JOURNAL OF
Materials
CHEMISTRY

Low dimensional magnetism of $M(VOPO_4)_2{\cdot}4H_2O$ layered compounds: the 2D ferromagnet $Cd(VOPO_4)_2{\cdot}4H_2O$ and the 2D antiferromagnet $Mg_{1-x}Zn_x(VOPO_4)_2{\cdot}4H_2O$ with $x \approx 0.28$

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Received 29th October 1998, Accepted 18th January 1999

A magnetic study has been carried on the non-magnetic cations intercalated vanadyl phosphates $Cd(VOPO_4)_2{\cdot}4H_2O$ and $Mg_{1-x}Zn_x(VOPO_4)_2{\cdot}4H_2O$ with $x \approx 0.28$. The susceptibility measurements are indicative of weak magnetic interactions within the negatively charged $[VO_{4/2}OPO_{4/2}]^{\infty-}$ layers, which are interpreted on the basis of a 2D square planar Heisenberg model. $Cd(VOPO_4)_2{\cdot}4H_2O$ is ferromagnetic with $J = +0.87$ cm^{-1} while $Mg_{0.72}Zn_{0.28}(VOPO_4)_2{\cdot}4H_2O$ is antiferromagnetic ($J = -1.93$ cm^{-1}). The obtained results are discussed in connexion with the structural features.

The layered vanadyl phosphate $VOPO_4{\cdot}2H_2O$ is well known to allow for redox intercalation chemistry.[1] Depending upon the preparative route and(or) the nature of the guest cation, a large number of reduced intercalates with general formula $M_x(VOPO_4)_y{\cdot}zH_2O$ has been isolated in recent years.[2–18] Whereas accurate structural features have been available for many years, very little has been published about the magnetic properties of these intercalates. It is only recently that Papoutsakis *et al.*[19] described the magnetic properties of the non-magnetic intercalated Na^+, K^+, Rb^+ and Sr^{2+} compounds and that Zheng and Lii[20] reported on the susceptibility data for the transition metal intercalated vanadyl phosphates $M(VOPO_4)_2$ $4H_2O$ with Co^{2+} and Ni^{2+} as guest cations. Both studies concluded that low dimensional ferromagnetic or antiferromagnetic interactions were present which correlated well with the structural features. Papoutsakis *et al.* used a simple two-dimensional Heisenberg model for a square planar lattice of interacting ions (V^{IV} and V^{V} centers in the case of Na^+, K^+ and Rb^+ with ferromagnetic interactions, only V^{IV} centers in the case of Sr^{2+} with antiferromagnetic interactions) to explain their magnetic data. By contrast, the magnetic susceptibility for $M(VOPO_4)_2{\cdot}4H_2O$ compounds ($M^{2+} = Co^{2+}$, Ni^{2+}) was mainly attributed, in connexion with the structural results, to linear trimers V=O–M–O=V which are present between the layers. By using an isotropic model for both compounds, Zheng and Lii have found strong ferromagnetic coupling within the trimers which fitted well the high temperature part of the susceptibility data ($T \geqslant$ *ca.* 100 K) especially in the case of the nickel compound. However, they could not fit the slight upturns from the low temperature part of the $\chi^{-1} = f(T)$ curves ($T \leqslant$ *ca.* 100 K) because the weak antiferromagnetic interactions within the layers were overlooked. We report here, magnetic susceptibility data for the intercalates $Cd(VOPO_4)_2{\cdot}4H_2O$ and $Mg_{1-x}Zn_x(VOPO_4)_2{\cdot}4H_2O$ ($x \approx 0.28$). The results obtained by using a simple 2D Heisenberg model for a square planar lattice of interacting ions are given and compared to those obtained by using a isolated isotropic cubane-like model.

Experimental

Both compounds were obtained from soft hydrothermal treatments in a 23 mL Teflon-lined pressure vessel at 235 °C for 60 h. The cadmium containing compound was prepared from the initial mixture $V_2O_5 : CdCO_3 : Cd^0 : TEACl : H_3PO_4 : H_2O$ introduced in the respective ratios 1 : 1.2 : 6.85 : 3.6 : 8.78 : 240, the zinc–magnesium compound was synthesized from a mixture with a 1.0 : 1.41 : 2.88 : 7.1 : 17.08 : ≈264 of $V_2O_5 : MgCO_3 : Zn^0 : TEACl : H_3PO_4 : H_2O$ molar ratio. The obtained greenish-blue products were characterized as single phases by X-ray powder diffraction using CuKα radiation. Water loss was monitored by thermogravimetric analysis at a heating rate of 1 °C min^{-1}. The observed weight loss was 14% for $Cd(VOPO_4)_2{\cdot}4H_2O$ (theoretical loss 14.2%) and 14% for $Mg_{0.72}Zn_{0.28}(VOPO_4)_2{\cdot}4H_2O$ (theoretical loss 14.8%). The magnetic susceptibility data were recorded on a 213.1 mg powder sample for $Cd(VOPO_4)_2{\cdot}4H_2O$ and 57.6 mg of crushed single crystals for the zinc–magnesium compound, over the temperature range 2–300 K in a magnetic field of 1 kG using a SQUID magnetometer.

Results and discussion

Various structural and magnetic features on related intercalates are listed in Table 1. Within the infinite layer $[VOO_{4/2}PO_{4/2}]^{\infty-}$, two sets of V–V distances are present which remain *quasi*-constant whatever the nature of the intercalated cation. The first set, $(V–V)_1$ distances, ranges from 4.69 Å (K^+ compound) to 4.48 Å (Zn, Mg compound) with an average value of 4.58 Å while the second set, $(V–V)_2$ distances, varies in the range $6.252 \leqslant (V–V)_2 \leqslant 6.376$ Å. Both sets are involved in the magnetic interactions of the superexchange type *via* phosphate bridges. One of the remarkable features is the shortest V–V interlayer bond distance $(V–V)_3$ which remains surprisingly unchanged for the different members in the series of intercalated compounds, with $(V–V)_3$ ranging from 5.900 to 6.093 Å. By contrast, the interlayer distance varies from 6.297 Å for $Ca(VOPO_4)_2{\cdot}4H_2O$ to 7.41 Å for neutral $VOPO_4{\cdot}2H_2O$. Given the V–V bond distances, the exchange parameters can be anticipated to be weak as is readily seen in Table 1.

The susceptibility data for $Cd(VOPO_4)_2{\cdot}4H_2O$ and $Mg_{0.72}Zn_{0.28}(VOPO_4)_2{\cdot}4H_2O$ (Fig. 1 and 2) are well described by a Curie–Weiss law $\chi = C/(T-\theta)$ with $C = 0.744$ for the cadmium compound and 0.758 for $Mg_{0.72}Zn_{0.28}(VOPO_4)_2{\cdot}4H_2O$ (theoretical value 0.75). The positive value

Table 1 Selected structural and magnetic features for $M(VOPO_4)_2\cdot4H_2O$ compounds. A fairly good fit of the susceptibility data was also obtained by considering an isolated cubane-like unit within the layer with the adjustable exchange parameter J_{cub}. The column with heading □ is for neutral $VOPO_4\cdot2H_2O$

	Ca[a]	Ba[a]	Sr[b]	ZnMg	Co[a]	Cd	Na[b]	K[b]	Rb[b]	□
$(V–V)_1$/Å	4.550–4.663	4.641–4.644	4.627–4.674	4.479–4.486	4.493	—[c]	4.550–4.660	4.530–4.690	—[c]	4.568
$(V–V)_2$/Å	6.348–6.350	6.365–6.376	6.377–6.489	6.252–6.258	6.264	—[c]	6.285–6.284	6.282–6.285	—[c]	6.202
$(V–V)_3$/Å	5.961	5.900	5.900	5.993	5.959	—[c]	6.093	6.054	—[c]	7.410
d_{inter}/Å	6.297	6.365	6.319	6.739	6.710	—[c]	6.529	6.380	—[c]	7.410
Dihedral angle δ/°	2.74	2.67–2.77	2.35	0.69	0	—[c]	0	0	0	0
J_{2D}/cm^{-1}	−0.45	−1.25	−1.73	−1.93	<0	0.87	0.42	0.41	0.44	—
J_{cub}/cm^{-1}	−1.4	−5	—[c]	−6.8	<0	3.7	—[c]	—[c]	—[c]	—
J_{cub}/J_{2D}	3.11	4	—[c]	3.52	—[c]	4.2	—[c]	—[c]	—[c]	—

[a] Full details awaiting publication. [b] From ref. 19. [c] Values not known.

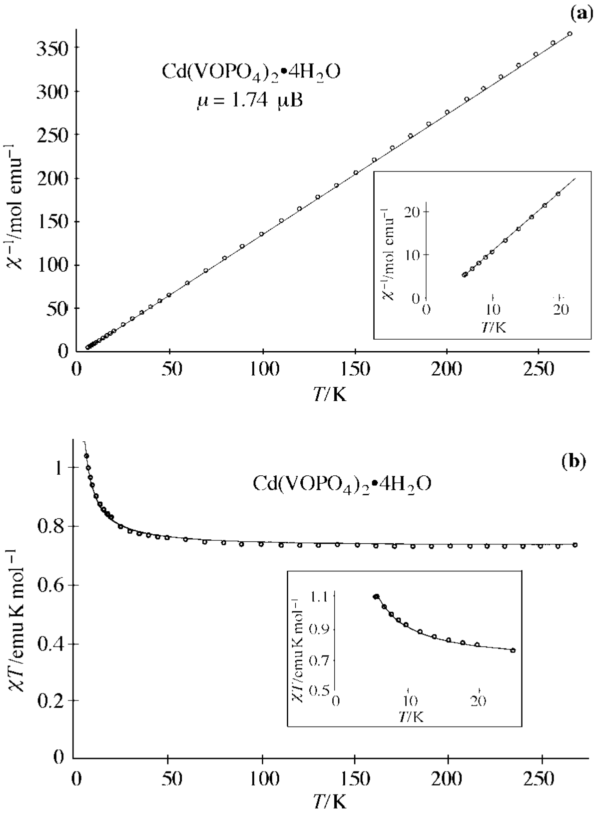

Fig. 1 Susceptibility data for $Cd(VOPO_4)_2\cdot4H_2O$: reciprocal susceptibility *versus* temperature curves (a) and the corresponding $\chi T=f(T)$ curve (b). Open circles are experimental points, a full line represents the fit according to the 2D Heisenberg model.

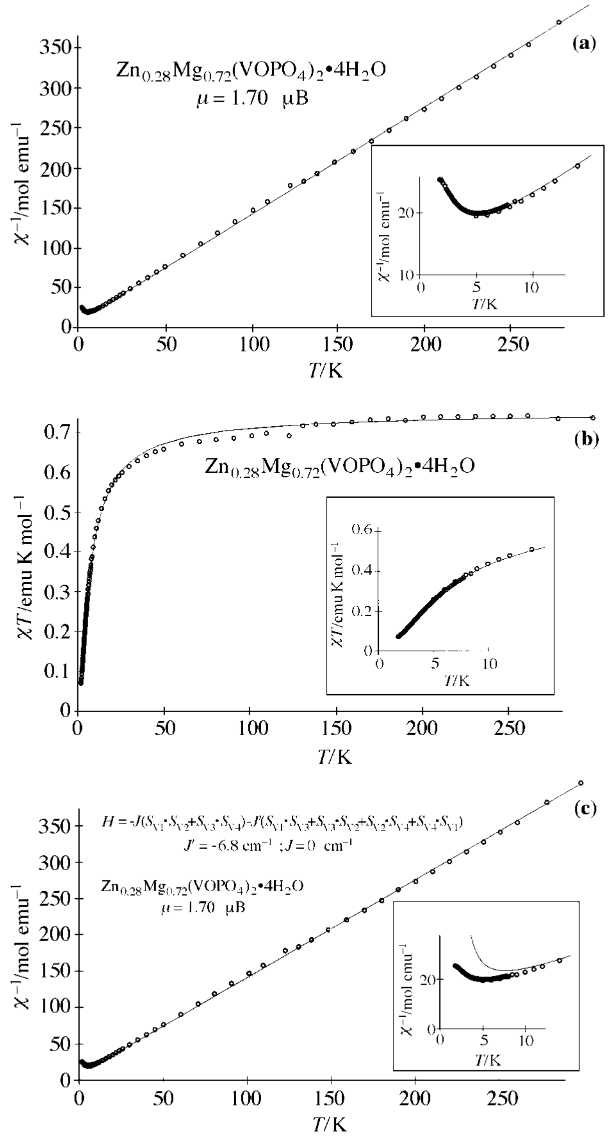

Fig. 2 Susceptibility data for $Mg_{0.78}Zn_{0.22}(VOPO_4)_2\cdot4H_2O$: reciprocal susceptibility *versus* temperature curves (a, c) and the corresponding $\chi T=f(T)$ curve (b). Open circles are the experimental points, a full line represents the fit according to the 2D Heisenberg model (a, b) and to the cubane-like model (c).

of θ ($\theta=1.5$ K) for $Cd(VOPO_4)_2\cdot4H_2O$ shows that the prevailing interactions are ferromagnetic within the $[VOO_{4/2}PO_{4/2}]^{\infty-}$ layer. By contrast, the negative value of θ ($\theta=-7.6$ K) for $Mg_{0.72}Zn_{0.28}(VOPO_4)_2\cdot4H_2O$ shows that the interactions are antiferromagnetic in nature.

Different models were carried out to take into account for the experimental curves:

Isolated isotropic cubane-like model

The $(V–V)_1$ and $(V–V)_2$ distances are respectively, the shortest and longest V–V distances for the cubane unit shown in Fig. 3(b). The experimental data were analyzed by using the zero-field spin hamiltonian $\boldsymbol{H}=-J(\boldsymbol{S}_1\cdot\boldsymbol{S}_2+\boldsymbol{S}_3\cdot\boldsymbol{S}_4)-J'(\boldsymbol{S}_1\cdot\boldsymbol{S}_3+\boldsymbol{S}_3\cdot\boldsymbol{S}_2+\boldsymbol{S}_2\cdot\boldsymbol{S}_4+\boldsymbol{S}_4\cdot\boldsymbol{S}_1)$ according to Khan.[21] The J and J' exchange parameters are joined to the longest $(V–V)_2$ and shortest $(V–V)_1$ distances within a unit. According to the $(V–V)_2/(V–V)_1$ ratio of *ca.* $\sqrt{2}$, the J parameter was allowed to vary within the range $0\leqslant2\cdot J\leqslant\sqrt{2}|J'|$. For both compounds, the best agreements were obtained for $J=0$. The experimental data are very well fitted for $Cd(VOPO_4)_2\cdot4H_2O$ ($R^2=1.0$ for χ^{-1} and χT curves). In the case of $Mg_{0.72}Zn_{0.28}(VOPO_4)_2\cdot4H_2O$, discrepancies appeared between the theoretical and experimental data for $T<10$ K as can be seen on the $\chi^{-1}=f(T)$ curve in Fig. 2(c) ($R^2=0.836$). Though the experimental data were fairly fitted especially for ferromagnetic

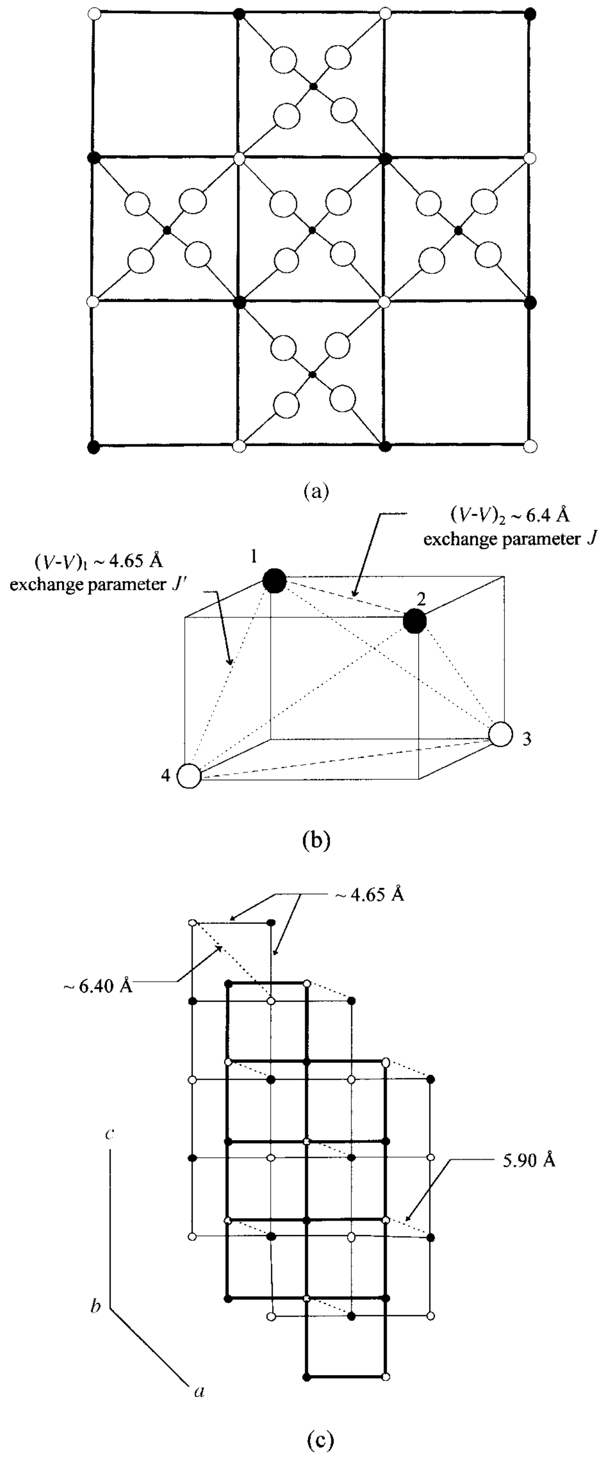

Fig. 3 Partial views of $Ba(VOPO_4)_2{\cdot}4H_2O$ along the [010] direction of the monoclinic unit-cell showing the cubane-like network within the $[VO_{4/2}OPO_{4/2}]^{\infty-}$ layers: (a) the PO_4 tetrahedra are drawn to emphasize the exchange pathways between the vanadium ions; (b) perspective view of the cubane unit; (c) two successive layers shifted from each other in the *ac* plane. The different sets of (V–V) distances are shown: $(V\text{–}V)_1 \approx 4.65$ Å, $(V\text{–}V)_2 \approx 6.40$ Å and $(V\text{–}V)_3 = 5.90$ Å. Large open circles: oxygen ions; small black circles: phosphorus ions; medium circles are vanadium ions with the open ones at $y = 0.5443$ and the black ones at $y = 0.4557$ for the first layer, $y = 1.0443$ and $y = 0.9557$ for the second one.

$Cd(VOPO_4)_2{\cdot}4H_2O$, the isolated cubane-like model did not take into account the 2D network within the layers.

2D square planar Heisenberg cooperative magnetism

For both compounds, the magnetic susceptibility data have been fitted by using the equation after Rushbrooke and Wood[22] for an $S = 1/2$ square planar Heisenberg lattice $\chi(1 - 2/x + 2/x^2 - 4/(3x^3) + 1/(4x^4) + 0.4833/x^5 + 0.003797/x^6) = Ng^2\beta^2/4k_BT$ with $x = k_BT/J$. The exchange parameter J was the unique adjustable parameter.

For $Cd(VOPO_4)_2{\cdot}4H_2O$, the best fit was obtained for $J = +0.87\ cm^{-1}$. The corresponding $\chi^{-1} = f(T)$ curves ($R^2 = 1.0$) and χT *vs.* T ($R^2 = 0.996$) are given in Fig. 1(a) and (b). The obtained exchange parameter agrees fairly well with the observed θ value of $+1.5$ K when considering, after de Jongh and Miedema,[23] the theoretical relation for an $S = 1/2$ square planar Heisenberg lattice $k_B\theta = 2.53|J|S(S+1)$. For $Mg_{0.72}Zn_{0.28}(VOPO_4)_2{\cdot}4H_2O$, the best fit was obtained for $J = -1.93\ cm^{-1}$. The corresponding $1/\chi = f(T)$ ($R^2 = 1.0$) and $\chi T = f(T)$ ($R^2 = 0.999$) curves are given in Fig. 2(a) and (b). The obtained value for the J parameter fits well with the observed T_{min} value of $+5.2$ K (theoretical $T_{min} = 1.90|J|/k_B = 5.27$ K).

No obvious correspondence can be made to correlate the obtained values of J with the shortest intralayer V–V distances. On the other hand, the exhange mechanisms are not as simple as previously reported[24] by taking into account the relative orientation of the vanadium polyhedra within the layer measured by the dihedral angle δ. With the exception of the cadmium compound for which no accurate structural data are available, the intralayer interactions are antiferromagnetic whatever the dihedral angle δ between adjacent V=O groups for divalent guest cations. The J values are ranging from $J = -1.93\ cm^{-1}$ for the zinc–magnesium compound with $\delta = 0.69°$ to $J = -0.45\ cm^{-1}$ for the calcium compound with $\delta = 2.74°$. The corresponding J values were not determined for the nickel and cobalt compounds for which $\delta = 0°$, nevertheless the slight upturns observed on the $1/\chi = f(T)$ for these compounds clearly indicate that the exchange interactions are also antiferromagnetic. By contrast, according to the results by Papoutsakis *et al.*, all the intercalates with monovalent cations are ferromagnetic with J values about $+0.4\ cm^{-1}$ and a dihedral angle $\delta = 0°$.

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Paper 8/08386J