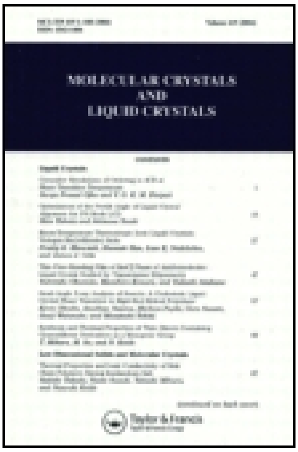

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Ferromagnetism, Antiferromagnetism and Paramagnetism in Vanadium Phosphates Prepared From Hydrothermal Conditions

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FERROMAGNETISM, ANTIFERROMAGNETISM AND PARAMAGNETISM IN VANADIUM PHOSPHATES PREPARED FROM HYDROTHERMAL CONDITIONS

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Abstract: Several metal phosphate solids have been prepared from hydrothermal reaction methods that involve vanadium and either alkali metal ions or organic amine templating agents. A variety of magnetic behavior is observed, depending on the structures of the solids that are isolated. Binuclear $[(VO)_2Cl_2(H_2O)_2(PhAsO_3H)_2Ph_4PCl]$, trinuclear $[(C_2H_5NH_3)_2(VO)_3H_2O(C_2H_5PO_3)_6]$, hexanuclear $[(C_2H_5)_4N_2(VO)_6(H_2O)_2(C_2H_5PO_3)_6]$, 16-atom cluster $[V_{16}O_{20}(OCH_2CCH_2O)_8(H_2O)_4]$ and polymeric $[AVOPO_4, A= Na, NH_3]$ materials have been prepared. Some materials exhibit long range antiferromagnetic phase transitions that result from strong lattice interactions between magnetic centers. Ferromagnetic behavior is also observed in $[H_3N(CH_2)_3NH_3(VO)_3(OH)_2(H_2O)_2(PO_4)_2]$ with a ferromagnetic phase transition at T_c=5K. The magnetic data are interpreted in terms of the molecular and crystallographic data.

INTRODUCTION

Hydrothermal methods utilize water under pressure and at temperatures above its normal boiling point as a means of speeding up reactions between solids. Such hydrothermal methods are finding increasing applications in material science and solid state chemistry. They are technologically important, both as a method of crystal growth and for the synthesis of new materials with useful properties. As a synthetic route to new structures, it is especially valuable for those structures which do not have high temperature stability.

Hydrothermal synthetic techniques have proven to be an extremely valuable procedure in the chemistry of microporous solids. Recent developments in the chemistry of polyoxovanadium clusters reflect their relevance to bioinorganic chemistry,[1-3] geochemistry,[4-5] sol-gel chemistry,[6-7] and catalysis and materials science.[8-10]

Several transition metal phosphate clusters have been prepared from hydrothermal reaction methods that involve vanadium and either alkali metal ions or organic amine templating agents. Binuclear, trinuclears, hexanuclear, decahexanuclear, and polymeric materials have been prepared. Some materials exhibit long range antiferromagnetic phase transitions that result from strong lattice interactions between magnetic centers. Ferromagnetic behavior is also observed. In this report, we describe several vanadium metal and vanadium metal phosphate complexes. A variety of magnetic behavior has been observed for these complexes, depending on the structures of the solids that are isolated. The magnetic data is interpreted in terms of the molecular and crystallographic data.

EXPERIMENTAL

Synthesis:

Several different starting precursor materials were mixed and placed in a 23 ml Teflon-lined Parr acid digestion bomb and heated at soft chemistry temperatures ($T \leq 200^oC$) with autogeneous pressure for around 48 hours depending on each sample. After allowing the resultant mixture to cool slowly to room temperature, crystalline product was filtered.

Magnetism:

Two instruments were used for the magnetic measurements: the Quantum Design, Inc. model MPMS-5S superconducting SQUID susceptometer, and the S.H.E. Corp. VTS-50 superconducting susceptometer. The magnetic susceptibility data were recorded on polycrystalline samples over the 2-300 K temperature region. Measurement and calibration techniques have been reported elsewhere.[11]

RESULTS AND DISCUSSION

$[V_{16}O_{20}\{(OCH_2)_3CCH_2OH\}_8(H_2O)_4]\cdot 3H_2O$ *(1)*

The neutral polyoxoalkoxyvanadium(IV) cluster with a hexadecametyalate core, has been synthesized by the hydrothermal technique. As shown in Figure 1, the structure of this complex **1** consists of two $[V_8O_8\{(OCH_2)_3CCH_2OH\}_4\cdot(H_2O)_2]^{4+}$ units connected through four oxo groups. There are several different vanadium(IV) environments in the crystalline material. Two pairs of V centers have very close contacts at 2.671 and 2.684 Å compared to a range of 3.03-3.30 Å for the distance between other V-V pairs.[12] More details about crystal structure analysis of this complex are available in reference 12. Variable temperature magnetic susceptibility data were recorded on a 17 mg polycrystalline sample of (**1**) over the temperature range of 2 to 300 K.

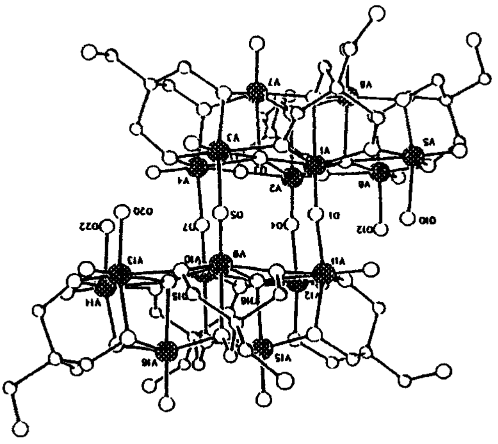

Figure 1. X-ray structure diagram of (1)

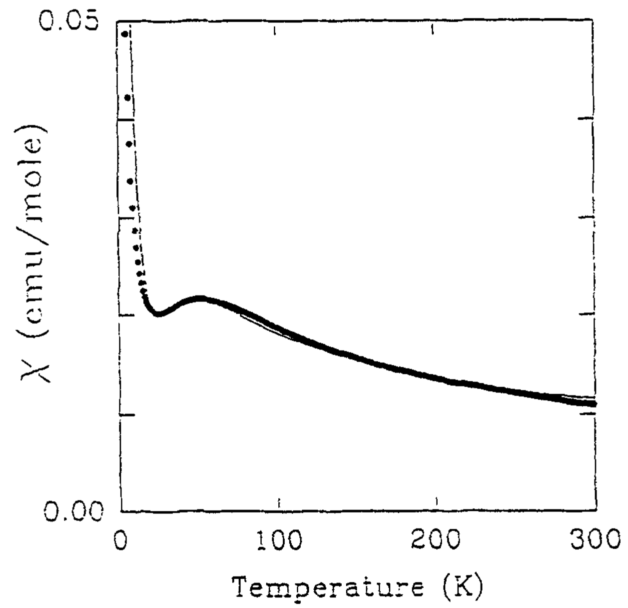

Figure 2. Temperature dependent magnetic susceptibility of (1). The curve shows the best fit of the data as described in the text.

The temperature dependent magnetic susceptibility data for this complex is shown in Figure 2 as magnetic susceptibility plotted as a function of temperature. The high temperature magnetic susceptibility data (T > 100K) was fitted with the expression describing Curie-Weiss paramagnetism with S=1/2 for a $V(IV)_{16}$ system, yielding C = 2.028 emu·K/mole, θ = -46 K, and TIP = 0.00528 emu/mole. The electron structure of the compound corresponds to one unpaired electron per vanadium. This results in an average Curie-Weiss g-value of g=1.16 for each of the sixteen V(IV) ions in the $V_{16}O_{20}$ cluster. The low g-value supports the assignment of two pairs of V(IV) binuclear units as strongly coupled and contributing essentially a diamagnetic component to the magnetic susceptibility.

At low temperatures an anomaly is observed in the temperature dependence of the magnetic susceptibility data. As temperature is lowered to around 50K, the magnetic susceptibility of the sample passes through a broad maximum expected for short range antiferromagnetic interactions and is consistent with magnetic exchange between a pair of vanadium(IV) binuclear units, while the remaining vanadium(IV) centers would be expected to show paramagnetic behavior that results from significantly less magnetic exchange.

The behavior expected in binuclear system of the vanadium(IV) cluster complex is the Heisenberg isotropic exchange Hamiltonian and may be written as $\mathcal{H} = -2JS_1 \cdot S_2$ where a negative J denotes a singlet ground state (antiferromagnetism) and positive J indicates a triplet ground state (ferromagnetism). The application of this spin Hamiltonian and $S_1=S_2=1/2$ system to the Van Vleck equation yields the Bleaney-Bowers equation for the magnetic susceptibility

$$\chi = [Ng^2\mu_B{}^2/kT][2e^{2x}/(1+3e^{2x})] \qquad (1)$$

where x = J/kT. Since 8 of the V(IV) ions have longer interatomic contacts, these would be expected to have weaker exchange interactions than the other V(IV) ions. The magnetic behavior of the weakly coupled V(IV) centers can be approximated as paramagnetic Curie law behavior. The behavior of the two pairs of V(IV) ions and the 8 paramagnetic V(IV) ions in the V_{16} cluster can be expressed by

$$\chi = [2Ng^2\mu_B{}^2/kT] + [4Ng^2\mu_B{}^2/kT]\cdot[e^{2J/kt}/(1+3^{2J/kt})] \qquad (2)$$

where all V(IV) ions are assumed to have the same g-value, the magnetic susceptibility is calculated per 16-V(IV) unit, and all of the parameters have their usual meaning.

Equation 2 neglects the internuclear magnetic exchange except the binuclear exchange parameter J. Although the contact distances are longer for the 8 paramagnetic V(IV) ions, it is reasonable to expect that these ions will exhibit weak magnetic interactions with each other and as well as with the two stronger coupled binuclear units.

The overall magnetic exchange is therefore quite complicated but a simple approximation can be attempted by treating all secondary magnetic exchange with a single parameter using the molecular field correction. The equation that describes the effect of a molecular exchange field on the magnetic susceptibility is:

$$\chi = \chi'/\{1 - (zJ'/Ng^2\mu_B{}^2)\chi'\} + TIP \qquad (3)$$

where χ' is the magnetic susceptibility of the material in the absence of the exchange field (eq.2) and χ is the molecular exchange field influenced magnetic susceptibility that is actually measured. The exchange field coupling parameter is zJ', where z is the number of exchange coupled neighbors. The addition of the molecular field exchange correction resulted in a substantial improvement of the fit to the data.

The results of a least square fit of equation 2 corrected for a molecular exchange field (eq. 3) yields the parameters g = 2.2, J/k = -44K, zJ'/k = -7.1K, and a correction for temperature independent paramagnetism TIP = 0.00695 emu/mole. The result of this fit is illustrated in Figure 2 as magnetic susceptibility plotted as a function of temperature and the smooth curve is the theoretical calculation.

At lower temperatures, the experimental data deviates slightly from the calculated values although Curie Weiss behavior is still followed. The deviation at the lowest temperature is expected since a variety of different weak magnetic interactions are all represented by only one parameter, zJ'. The overall prediction of our model is quite good, especially when one considers the simplicity of the model. The theoretical model gives excellent agreement with the magnetic data from room temperature to temperatures below the maximum in the magnetic susceptibility. Since the behavior of the magnetic susceptibility is so well predicted in the vicinity of the maximum, the fitted value of the binuclear coupling parameter (J) is an excellent representation of the coupling between these magnetic centers.

$Rb_2[V_6O_7(OH)_3\{(OCH_2)_3CCH_3\}_3]$ *(2)*

A new organically templated vanadium complex of the formula (2) has been prepared and consists of octahedral V^{IV} units as shown in Figure 3. The temperature dependent magnetic susceptibility data for this complex is shown in Figure 4 plotted as a function of temperature. As the temperature is lowered to around 40K, The magnetic susceptibility of the sample passes through a broad maximum and begins to decrease a lower temperatures. This behavior is expected for short-range antiferromagnetic exchange and is consistent with magnetic exchange between the six vanadium(IV) ions occupying the

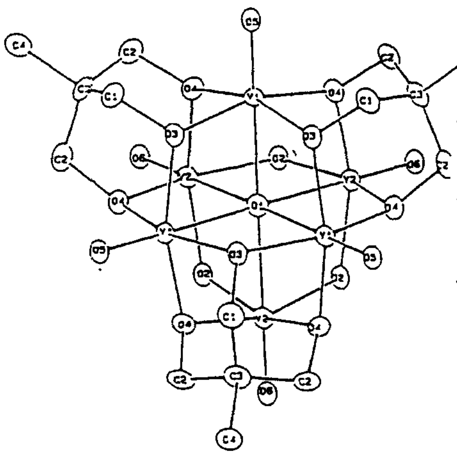

Figure 3. X-ray structure diagram of the hexameric complex (2).

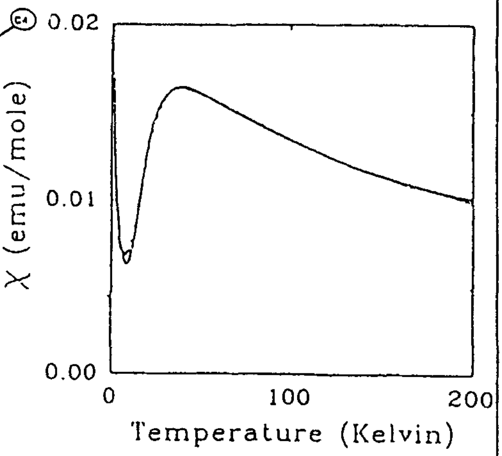

Figure 4. Temperature dependent magnetic susceptibil;ity of (2). The curve shows the fit of the data using the isotropix hexameric spin Hamiltonian.

corners of an octahedron. Within the context of the crystal structure of this material, the exchange from this spin Hamiltonian may be propagated via an isotropic octahedral six atom cluster magnetic exchange interaction. Since the hexamer may be approximated as an octahedron, a summation may be taken over all possible V-V interactions within the cluster and all J values are restrained to be same.

The behavior of the totally isotropic and symmetric six atom spin S=1/2 magnetic exchange may be described by the following magnetic susceptibility equation

$$\chi = \frac{Ng^2\mu_B{}^2}{kT} \; \frac{56e^{2x}+200e^{6x}+196e^{12x}+60e^{20x}}{14+84e^{2x}+100e^{6x}+496e^{12x}+9e^{20x}} \qquad (4)$$

where the magnetic susceptibility is calculated per hexamer unit and x=J/kT.

The magnetic susceptibility data recorded at the lowest temperatures indicates the presence of a paramagnetic impurity. The magnetic susceptibility data were fit over the entire temperature region to the isotropic, symmetric hexamer magnetic exchange model corrected for the presence of the paramagnetic impurity. The fitted parameters are g=1.88, J/k=-32.1, and TIP= 0.00329 emu/mole, with 1.2% paramagnetic impurity. The smooth line drawn through the data points in Figure 4 is the theoretical curve calculated from eq4 with the parameters indicated.

$(C_2H_5NH_3)_2[V_3O_3(H_2O)(PhPO_3)_4$ (3)

The organically-templated vanadium-oxide organophosphonate phase (3) was prepared and the structure analysis of this complex shows an alternating inorganic and organic layered structure. The layered solid material consists of alternating organic and inorganic domains and exhibit useful sorptive and catalytic properties[13-15].

The magnetic susceptibility data were recorded on a 13.42 mg polycrystalline sample of this complex over the 1.7-300 K temperature region. The high temperature magnetic susceptibility data (T>20K) exhibit Curie-Weiss paramagnetism with C=1.075 emu·K/mole, θ = -14K, and TIP = 0.00036 emu/mole as shown in Figure 5. The electron structure of (3) corresponds to one unpaired electron per vanadium(IV)ion with spin S=1/2. This results in an average Curie-Weiss g-value of g=1.95 for each of the V(IV) ions.

The large negative Weiss constant indicates that there is a substantial amount of antiferromagnetic exchange in this complex. At lower temperatures the magnetic susceptibility begins to deviate from Curie-Weiss law, but there is no characteristic magnetic anomaly to allow a precise determination of the strength and nature of the magnetic coupling.

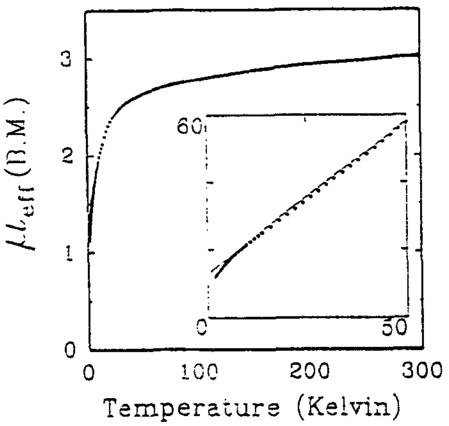

Figure 5. Temperature dependent - μ_{eff} and χ^{-1} (inset) for (3). The data show Curie-Weiss behavior.

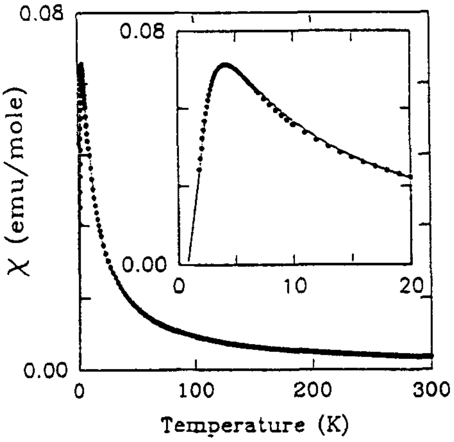

Figure 6. Temperature dependent magnetic susceptibility of (4). The inset shows an expansion of the 0 - 20 K region.

$[V_2O_2Cl_2(H_2O)_2(PhAsO_3H)_2][Ph_4PCl]_2$ (4)

From the hydrothermal method, compound (4) was synthesized and X-ray structure analysis was obtained. The magnetic susceptibility data were recorded on 37.13 mg polycrystalline sample of 6 over 1.7-300 K temperature region. The magnetic data are shown in Figure 6 as molar magnetic susceptibility plotted as a function of temperature.

The high temperature magnetic susceptibility data (T>100K) exhibit Curie-Weiss paramagnetism with C= 0.786 emu·K/mole, θ = -9.0K, and TIP= 0.000267 emu/mole. The electron structure of compound 4 corresponds to one unpaired electron per vanadium. This results in an average Curie-Weiss g-value of g=2.04 for each of the V(IV)ions. As the temperature is lowered to below 10K, the magnetic susceptibility of the sample passes through a broad maximum and begins to decrease. The broad maximum is expected for short range antiferromagnetic exchange and is consistent for vanadium(IV) binuclear units. Although the contacts are longer for the inter-binuclear distances as opposed to the intra-binuclear distance, there is a bonding pathway through the phosphate bridges that allows for inter-binuclear magnetic exchange.

The analysis with the binuclear model corrected for a molecular exchange field yields the parameters g=1.95, J/k = -3.6, zJ'/k = -2.0 K. The result of this fit is illustrated in Figure 6 as magnetic susceptibility plotted as a function of temperature and the smooth curve is the theoretical calculation.

$(CH_2)_3NH_3[(VO)_3(OH)_2(H_2O)_2(PO_4)_2]$ *(5)*

The magnetic susceptibility data of (5) have been recorded and display interesting and complicated magnetic properties. The high temperature magnetic susceptibility data (T>50K) exhibit Curie-Weiss paramagnetism with C= 0.9751 emu·K/mole and θ = 20.7K. This results in an average g-value of g=1.86 for each of the three V(IV) ions the V_3O_3 cluster. At room temperature the V atoms display an effective magnetic moment near 3 consistent with three noninteracting S = 1/2 V(IV) centers.

As the sample is cooled, deviation from Curie-Weiss behavior become apparent below 50K and the magnetic moment begins to decrease. Studies of the susceptibility of this complex as a function of temperature and applied measuring field are shown in Figure 7. The decrease in χ below 50 K manifests itself as a broad local maximum near 6.5 K, as shown in Figure 7b, suggesting short range antiferromagnetic ordering possibly attributable to the antiferromagnetic coupling of the spins between the trimers. Near 5.2 K the material undergoes an ordering into a weakly ferromagnetic state. The transition is extremely sensitive to the magnitude of the measuring field and χ below the ferromagnetic transition is initially suppressed as the field is decreased as shown in Figure 7a,b, but this trend is reversed as the measuring field is increased above 2.5 kG, the lower temperature susceptibility once again begins to increase (Figure 7c) and continues increasing at the highest fields (*ca.* 20 kG). When samples are cooled in cooling fields near zero and then measured upon warming in small applied fields (Figure 7d), there are indications of a still more complicated magnetic phase diagram.

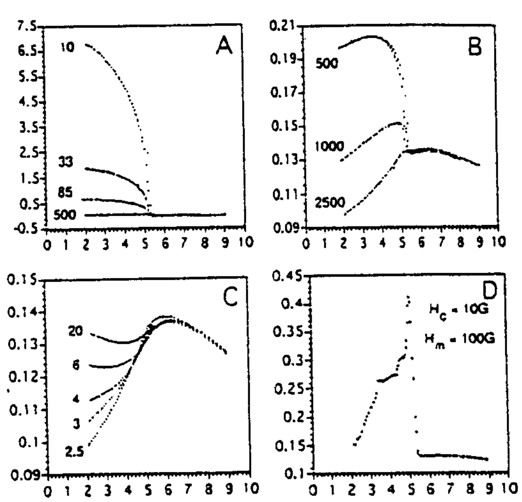

Figure 7 . Figures A, B, and C show the dc-magnetic data of (5) measured at several magnetic field strengths. D shows the data for the zero field cooled experiment.

An interesting question is the nature of the longer range interactions developing, even though the magnetically active trimmers are separated from one another by the insulating phosphate groups. In the crystal structure, the vanadyl oxygen atoms of the octahedral VO_6 at both end of the trimers have contacts at 2.81 Å which is essentially the van deer Waals radius for oxygen. Polarization of the electrons of the V=O groups could provide a possible exchange pathway for the longer range interactions.

$NaVOPO_4$ (6) and NH_4VOPO_4 (7)

Two vanadyl phosphates have been prepared by hydrothermal technique. The X-ray crystal analysis for these complexes have been conducted showing linear chain structures of corner sharing VO_6 octahedra in Figure 8. The temperature dependent magnetic susceptibility data for these complexes are shown in Figure 9a and 9b for **6** and **7**, respectively, as magnetic susceptibility plotted as a function of temperature. The high temperature magnetic susceptibility data (T>100K) for $NaVOPO_4$ (**6**) and (T>25K) for NH_4VOPO_4 (**7**) exhibit Curie-Weiss paramagnetism with C = 0.416 emu·K/mole, θ = -31 K for complex 6 and C = 0.417 emu·K/mole, θ = -4.72 K for complex 7. The electron structure of both complexes corresponds to one unpaired electron per VO formula unit with spin S = 1/2. This results in an average Curie-Weiss g-value of g = 2.1 for each of the V(IV) ions in the cluster. The large negative Weiss constants indicate that there are substantial amounts of antiferromagnetic exchange in these materials.

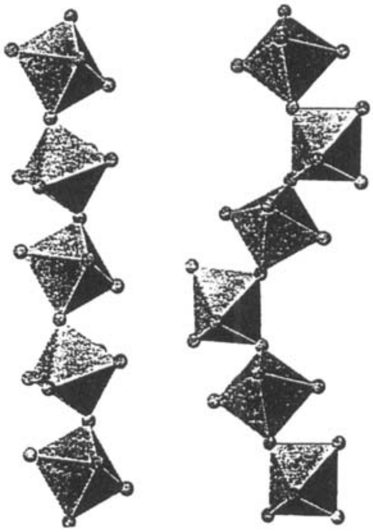

Figure 8. X-ray structure of the linear chain compounds $AVOPO_4$.

At lower temperatures the magnetic susceptibility data show temperature dependent behavior that begins to deviate from Curie-Weiss law. At around 20 K for the $NaVOPO_4$ complex, the magnetic susceptibility of the sample passes through a broad maximum and begins to decrease a lower temperatures (Figure 9a). The behavior is expected for short-range antiferromagnetic exchange. The magnetic exchange for this complex is the isotropic Heisenberg spin Hamiltonian. Within the context of the crystal structure of this material, the exchange from this spin Hamiltonian may be propagated via a one dimensional magnetic exchange interaction along the structural chain axis. The Bonner-Fisher Heisenberg linear chain calculation was done for this antiferromagnetically coupled one dimensional vanadium complex, and gives the fitted parameters as g=2.00, J/k=-18.6, TIP=0.00009 emu/mole, and 2% paramagnetic impurity. The smooth line drawn through the data points in Figure 9a is the theoretical curve with the parameters indicated.

The Bonner-Fisher calculation was not as successful for the NH_4VOPO_4 complex which shows an abrupt deviation of the magnetic susceptibility data at about 3.71K (Figure 9b). This can be explained by the structure analysis. Both materials are structural

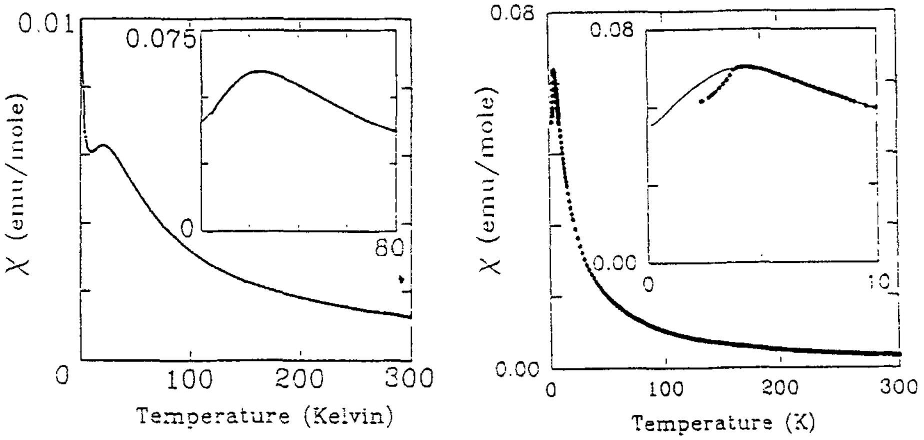

Figure 9. Temperature dependent magnetic data for (a) $NaVOPO_4$ (**6**) and (b) NH_4VOPO_4 (**7**). The curves represent the best fits of the data to the linear chain model as described in the text.

linear chains that are propagated along cornet sharing VO_6 bonding pathway. However the complex **6** exhibits only trans coordination within the chain while the complex **7** exhibits alternating cis-trans coordination along the chain.

The molecular field corrected to the linear chain model was used to approximate the effect of inter-chain magnetic interaction, and gives the fitted parameters as g=2.10, J/k= -3.26, zJ'/k=-2.1K for **7**. The model shows excellent agreement of the calculated values with the measured magnetic susceptibility data until the onset of long range order at T= 3.71K.

CONCLUSION

Several vanadium complexes have been prepared from hydrothermal techniques. Magnetic measurements were conducted in the SQUID magnetometer for these complexes showing either a variety of magnetic . In these vanadium complexes, direct exchange is not important because most of the these vanadium complexes are linked with oxygen ligand which promotes a superexchange mechanism. The magnetic models that were used to analyze the data were developed from consideration of the molecular structure and bonding obtained from the crystal structure analysis. The vanadium oxide coordination sphere and three dimensional crystal contacts promote the onset of magnetic phase transitions in several of the complexes.

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REFERENCES

1. D.Rehder, *Angew.Chem., Int.Ed.Engl.9,* **1991**, *30*, 148.
2. D.C.Crans, C.M.Simons, J.S.Blenchard, *J.Am.Chem.Soc.,* **1992**, *114*, 4926.
3. A.Butler, C.J.Carrano, *Coord.Chem.Rev.,* **1991**, *109*, 61.
4. H.T.Evans,Jr., J.S.White,Jr., *Mineral.rec.,***1988**, *18*, 333.
5. H.T.Evans,Jr. S.Landergren, In *Handbook of Geochemistry,* K.H.Wedepohl,Ed., Springer, Berlin, **1978**, Vol.II/2, Chapter 23.
6. C.J.Brinker, G.W.Scherer, *SolGel Science*, Academic Press, New York, **1991.**
7. J.Livage, *Chem.Mater.,* **1991**, *3*, 579.
8. B.I.Whittington, J.R.Anderson, *J.Phys.Chem.,* **1993**, *97*, 1032; D.Patel, P.J.Anderson, H.H.Kung, *J.Catal.* **1990**, *125*, 132.
9. J.-M.Aamarilla, B.Casal, J.-C. Galvan, E.Ruiz-Hitzky, *Chem.Mater,* **1992**, *4*, 62.
10. R.T.K.Baker, L.L.murrell, Eds.New.Materials in *Heterogeneous Catalysis;* American Chemical Society, Washington,DC, **1990.**
11. C.J.O'Connor, *Prog. Inorg. Chem.,* **1982**, *29*, 203.
12. M.I.Khan, Y.-S. Lee, C.J.O'Connor, and J.Zudieta,
13. M.B.Dines, R.E.Cooksey, P.C.Griffith, *Inorg.Chem.,* **1983**, *22*, 567.
14. G.Cao, T.E.Mallouk, *Inorg.Chem.,* **1991**, *30*, 1434.
15. G.L.Rosenthal, J.Caruso, *Inorg.Chem.,* **1992**, *31*, 3104.
16. V.Soghomonian, Q.Chen, R.C.Haushalter, J.Zubieta, C.J.O'Connor, and Y.-S. Lee, *Chem.Mater.* **1993**, *5*, 1690-1691.