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Notes

Magnetic Properties of a Dodecanuclear Polyoxovanadate with Exchange and Electron Delocalization Effects

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Introduction

The magnetic properties of metal clusters in which both exchange interactions and electron-transfer processes are operative are the focus of active research. On one side, these materials are used as models of biological systems in which such processes coexist, like in iron–sulfur proteins,[1] and they are also investigated as possible candidates to yield molecular based magnetic materials,[2] taking advantage of the spin polarization effects determined by electron transfer (double exchange).

Recently, one of us reported a series of polyoxovanadates, containing up to 34 vanadium atoms,[3–6] with varying numbers of vanadium(IV) and vanadium(V). We have already reported some preliminary information on a cluster containing 15 localized vanadium(IV) ions.[7] We wish to report here the magnetic properties of $K_6[H_3KV_{12}As_3O_{39}(AsO_4)]\cdot 8H_2O$ (V3 + 1), which contains[8] anions which can be described as fragment of sphere capped by a potassium ion, as shown in Figure 1. It is formally built up by nine VO_6 octahedra, three VO_4 tetrahedra, and four AsO_4 tetrahedra. The number of vanadium(IV) centers, which are expected to be 4 for charge compensation, was confirmed by manganometric titration.

The identification of the vanadium(IV) centers in the structure is by no means an obvious task. Valence bond summations[9] suggest that V10, V11, and V12 are localized vanadium(IV) ions, while the fourth vanadium(IV) is delocalized over the V1, V2, and V3 sites. However, additional evidence would be required in order to confirm this assignment and also to evaluate the reliability of the method in view of using it for more complex materials. We feel that magnetic measurements, depending on the topology of the magnetic ions, can be a valid test of the ability of the valence bond summations to correctly individuate the localized and delocalized vanadium(IV) centers in polyoxovanadates.

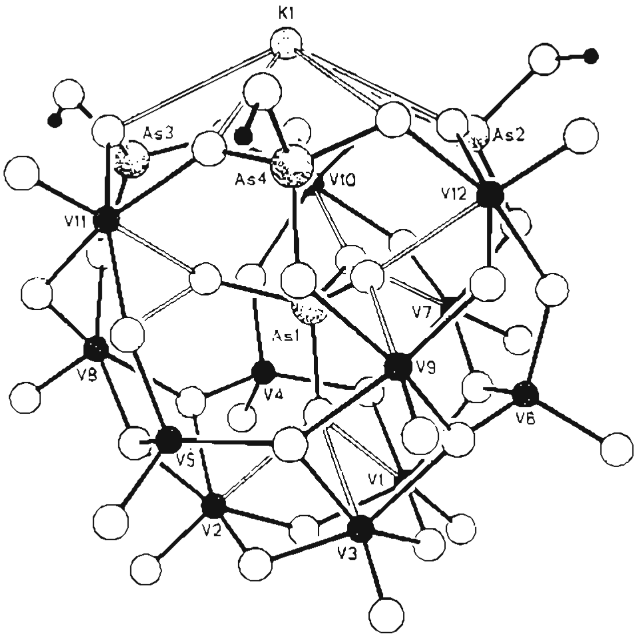

Figure 1. Structure of the $[H_3KV_{12}As_3O_{39}(AsO_4)]^{6-}$ anion.

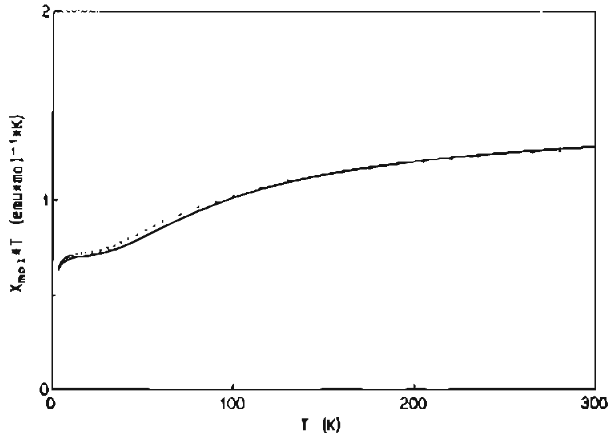

Figure 2. Temperature dependence of χT for $[H_3KV_{12}As_3O_{39}(AsO_4)]^{6-}$.

Experimental Section

The compound was prepared as previously described.[8] Microcrystalline samples were satisfactorily analyzed. The magnetic susceptibility in the range 4–300 K was measured with a Metronique Ingenierie SQUID Magnetometer. The experimental data were corrected for diamagnetic contributions using standard Pascal constants. EPR spectra were recorded with a Varian E9 spectrometer, equipped with an ESR9 Oxford Instruments continuous-flow cryostat, and with a high-field spectrometer previously described.[10]

Results and Discussion

The value of χT of V3 + 1 at room temperature, 1.26 emu mol^{-1} K (Figure 2), is very close to the value expected for four uncoupled electrons (1.5 emu mol^{-1} K for $g = 2$), thus confirming the total number of vanadium(IV) ions deduced from charge compensation considerations. On decrease of the temperature, χT gradually decreases and in the 10–20 K range it makes a

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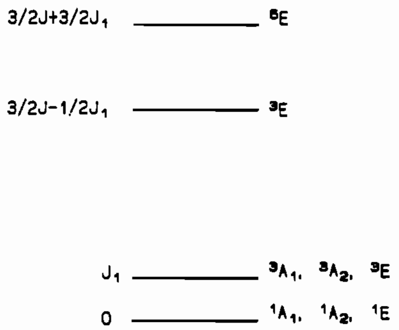

Figure 3. Energy levels for $[H_3KV_{12}As_3O_{39}(AsO_4)]^{6-}$.

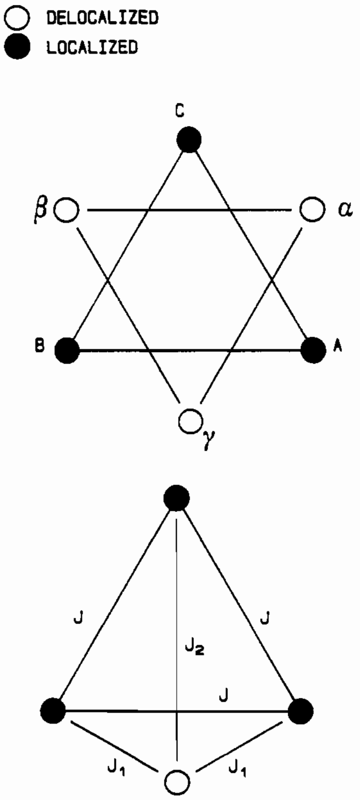

Figure 4. (a) Top: Scheme of magnetic sites in $[H_3KV_{12}As_3O_{39}(AsO_4)]^{6-}$. (b) Bottom: Scheme of exchange pathways in $[H_3KV_{12}As_3O_{39}(AsO_4)]^{6-}$.

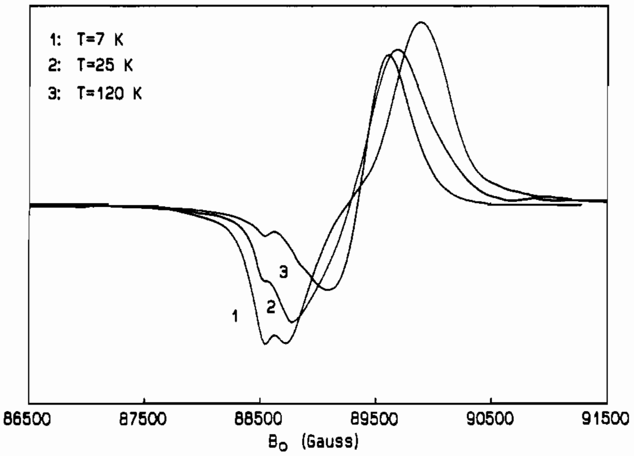

Figure 5. Polycrystalline powder EPR spectra of $[H_3KV_{12}As_3O_{39}(AsO_4)]^{6-}$ at various temperatures. The exciting frequency was 240 GHz.

small plateau, at a value close to that expected for two unpaired electrons, before decreasing again. This result indicates the presence of an antiferromagnetic exchange interaction between the three localized vanadium(IV) ions and, at best, a very weak interation between them and the delocalized center. This result is not unexpected because V10, V11, and V12 are far from the V1, V2, and V3 sites, with no efficient bridge connecting them. The exchange within the three localized vanadium(IV) can be transmitted through arsenato, O–As–O, bridges. On the other hand, the three vanadium centers in the delocalized triangle are close to each other, 3.177 (2), 3.217 (4), and 3.207 (5) Å, and are bridged by μ-oxo groups. Therefore, we may assume that electron transfer is efficient among them.

The simplest quantitative model for the magnetic properties of the cluster takes into account an antiferromagnetic coupling constant J between the three localized vanadium(IV) ions and an effective coupling constant, J', between the localized and delocalized vanadium(IV) centers. The energies of the spin levels can be easily calculated using the Kambe approach.[11] The coupling within the localized triangle gives two degenerate spin doublets and a quartet, separated by $^3/_2J$. The interaction of these with the spin of the delocalized vanadium(IV) splits the quartet in a quintet and a triplet, separated by $2J'$. The two doublets give two singlets and two triplets, separated by J'. The scheme of the levels is shown in Figure 3.

We used this model to fit the experimental thermal variation of χT, as shown in Figure 2. The best fit parameters were J = 63 (3) cm^{-1} and J' = 1.0 (2) cm^{-1}. The value of J is higher than usually observed for μ-O,O′-bridged phosphates.[12-15] In fact J = 32 cm^{-1} was reported[15] for bis(μ-O,O′) phosphate bridges in $(VO)_2P_2O_7$, and J = 16 cm^{-1} for $VO(HPO_4)\cdot 2H_2O$.[14] These data indicate that the coupling constants depend dramatically on the geometry of the complexes, thus making it possible in principle that the high J value observed here is feasible. Further, there can be an enhancement of the magnetic coupling due to the interaction with the delocalized electron.

At low temperature, as far as the magnetic behavior is concerned, it is not possible to rule out that weak intermolecular exchange interactions play some role; therefore, the J' value must be considered at best as an effective coupling constant.

The model we used is not really sensitive to the delocalized nature of the fourth vanadium(IV), and it would be essentially the same for both strong delocalization and for a localized case. In fact, taking into account delocalization effects of one d^1 ion over three equivalent sites, using the scheme previously reported,[16] gives rise to three spin doublet states, which in C_{3v} symmetry can be labeled as $^2A_1$ and ^2E. The energy separation between these levels is $3P$, where P is the parameter associated with the electron-transfer process. For positive P the ground state is ^2E.

In the assumption of large P, i.e. of strong delocalization, the energies of the low-lying spin states are calculated as shown in Figure 3, with J_1 which is the average between J_1 and J_2, the topologically different coupling constants connecting one of the delocalized centers with the localized ones, as schematized in Figure 4.

Therefore, the magnetic data alone cannot determine whether the fourth spin is localized or delocalized. In order to try to solve this problem, we recorded polycrystalline powder EPR spectra at various frequencies and temperatures.

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The 9-GHz spectra do not show any substantial variation with temperature. They have an isotropic $g = 1.96$ and also show a weak transition at half-field. This is a clear indication that the observed spectrum is the result of an averaging process over several spin multiplet states. The g isotropy arises from the averaging of the **g** tensors of all the vanadium(IV) ions. The fact that a half-field transition is observed is an indication that the complete exchange narrowing regime is not achieved.[17]

The 240-GHz spectra at 4.2 K show a more anisotropic signal centered at $g = 1.96$. An increase in temperature shows an overall decrease in the width of the signal, which becomes more isotropic, as shown in Figure 5. Attempts were made to fit the anisotropic spectra by introducing the anisotropic **g** tensor, but no satisfactory fit was obtained. In fact the spectra at 7 K can be reproduced with $g_1 = 1.95$, $g_2 = 1.96$, and $g_3 = 1.97$ but with very anisotropic line widths, 250, 1050, and 350 G, respectively, and with a calculated decay of the signal in the tails of the spectrum which is much slower than experimentally observed.

Our interpretation is that on a decrease of the temperature, in a strong external field, the averaging process becomes less effective, and the spectra move toward those of a triplet. This can be possible if the strong external field stabilizes one triplet over the singlet and over the other triplet states. It must be recalled that in a field of 8 T the lowest component of a triplet lowers its energy by ca. 7 cm^{-1}. Similar effects have been observed in other polyoxovanadates, which will be reported later.

Conclusions

The analysis of the magnetic properties of V3 + 1 showed that it is possible to identify the localized or delocalized nature of the vanadium centers in polyoxovanadates using valence bond summations. This is a very important result for the analysis of the numerous and complex vanadates so far reported which show valence delocalization effects.

Although structural data at room temperature indicate the presence of one vanadium(IV) center delocalized over three equivalent sites, the magnetic and EPR data do not allow us to reach any safe conclusion about the nature of this center at low temperature, because the weak magnetic interaction which couples it to the localized centers does not provide enough information.

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