a single phase of $\text{Ni}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ was obtained. For $\text{Co}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$, a mixture of 0.20 g of CoO , 0.20 g of V_2O_3 , 0.243 g of V_2O_5 , and 10 mL of 0.667 M H_3PO_4 (molar ratio $\text{Co} : \text{V} : \text{P} = 1 : 2 : \sim 2.5$) was heated at 230°C for 5 days before slow cooling at 10°C/h to room temperature. The product was a mixture of green tabular crystals of the title compound and unidentified materials. We were unable to find reaction conditions capable of suppressing the formation of the impurity phases. The green tabular crystals were thus manually selected for further magnetic susceptibility measurements. The X-ray powder pattern of the sample compared well with that calculated from the single-crystal data.

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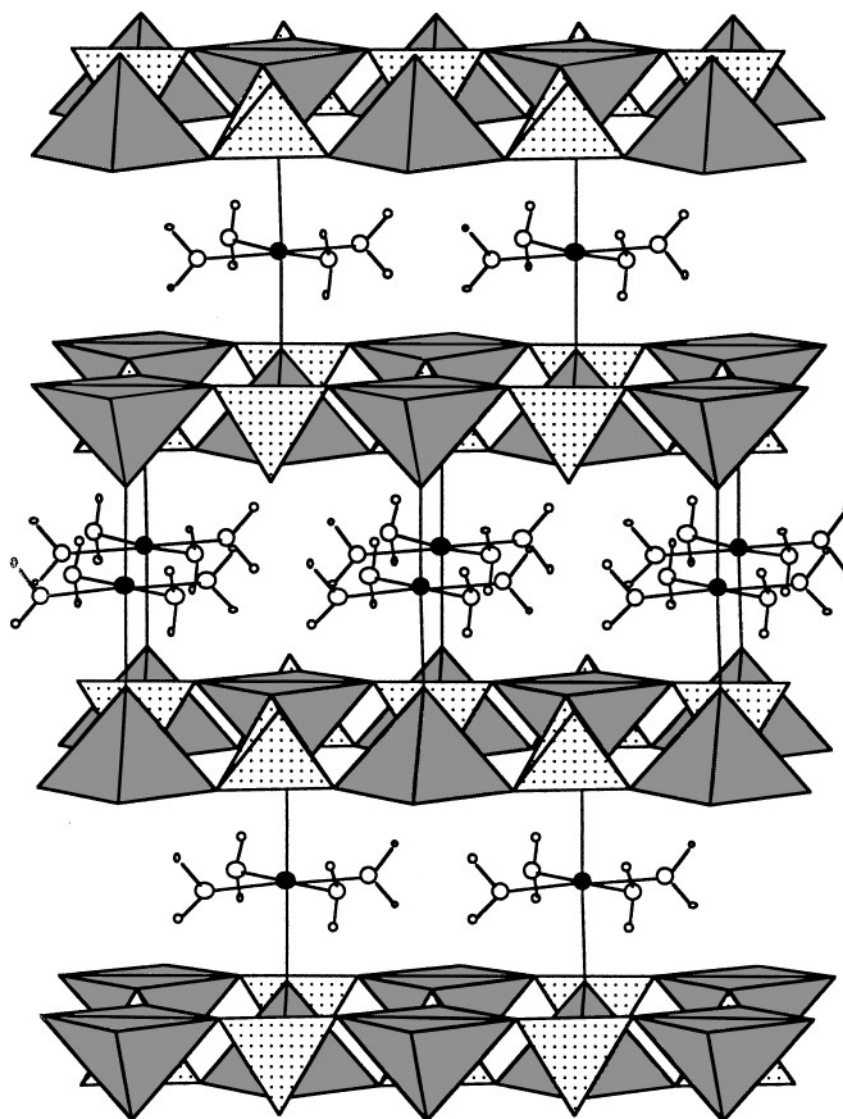


FIG. 1. Polyhedral view (*c* vertical) of $\text{Ni}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ with the nickel, water oxygen, and hydrogen atoms shown as solid, large open, and small open circles, respectively.

The magnetic susceptibility data were recorded on a 121.76-mg polycrystalline sample of $\text{Ni}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ or a 17.56-mg powder sample of $\text{Co}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ over the temperature range 2–300 K in a magnetic field of 5 kG using a SQUID magnetometer. Corrections for the diamagnetism were estimated from Pascal's constants. TIP values were taken as $100 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$ for the Ni(II) monomer, $130 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$ for the V(IV) monomer, and zero for the Co(II) monomer.

RESULTS AND DISCUSSION

The magnetic behavior of a powdered sample of $\text{Ni}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ is shown in Figs. 2 and 3 in the forms

of $1/\chi_m$ versus T and $\chi_m T$ versus T plots, respectively. χ_m is the molar magnetic susceptibility. At 300 K, the effective magnetic moment (μ_{eff}) per $\text{Ni}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$, calculated from $\mu_{\text{eff}} = 2.828(\chi_m T)^{1/2}$, is $4.15 \mu_B$, which is greater than that of the spin-only value expected for a $\text{V}^{\text{IV}}_2\text{Ni}^{\text{II}}$ species containing noninteracting metal centers ($3.74 \mu_B$). The Weiss constant determined in the temperature range of 300–140 K, based on the equation $\chi_m = C/(T - \Theta)$, is $+16.3 \text{ K}$, which suggests the presence of ferromagnetic near-neighbor exchange. This ferromagnetic exchange is further confirmed by a slow increasing of $\chi_m T$ upon cooling from room temperature. When the temperature is even lower, however, the value of $\chi_m T$ passes through a maximum around 50 K and then decreases with decreasing temperature, indicating an

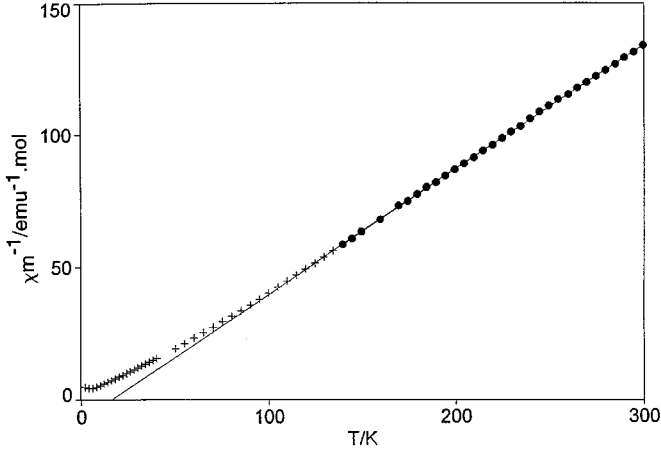


FIG. 2. Temperature dependence of the reciprocal magnetic susceptibility for $\text{Ni}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$.

antiferromagnetic coupling and/or an influence of a zero-field splitting of the ground state.

The structure of $\text{Ni}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ consists of VOPO_4 layers linked by NiO_6 octahedra (6, 8). Within the layers, the magnetic interaction is weak since the magnetic centers of V^{4+} are bridged via PO_4 anions. The bulk magnetic susceptibility is therefore mainly attributed to the linear trimer of $\text{V}=\text{O}-\text{Ni}-\text{O}=\text{V}$ between the sheets. For such an isolated linear trimer, the spin Hamiltonian can be expressed as

$$\hat{H} = -2J(\hat{S}_{\text{V1}} \cdot \hat{S}_{\text{Ni}} + \hat{S}_{\text{Ni}} \cdot \hat{S}_{\text{V2}}) + \beta[g_{\text{V}}(\hat{S}_{\text{V1}} + \hat{S}_{\text{V2}}) + g_{\text{Ni}}\hat{S}_{\text{Ni}}] \cdot \vec{H} \quad [1]$$

Here, it is assumed that the interaction between the nearest neighbors is purely isotropic and that between the terminal centers is neglected. The relative energies of the low-lying

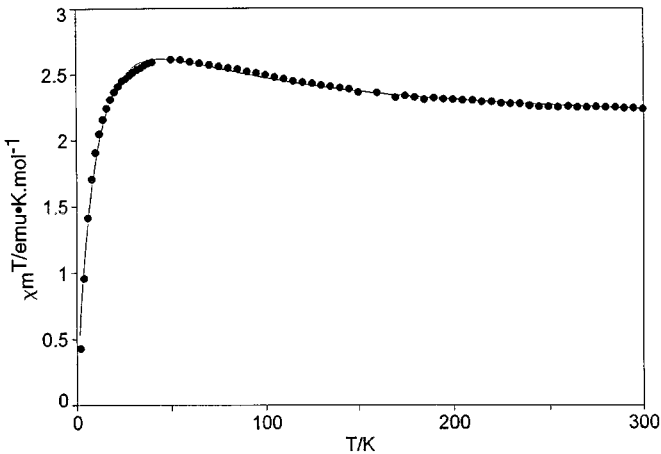


FIG. 3. Thermal variation of $\chi_m T$ for $\text{Ni}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$. The solid line shows the best fit using Eq. [2].

states are easily calculated following Kambe's approach (9). As ferromagnetic exchange ($J > 0$) is expected, the ground state is assumed to be $S = 2$. A theoretical expression of the magnetic susceptibility is then derived:

$$\chi_m = \frac{N\beta^2 g^2}{kT} \times \frac{10 + 2\exp\left(-\frac{2J}{kT}\right) + 2\exp\left(-\frac{4J}{kT}\right)}{5 + 3\exp\left(-\frac{2J}{kT}\right) + 3\exp\left(-\frac{4J}{kT}\right) + \exp\left(-\frac{6J}{kT}\right)}$$

$$\chi'_m = \chi_m / (1 - zJ'\chi_m), \quad [2]$$

where N is the Avogadro constant, g is the g factor, β is the Bohr magneton, k is the Boltzmann constant, and J is the exchange coupling constant. The contribution from the zero-field splitting of the ground state is not taken into account because it is normally found to be very small compared to $2J$. A correction factor zJ' is introduced to account for the possible intertrimer interactions through phosphate bridges. The g_{V} and g_{Ni} factors are presumed to be isotropic and equal to g for the sake of simplicity. A good fit of the data was obtained, affording the solid line in Fig. 3, with $g = 2.18$, $2J = 37.6 \text{ cm}^{-1}$, and $zJ' = -2.7 \text{ cm}^{-1}$. The coefficient of determination (r^2) is 0.9894.

With replacement of Ni^{2+} by Co^{2+} , a very similar magnetic behavior is observed. Figure 4 shows plot of $\chi_m T$ vs T for $\text{Co}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ over the temperature range 2–300 K. At 300 K, the effective magnetic moment per molecule is $5.70 \mu_{\text{B}}$, which is much higher than that of the spin-only value expected for a $\text{V}^{\text{IV}}_2\text{Co}^{\text{II}}$ unit containing noninteracting metal centers ($4.58 \mu_{\text{B}}$). The significant deviation of μ_{eff} can be caused by the spin-orbit coupling of $\text{Co}(\text{II})$ in an axially distorted octahedral environment (10). However, the positive Weiss constant of $+22.4 \text{ K}$ (120–300 K), as well as the slowly increasing value of $\chi_m T$ on cooling from room temperature to 54 K, clearly indicates a bulk ferromagnetic coupling. Analogously, this ferromagnetic coupling is attributed to the existence of $\text{V}=\text{O}-\text{Co}-\text{O}=\text{V}$ trimers. Assuming the ground state is $S = 5/2$, the following theoretical equation may be derived:

$$\chi_m = \frac{N\beta^2 g^2}{4kT} \times \frac{35 + 10\exp\left(-\frac{3J}{kT}\right) + 10\exp\left(-\frac{5J}{kT}\right) + \exp\left(-\frac{8J}{kT}\right)}{3 + 2\exp\left(-\frac{3J}{kT}\right) + 2\exp\left(-\frac{5J}{kT}\right) + \exp\left(-\frac{8J}{kT}\right)}$$

$$\chi'_m = \chi_m / (1 - zJ'\chi_m), \quad [3]$$

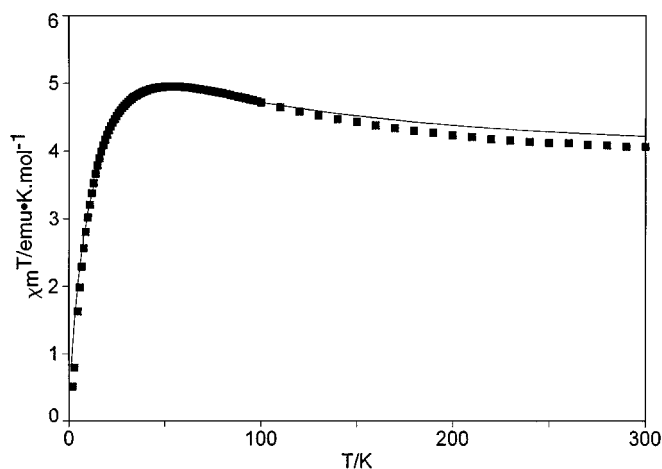
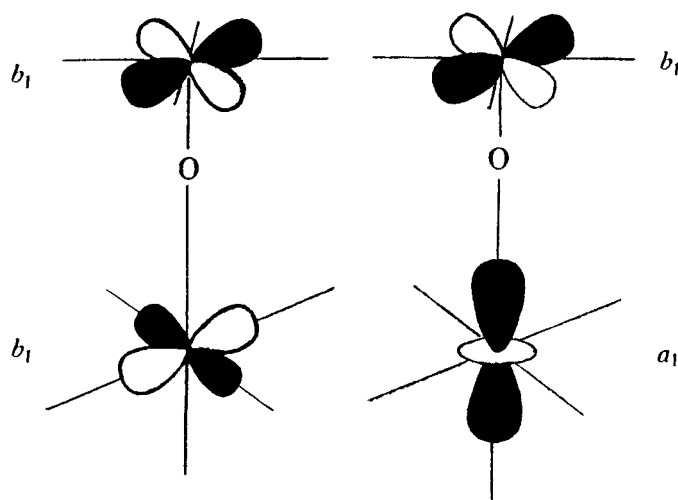


FIG. 4. Thermal variation of $\chi_m T$ for $\text{Co}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$. The solid line shows the best fit using Eq. [3].

where the parameters have the same meanings as in the Ni^{2+} compound. The g factors are assumed to be isotropic and $g_V = g_{\text{Co}} = g$. A fit of the magnetic data leads to the parameters of $g = 2.42$, $2J = 38.6 \text{ cm}^{-1}$ and $zJ' = -1.7 \text{ cm}^{-1}$. The coefficient of determination is 0.9774.

The structures of both $\text{Ni}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ (6, 8) and $\text{Co}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ (5) are closely related to that of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. The incorporation of metal cations accompanies the reduction of V^{5+} to V^{4+} , although the basic tetragonal structure of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ is unchanged (Fig. 1). The intercalated metal cations bring the layers closer to each other by electrostatic interactions, and the interlayer separation in $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (7.43 Å) (11) is shortened. Compared with the interlayer separations in $M(\text{VOPO}_4)_2 \cdot n\text{H}_2\text{O}$ ($M = \text{Na}, \text{K}, \text{Rb}, \text{Ca}, \text{Sr}, \text{Pb}; n = 3, 4$) (6.30–6.53 Å), those in $\text{Co}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ (6.714 Å) and $\text{Ni}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ (6.667 Å) are significantly longer. In contrast, the magnetic exchanges mediated between the layers are much stronger in the latter cases. As already mentioned, it is the linear trimer of $\text{V}=\text{O}-\text{M}-\text{O}=\text{V}$ ($M = \text{Ni}, \text{Co}$) that is responsible for the bulk magnetic susceptibility of $M(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($M = \text{Ni}, \text{Co}$). Ferromagnetic exchange may be simply explained by the nature of the magnetic orbitals involved in $\text{V}^{4+}-\text{M}^{2+}$ interactions within the trimer, as in the Ni compound, for instance.

The exchange constant J in Eq. [1] refers to the coupling between a pair of V^{4+} and Ni^{2+} . It is therefore justified that the symmetry of the $\text{V}=\text{O}-\text{Ni}$ dimer, which is close to C_{4v} , is considered instead of the symmetry of trimer, which is close to D_{4h} . We assume that the z -axis is parallel to the $\text{V}-\text{Ni}-\text{V}$ direction and that the x - and y -axes are along the $\text{Ni}-\text{OH}_2$ bonds. Under C_{4v} symmetry, the one unpaired electron around V^{4+} that occupies a $d_{x^2-y^2}$ orbital could be transformed as b_1 , and the two unpaired electrons around Ni^{2+} arising from the e_g configuration that occupy the $d_{x^2-y^2}$ and



SCHEME 1

d_{z^2} magnetic orbitals could be transformed as b_1 and a_1 , respectively. The magnetic orbitals may be schematized as shown in Scheme 1. The strict orthogonality is thus achieved only with the $d_{x^2-y^2}$ orbital of V^{4+} and the d_{z^2} orbital of Ni^{2+} . $J = J(\text{F}) + J(\text{AF})$. The antiferromagnetic interaction, caused by the direct overlap of the $d_{x^2-y^2}(\text{Ni}^{2+})$ and $d_{x^2-y^2}(\text{V}^{4+})$ magnetic orbitals, would be expected to be very weak because the electrons are largely localized in their equatorial planes and, as a result, the overlap could be neglected. The ferromagnetic contribution, $J(\text{F})$, therefore is dominant, which is in agreement with the experimental results.

The obvious ferromagnetic coupling between Ni^{2+} and V^{4+} in $\text{Ni}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ is stronger than those in other $\text{V}^{4+}-\text{Ni}^{2+}$ systems such as $[(\text{VO})\text{LNi}(\text{H}_2\text{O})_2](\text{ClO}_4)_2$, $[(\text{VO})\text{LNi}(\text{Py})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, and $[(\text{VO})\text{LNi}(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O} \cdot 2.5\text{CH}_3\text{OH}$, where L is a macrocyclic tetramine-diphenol ligand ($2J = 4-24 \text{ cm}^{-1}$) (12). These systems also involve orthogonal magnetic orbitals but the vanadyl oxygen remains as a terminal ligand. The relatively efficient ferromagnetic exchange pathway in the former case may arise from the precise linear nature of $\text{V}=\text{O}-\text{Ni}-\text{O}=\text{V}$ and, hence, the delocalization of the $d_{z^2}(\text{Ni}^{2+})$ magnetic orbital toward the oxygen could be largely achieved while the antiferromagnetic contribution is nearly ignored. In the latter case, the fact that the V^{4+} ion is pulled out of the equatorial plane toward the oxygen of the vanadyl group may decrease the overlap density and, consequently, exhibit weak interactions between the magnetic centers.

For $\text{Co}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$, the three unpaired electrons around Co^{2+} occupy $d_{x^2-y^2}$, d_{z^2} , and d_{xy} orbitals, which, under C_{4v} symmetry, could be transformed as b_1 , a_1 and b_2 , respectively. Strict orthogonality is again achieved with the $d_{x^2-y^2}$ orbital of V^{4+} and the d_{z^2} and d_{xy} orbitals of Co^{2+} . Accordingly, ferromagnetic interactions could be favorable

within the trimer. The calculated coupling constant ($2J = 38.6 \text{ cm}^{-1}$) could be compared with that of $\text{Ni}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($2J = 37.6 \text{ cm}^{-1}$). A comparison to other Co^{2+} - VO^{2+} compounds is not available because, as far as we are aware, there have been no reports on the magnetic behaviors of such systems up till now.

At lower temperatures ($< 50 \text{ K}$), both $\text{Ni}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ exhibit a monotonous decrease of $\chi_m T$. Such a decrease could be caused by the antiferromagnetic interactions between the trimers, which are mediated through the phosphate bridges within the layers. The zJ' values, which infer this interaction, are small and comparable to the exchange constant in $\text{Sr}(\text{VOPO}_4)_2 \cdot 4\text{H}_2\text{O}$ (-1.7 cm^{-1}). The intralayer antiferromagnetic interactions in the Sr compound are claimed to be correlated with the canted $(\text{VO})\text{O}_4$ basal planes (4). Nevertheless, in Ni and Co compounds, the $(\text{VO})\text{O}_4$ basal planes are parallel to each other by symmetry. It is worth noting that the zero-field splitting as well as the spin-orbit coupling (especially in the Co compound) would make significant contributions to the magnetic behaviors of the title compounds at low temperature (10). Taking into account the difficulty of considering these effects together, the exchange parameters obtained in this paper are approximate values. The results, however, clearly point out the ferromagnetic coupling nature within the $\text{V}=\text{O}-M-\text{O}=\text{V}$ ($M = \text{Ni}, \text{Co}$) trimers.

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