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Magnetic Properties of the Trirutile Compound $LiMnVF_6$

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The magnetic susceptibility from 4.2 to 300 K and spontaneous magnetization up to T_c of the trirutile compound $LiMnVF_6$ were measured. A plot of χ^{-1} vs. T displays two linear regions. One possible explanation for this phenomenon employs a binuclear model in which the intradimer interaction (J_1) is 1 order of magnitude or more greater than the interdimer interaction (J_2). This model presumes Mn^{2+} and V^{3+} ions are ordered within the trirutile lattice such that all nearest- and second-nearest-neighboring magnetic ions of Mn^{2+} are V^{3+}, and vice versa. Intracoupling between nearest-neighboring Mn^{2+}-V^{3+} pairs occurs first, forming magnetically ordered dimers. These dimers then behave as paramagnetic ions, giving rise to a quasi-paramagnetic region. At lower temperatures, intercoupling of the dimers leads to three-dimensional, long-range ordering with a predictable spontaneous magnetic moment. The experimental magnetic constants for $LiMnVF_6$ are $C_M = 5.32$ cm^3 K mol^{-1}, $C_M' = 1.92$ cm^3 K mol^{-1}, $\Theta = -25$ K, $\Theta' = +18.5$ K, $T_c = 23$ K, and $\sigma_0 = 2.6\ \mu_B$. Values of the exchange constants that were fitted to the susceptibility data are $J_1/k = -26 \pm 3$ K and $J_2/k = -0.83 \pm 0.05$ K.

Introduction

Most combinations of divalent and trivalent first-row transition-metal fluorides (which are thermodynamically compatible) will combine with LiF 1:1:1 to form a trirutile lattice with composition $LiM^{II}M^{III}F_6$.[1-9] Noted exceptions are as follows: $LiMnCrF_6$ and $LiMnFeF_6$, which form hexagonal lattices of the Na_2SiF_6 type;[7] the $LiCuM^{III}F_6$ phases, which form solid solutions in the rutile lattice;[6] the $LiCrM^{III}F_6$ phases, which form a structure yet to be determined.[10]

The mineral tapiolite ($FeNb_{0.2}Ta_{1.8}O_6$) and numerous synthetic oxides of the general formula $M^{II}M^{V}{}_2O_6$ crystallize in a trirutile lattice that belongs to space group $P4_2/mnm$ (D_{4h}^{14}).[11] In these oxides, M^{2+} ions occupy 2a sites and M^{5+} ions occupy 4e sites. The fluorides mentioned above have often been reported to belong to the same space group as the oxides.[2,3,5,6] This would mean the Li^+ ions occupy 2a sites and the M^{2+} and M^{3+} ions randomly occupy 4e sites.

Recently, it was established that in fluoride analogues of tetragonal tungsten bronze of composition $KM^{II}M^{III}F_6$ the M^{2+} and M^{3+} ions are not random but occupy unique lattice positions.[12-14] This ionic ordering lowers the symmetry in the bronze structure from $P4/mbm$ (D_{4h}^5) (oxides) to $P4_2bc$ (C_4^8) (fluorides).[12] In fluorides having the trirutile lattice, ordering of M^{2+} and M^{3+} ions should also lower the crystal symmetry.

Crystal structures of fluorides that form a trirutile lattice have been determined for $Li_{0.75}Zn_{0.25}(Zn_{1.25}Cr_{0.75})F_6$[6] and LiV_2F_6.[9] In both cases, the space group was found to be $P4_2/mnm$. Neither of these compounds, however, is representative of the general class $LiM^{II}M^{III}F_6$. In $Li_{0.75}Zn_{0.25}(Zn_{1.25}Cr_{0.75})F_6$, the stoichiometry is not 1:1:1, and not only is LiV_2F_6 a mixed valence compound but it also has a unique electronic structure.

Figure 1a shows the location of cations in rutile (MF_2), Figure 1b illustrates trirutile ($LiM^{II}M^{III}F_6$) in which M^{2+} and M^{3+} ions are random, and Figure 1c illustrates a possible ordered arrangement of M^{2+} and M^{3+} ions within the trirutile lattice. In these structures, the F^- ions are located between neighboring cations such that ~90° M-F-M interactions occur between nearest neighbors and ~135° M-F-M interactions occur between second-nearest neighbors. In MF_2 (Figure 1a), each M^{2+} ion has two nearest neighbors and eight second-nearest neighbors. In $LiM^{II}M^{III}F_6$ (Figure 1b), each paramagnetic ion has only one nearest neighbor and four second-nearest neighbors which are also paramagnetic. If M^{2+} and M^{3+} are order as illustrated in Figure 1c, the situation becomes more interesting as the nearest neighbor and four second-nearest neighbors to an M^{2+} ion are M^{3+} ions, and vice versa. The ordered arrangement of ions in Figure 1c would lower the symmetry of the crystal from space group $P4_2/mnm$ (D_{4h}^{14}) to probably $P4_2nm$ (C_{4v}^4).[15] Wintenberger et al.,[16] in fact, suggested this may be the correct space group for $LiFe_2F_6$ on the basis of their determination of its magnetic structure. However, they were not able to distinguish between a randomly disordered distribution of Fe^{2+} and Fe^{3+} ion and an ordered one.

In LiV_2F_6,[9] a unique situation exists in that nearest-neighboring vanadium ions share an electron and the two rapidly alternate oxidation states. This model is based on single-crystal X-ray results which indicate that vanadium ions occupy a single lattice site, and the magnetic data which suggest both V^{2+} and V^{3+} species are present in the paramagnetic region. The strength of the nearest-neighbor magnetic interaction (J_1) is 1 order of magnitude, or more, greater than that of the second-nearest-neighbor magnetic interaction (J_2). This causes magnetic ordering to occur in steps: dimers form first, followed at lower temperatures by three-dimensional, long-range ordering. This feature gives rise to a temperature range (quasi-paramagnetic region) where the dimers behave as paramagnetic ions. In LiV_2F_6, the sign of J_1 is positive, hence, intradimer coupling is ferromagnetic; J_2 is negative, so interdimer coupling is antiferromagnetic, thus canceling any spontaneous magnetic moment.

In a search for $LiM^{II}M^{III}F_6$ compounds that will have $|J_1| >> |J_2|$, it is appropriate to examine M^{2+}, M^{3+} combinations in which (1) overlapping t_{2g} orbitals are each half-filled or (2) one of the t_{2g} orbitals is half-filled and the other is empty. Candidates for M^{2+} include $V^{2+}(d^3)$ and Mn^{2+} (d^5); candidates for M^{3+} include $V^{3+}(d^2)$, $Cr^{3+}(d^3)$, and $Fe^{3+}(d^5)$, all of which should have "spin-only" magnetic moments in the trirutile lattice. Of these six combinations, V^{2+}-V^{3+} has been studied;[9] it is questionable that V^{2+}-Cr^{3+} and V^{2+}-Fe^{3+} are thermodynamically stable; Mn^{2+}-Cr^{3+}

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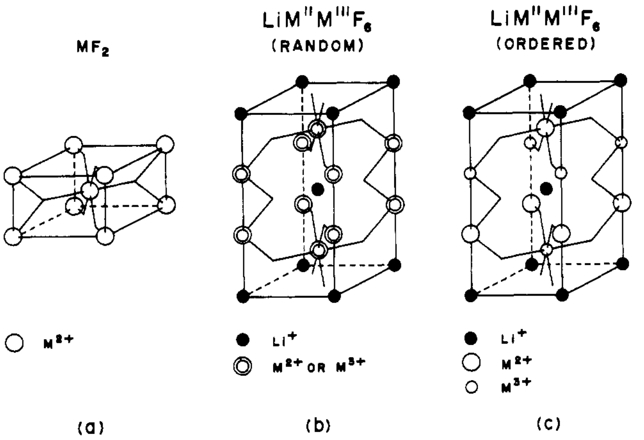

Figure 1. (a) The rutile structure, (b) the random trirutile structure, and (c) the proposed ordered trirutile structure.

Table I. Magnetic Constants of $LiMnVF_6$

C_M(obsd) = 5.32 cm^3 K mol^{-1}	C_M'(obsd) = 1.92 cm^3 K mol^{-1}
C_M(calcd) = 5.38 cm^3 K mol^{-1}	C_M'(calcd) = 1.88 cm^3 K mol^{-1}
$\theta = -25$ K	$\theta' = 18.5$ K
$T_c = 23$ K	$J_1/k = -26 \pm 3$ K
$\sigma = 2.60\ \mu_B$	$J_2/k = -0.83 \pm 0.05$ K

and Mn^{2+}–Fe^{3+} form the Na_2SiF_6 structure.[5] The sole candidate remaining is $LiMnVF_6$; hence, it is the topic of this paper.

Experimental Section

Appropriate quantities of thoroughly mixed LiF, MnF_2, and VF_3 were vacuum encapsulated in a 0.75 in. diameter × 1.25 in. height Mo capsule by means of electron-beam welding techniques. The MnF_2 and VF_3 were prepared in this laboratory by using methods previously described by Stout and Boo.[17,18] Optical grade LiF was obtained commercially. The sealed capsule was fired inside a nickel tube heated by a Lindberg Hevi-duty furnace at 850 °C for 13 days. The product was analyzed optically by stereoscopic and polarized microscopy. The sample was characterized by X-ray diffraction using both Cu $K\alpha_1$ and Cr $K\alpha_1$ radiations with a Guinier–Hagg camera. The X-ray data were refined by least squares on a DEC-10 computer. Magnetic measurements were made from 4.2 to 300 K between 0.14 and 10 kG with a Foner type PAR vibrating-sample magnetometer equipped with a Janis liquid-helium Dewar and gallium arsenide temperature controller. Magnetic fields were measured with a F. W. Bell Hall-probe gauss meter, Model 8860.

Results

Optical examination of the $LiMnVF_6$ product revealed that it consisted mostly of highly birefringent, emerald green crystals with ~1% light green crystals, which were also highly birefringent. The latter phase was separated from the sample by Pasteur's method before X-ray photographs and magnetic measurements were made. All lines on Guinier–Hagg X-ray photographs of the emerald green crystals were fitted to a trirutile lattice of dimensions $a = 4.739$ (2) Å and $c = 9.411$ (5) Å. X-ray photographs of the light green crystals confirmed they were VF_3.

A plot of the inverse magnetic susceptibility of a randomly oriented powder sample of $LiMnVF_6$ vs. temperature from 4.2 to 150 K is shown in Figure 2. The spontaneous moment extrapolated to zero field is included in the insert. A tiny single crystal (approximately 0.5 mg) was measured at 4.2 K to determine whether the spontaneous magnetic moment has a preferred direction or if it aligns itself with the field. The moment has a preferred orientation, so the spontaneous moment of 2.6 μ_B contains the factor $3^{1/2}$. The magnetic constants of $LiMnVF_6$ are summarized in Table I.

Discussion

The Guinier–Hagg X-ray data confirm that $LiMnVF_6$ crystallizes in a trirutile lattice. The powder data, however, do not provide information leading to a unique space group. From conditions limiting possible reflections, given in ref 15, it is not possible to distinguish between space groups $P4_2/mnm$ and $P4_2nm$. For both space groups, the general conditions are the same ($0kl$, $k + l = 2n$). For $P4_2/mnm$, the Li^+ ions should occupy 2a positions, Mn^{2+} and V^{3+} ions should randomly fill 4e positions, and F^- ions should be on 4f positions. For $P4_2nm$, Li^+, Mn^{2+}, and V^{3+} ions should each occupy unique 2a positions and F^- ions three sets of 4c positions. In both space groups, all special conditions for the cation sites are the same (hkl, $h + k + l = 2n$), with no special conditions for F^- sites.

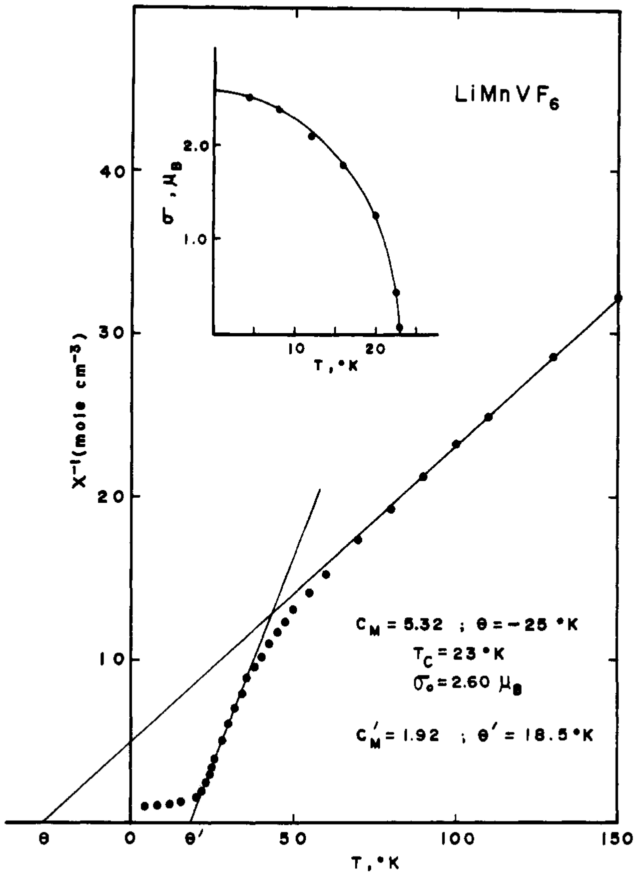

Figure 2. Inverse susceptibility vs. temperature, and spontaneous moment vs. temperature (insert), of a randomly oriented powder sample of $LiMnVF_6$.

The plot of χ^{-1} vs. T for $LiMnVF_6$ shown in Figure 2 displays two linear regions. If we assume a binuclear model for an explanation, the criterion $|J_1| >> |J_2|$ appears to be met in this compound. Since Θ' is positive, we conclude the interaction between dimers is ferromagnetic and J_2' is positive. The value of Θ is more negative than Θ'; hence, J_1 must be negative and nearest-neighboring Mn^{2+}–V^{3+} pairs couple in an antiparallel manner. The value of C_M is greater than that of C_M', and a sizeable spontaneous moment was observed at low temperatures. All of these qualitative aspects are consistent with the surmise that Mn^{2+} and V^{3+} ions in $LiMnVF_6$ are ionically ordered as illustrated in Figure 1c. The observable values of C_M, C_M', and σ are consistent with the model. Experimental values for the two Curie constants are C_M(obsd) = 5.32 cm^3 K mol^{-1} and C_M'(obsd) = 1.92 cm^3 K mol^{-1}, vs. calculated values C_M(calcd) = 5.38 cm^3 K mol^{-1} and C_M'(calcd) = 1.88 cm^3 K mol^{-1}. The observed spontaneous moment, shown in the insert of Figure 2, is σ_0(obsd) = 2.6 μ_B. The calculated spontaneous moment is σ_0(calcd) = 3 μ_B.

If certain conditions are met, it is possible to obtain accurate values of J_1 and J_2 from magnetic susceptibility data. O'Connor[19] has derived magnetic susceptibility equations for isotropic, binuclear complexes based on a simplified form of the Van Vleck

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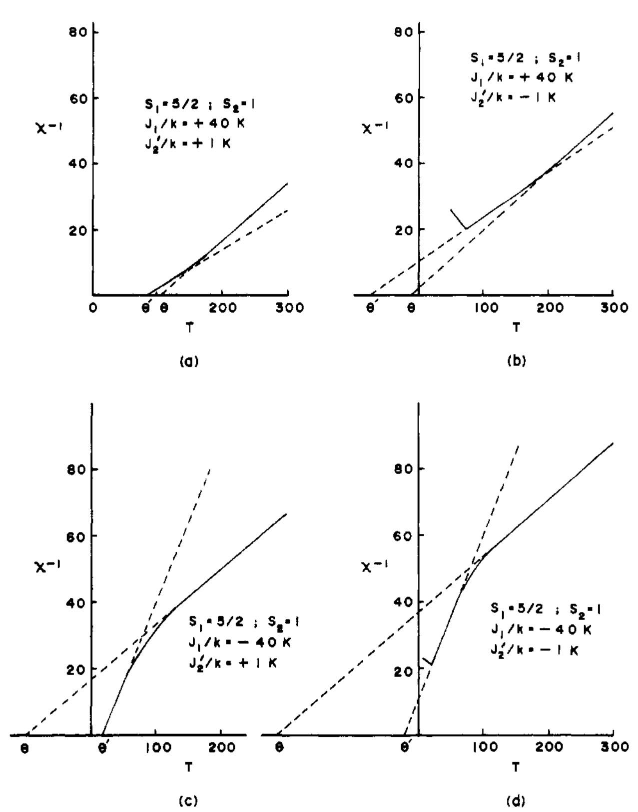

Figure 3. Four possibilities for two paramagnetic regions in trirutile: (a) $J_1/k = +40$ K, $J_2'/k = +1.0$ K; (b) $J_1/k = +40$ K, $J_2'/k = -1.0$ K; (c) $J_1/k = -40$ K, $J_2'/k = +1.0$ K; (d) $J_1/k = -40$ K, $J_2'/k = -1.0$ K.

equation.[20] These equations include ions with various combinations of spin quantum numbers under the effects of Heisenberg intracluster magnetic exchange. For dimers with $S_1 = 1$ and $S_2 = {}^5/_2$, the equation is

$$\chi_0 = C\frac{10 + 35e^{5x} + 84e^{12x}}{4(2 + 3e^{5x} + 4e^{12x})}$$

where $C = Ng^2\mu_B{}^2/kT$ and $x = J_1/kT$. Furthermore, if weak intercluster exchange interactions are present, the exchange-corrected susceptibility is given by

$$\chi = \frac{\chi_0}{1 - (2_zJ_2'/Ng^2\mu_B{}^2)\chi_0}$$

O'Connor warns, however, that the effectiveness of the molecular field exchange parameter is limited by the requirement that the primary interaction, J_1, should be at least 5–10 times the magnitude of zJ_2'.

A typical J_2'/k value might have a magnitude of 1 K. Since z is 8, and J_1 is required to be at least 5 times zJ_2', a marginal value for J_1/k would have the magnitude 40 K. Plots of χ^{-1} vs. T, values of the four possible combinations of J_1/k and J_2'/k being either positive or negative with magnitudes 40 and 1 K, respectively (calculated from the two equations above), are illustrated in Figure 3. It is clear that the plot of χ^{-1} vs. T for LiMnVF$_6$ shown in Figure 2 is similar to that in Figure 3c.

If we assume J_1 in LiMnVF$_6$ is negative, the resultant spin of the dimer after coupling is $^3/_2$. From the relationship

$$\Theta' = \frac{2S(S + 1)zJ_2'}{3k}$$

where $\Theta' = 18.5$ K and $S = {}^3/_2$, we obtained the value $J_2'/k = +0.93 \pm 0.05$ K. Substitution of this value into the preceding equations gives a fit to the experimental data with $J_1/k = -26 \pm 3$ K. Figure 4 is a plot of χT vs. T in which the solid line represents calculated values and the solid circles are observed values. An exact fit to each susceptibility point gives J_1/k values that vary from −29 K at 300 K to −24 K at low temperatures. It is not surprising that J_1 is a function of T, as one would expect shrinkage along the c axis to occur in the trirutile lattice as magnetic ordering sets in. This was found to be the case in the MF$_2$ compounds (M = V, Mn, Fe, Co, Ni) independent of the sign or magnitude of J_1.[21,22] One must not, however, overlook the fact that J_1/zJ_2' is only 3.3 and the accuracy of J_1/k may, therefore, be somewhat uncertain. Since magnetic ordering resulting from the binuclear model clearly describes an ideal ferrimagnet, the possibility must not be dismissed that the data may be more correctly interpreted by a ferrimagnetic model.

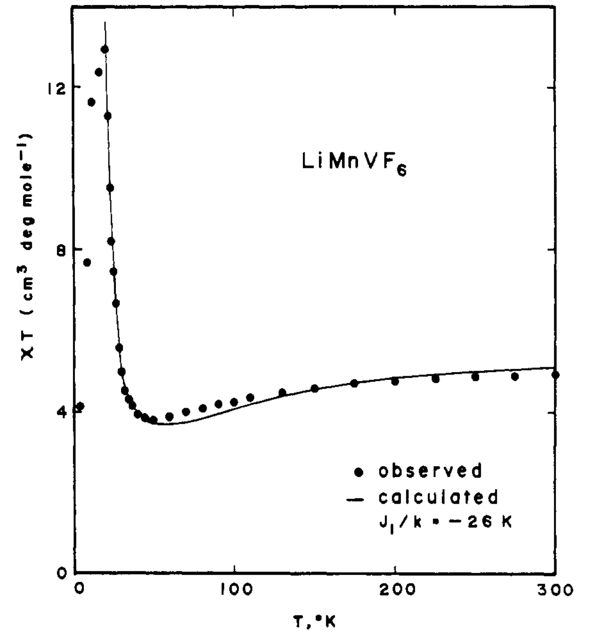

Figure 4. Experimental and calculated values of χT vs. temperature for LiMnVF$_6$.

One alteration is necessary with regard to the second-nearest-neighbor interaction. For mathematical reasons, we have assumed that after coupling occurs within the dimer, the behavior of the dimer can be explained simply as that of an ion with a resultant spin $^5/_2 - 1 = {}^3/_2$. The physical model of the dimer, however, is that the electrons of each Mn^{2+} and V^{3+} ion are localized; consequently, the second-nearest-neighbor interaction is actually a superexchange interaction between Mn^{2+}(d^5) and V^{3+}(d^2). The corrected J_2/k value is obtained from the relation

$$|\Theta'| = \frac{2[S_1(S_1 + 1)S_2(S_2 + 1)]^{1/2}zJ_2}{3k}$$

where S_1 and S_2 are the spins of V^{3+} and Mn^{2+}, respectively. The value of J_2/k, which is a ~135° Mn^{2+}–F$^-$–V^{3+} interaction, is −0.83 ± 0.05 K.

One surprise is the sign of J_1. In LiMnVF$_6$, we believe a half-filled t$_{2g}$ orbital of Mn^{2+} overlaps with the emtpy t$_{2g}$ orbital of V^{3+}. One would expect, as in LiV$_2$F$_6$, this direct exchange to be the dominant effect that would give rise to a ferromagnetic interaction. The Mn^{2+} and V^{3+} ions, however, couple antiparallel in forming the dimer, indicating J_1 is negative. A similar dilemma exists in the compounds NaMnCrF$_6$ and LiMnCrF$_6$.[23] Although these two compounds crystallize in modified forms of the Na$_2$SiF$_6$ structure rather than trirutile, these structures are similar to trirutile in that octahedra are both corner and edge sharing and have M^{2+}–F$^-$–M^{3+} bond angles of ~90 and ~135°. Again, one

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might speculate that the major contribution to the ~90° Mn^{2+}–F^-–Cr^{3+} interaction would be the direct overlap of half-filled t_{2g} orbitals located between the two ions, which should result in a medium-strength antiferromagnetic interaction. Surprisingly, this interaction is ferromagnetic, although quite weak. Equally surprising is the fact that the ~135° Mn^{2+}–F^-–Cr^{3+} and Mn^{2+}–F^-–V^{3+} interactions are antiferromagnetic, since 135° interactions are usually approximately the same as 180° interactions. We found that ~180° interactions in $KMnCrF_6$[14] and $KMnVF_6$[24] are ferromagnetic, which is explained very nicely by the Goodenough–Kanamori rules.[25,26]

The ~90° interactions of Mn^{2+} with Cr^{3+} or V^{3+} are not consistent with predictions based on the direct overlap of half-filled t_{2g} orbitals or of a half-filled t_{2g} orbital with an empty t_{2g} orbital, respectively. The most obvious correlation mechanism would involve the half-filled e_g orbitals of Mn^{2+} and the half-filled or empty t_{2g} orbitals of Cr^{3+} or V^{3+}, respectively. This mechanism, however, is not consistent with the Goodenough–Kanamori rules, as the sign is incorrect in both cases. One possibility of resolving this question is to gather more information. The most obvious systems that should be studied are the trirutile compounds $LiNiVF_6$, $LiNiCrF_6$, and $LiNiFeF_6$, all of which have been reported to exist.[3,7] On the basis of results from $LiMnVF_6$, $LiMnCrF_6$, and $NaMnCrF_6$, the compounds $LiNiVF_6$, $LiNiCrF_6$, and $LiNiFeF_6$ should have strong nearest-neighbor interactions that are negative, positive, and positive, respectively. A study of these three compounds is in progress in our laboratory.

Conclusions

The trirutile compound $LiMnVF_6$ is ionically ordered such that all nearest- and second-nearest-neighboring paramagnetic ions to an Mn^{2+} ion are V^{3+}, and vice versa. The correct space group for $LiMnVF_6$, therefore, is not $P4_2/mnm$, but the structure is of lower symmetry, perhaps $P4_2nm$. A second condition that persists in $LiMnVF_6$, as well as LiV_2F_6, is $|J_1| >> |J_2|$. This condition leads to two linear regions in a χ^{-1} vs. T plot, and all evidence supports the conclusion that magnetic coupling first forms dimers between nearest neighbors, followed at lower temperatures by cooperative, three-dimensional, long-range ordering. Finally, the ~90° Mn^{2+}–F^-–V^{3+} interaction is antiferromagnetic with $J_1/k \approx -26$ K and the ~135° Mn^{2+}–F^-–V^{3+} interaction is antiferromagnetic with $J_2/k \approx -0.83$ K.

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Supplementary Material Available: A table of measured magnetic susceptibilities of $LiMnVF_6$ vs. T from 4.2 to 300 K (1 page). Ordering information is given on any current masthead page.

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Preparation and Electrochemical Investigation of Monomeric Complexes of Molybdenum(0–VI) with the Ligand 1,4,7-Trimethyl-1,4,7-triazacyclononane (L). Crystal Structure of $[Mo^{IV}LBr_3](PF_6)$

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The oxidation of $LMo(CO)_3$, where L represents the facially coordinating triamine 1,4,7-trimethyl-1,4,7-triazacyclononane ($C_9H_{21}N_3$), by various oxidants such as Br_2, I_2, and nitric acid affords a variety of mononuclear complexes of molybdenum in the oxidation states II–VI: $[LMo^{II}(CO)_3X]^+$ (X = Br, I), $[LMo^{III}X_3]$ (X = Cl, Br, I, NCS), $[LMo^{IV}Br_3]^+$, $[LMo^{V}OX_2]^+$ (X = Cl, Br, I), and $[LMoO_2Br]^+$. The electrochemistry of $LMoX_3$ species in acetonitrile has been investigated. Reversible one-electron oxidation–reduction of $[LMo^{III}X_3]$ complexes has been found. Formal redox potentials measured in acetonitrile vs. the ferrocenium/ferrocene (Fc^+/Fc) couple are as follows: X = Cl, +0.395 V; X = Br, +0.50 V; X = I, +0.525 V. $[LMo(SCN)_3]$ exhibits two reversible one-electron-transfer processes at +0.53 and −2.00 V. The latter process corresponds to the couple Mo(III/II). $[LMo(CO)_3]$ in the absence of coordinating anions is found to be reversibly oxidized in acetonitrile; the formal redox potential of the couple $[LMo(CO)_3]^+/[LMo(CO)_3]$ is −0.245 V vs. Fc^+/Fc. $[LMo^{V}OX_2]^+$ species are reversibly reduced in acetonitrile to the $[LMo^{IV}OX_2]^0$ complexes ($E_{1/2}$ = −0.52 V for X = Cl and −0.40 V for X = Br vs. Fc^+/Fc). The redox potential of the couple $[LMoO_2Br]^{+/0}$ has also been measured to be −0.695 V vs. Fc^+/Fc in acetonitrile. The crystal structure of $[LMoBr_3](PF_6)$ has been determined. The compound crystallizes in the orthorhombic space group *Pbcm* with a = 7.642 (2) Å, b = 15.232 (4) Å, c = 16.275 (2) Å, V = 1890 Å^3, ρ_{calcd} = 2.29 g cm^{-3} for Z = 4, and molecular weight 651.9. The structure was solved by conventional techniques using 1048 unique reflections resulting in a final R factor of 0.076. The structure consists of pseudooctahedral $[LMoBr_3]^+$ cations and discrete PF_6^- anions.

Introduction

The structural chemistry of complexes of molybdenum(V), -(IV), and -(III) with simple O,N donor ligands in aqueous solution is dominated by dimeric and oligomeric oxo- and/or hydroxo-bridged species, containing for instance structural units such as $Mo^{V}{}_2O_4{}^{2+}$, $Mo^{IV}{}_3O_4{}^{4+}$, and $Mo^{III}{}_2(OH)_2{}^{4+}$.[1] The propensity to oligomerize is thought to be due to the formation of relatively strong metal–metal bonds. Thus, well-characterized stable monomeric complexes of molybdenum(III) and -(IV) with simple O,N donor ligands are still rather scarce. We have been investigating the ligating properties of the small macrocycle 1,4,7-triazacyclononane with some early transition metals in high and low oxidation states. With use of this ligand a series of dinuclear species of molybdenum(V) and -(III) containing metal–metal bonds have been characterized by X-ray crystallography[2,3] where

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