Magnetic Properties of Isostructural Dodecanuclear Polyoxovanadates with Six and Eight Vanadium(IV) Ions

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Received August 27, 1992

We investigated the magnetic properties of two polyoxovanadate anions, $[V_{12}As_8O_{40}(HCO_2)]^{3-}$ (I) and $[V_{12}As_8O_{40}(HCO_2)]^{5-}$ (II). Both I and II comprise four localized vanadium(IV) ions while two vanadium(IV) ions in I and four in II are delocalized on eight sites, the remaining ions formally being vanadium(V). The temperature dependence of the magnetic susceptibility for the two compounds was fitted with a model which takes into account an antiferromagnetic coupling between the localized vanadium(IV) ions. In II the delocalized vanadium(IV) ions are strongly coupled to give a ground $S = 0$ level by exchange and delocalization effects, while in I the delocalized vanadium(IV) must be considered to be ferromagnetically coupled to the localized ones. The magnetic behavior correlates with the geometry and the topology of the clusters. EPR spectra were recorded both at X-band frequency and with a high-field spectrometer using a far-infrared laser. The spectra of I and II show opposite behaviors at low and high fields, presumably due to field-dependent relaxation effects.

Introduction

The magnetic properties of large spin clusters, which provide a bridge between simple paramagnets, formed by isolated molecular moments, and magnetic materials where infinite assemblies of individual magnetic moments behave cooperatively are currently the focus of active research.[1-6]

In this frame, molecular polyoxovanadates are particularly exciting,[7] because they provide a large variety of high-nuclearity spin clusters, HNSC, containing up to more than 30 vanadium centers, with different topologies, and isostructural species with different electron populations are also known.[8-13] In fact, in these systems it is easy to produce charge fluctuations giving rise to varying ratios of vanadium(IV) and vanadium(V), thus providing systems in which it is possible to investigate the interplay of magnetic interactions and electron transfer.

We report here the investigation of the magnetic properties of $[V_{12}As_8O_{40}(HCO_2)]^{3-}$ (I) and $[V_{12}As_8O_{40}(HCO_2)]^{5-}$ (II), two isostructural dodecanuclear clusters containing six and eight vanadium(IV) ions, respectively, the remainder of the ions being vanadium(V).[8] The structures of I and II suggest that in both compounds four vanadium(IV) ions are localized, while two vanadium(IV) ions in I and four in II are delocalized on eight sites. The assignment of the oxidation states is made using standard bond valence summations.[14] A detailed theoretical model of the interplay of electron-transfer and -exchange interactions in this type of clusters has been published elsewhere.[15] Here we will show the results of temperature-dependent magnetic susceptibility measurements and EPR spectra, recorded both with a conventional spectrometer and with a high-field apparatus with an exciting frequency in the far-infrared region.

Experimental Section

The compounds were synthesized as previously described.[7] Magnetic susceptibility measurements were performed with a Metronique Ingenierie SQUID susceptometer. EPR spectra were recorded with a VARIAN E9 spectrometer operating at 9 GHz, equipped with an Oxford Instruments ESR9 liquid-helium continuous-flow cryostat. High-field EPR spectra were recorded with the apparatus previously described.[16]

Results

Structures. $[V_{12}As_8O_{40}(HCO_2)]^{3-}$ (I) and $[V_{12}As_8O_{40}(HCO_2)]^{5-}$ (II) have very similar structures, in such a way that one of them is sufficient to describe both. In Figure 1 we show the structure of I. The twelve vanadium atoms can be divided into three cluster fragments of four, (V_7, V_8, V_9, V_{12}'), (V_{10}, V_{11}, V_{10}', V_{11}'), (V_7', V_8', V_9', V_{12}), corresponding to three squares of sides 3.4, 5.2, and 3.4 Å, respectively. The external squares are

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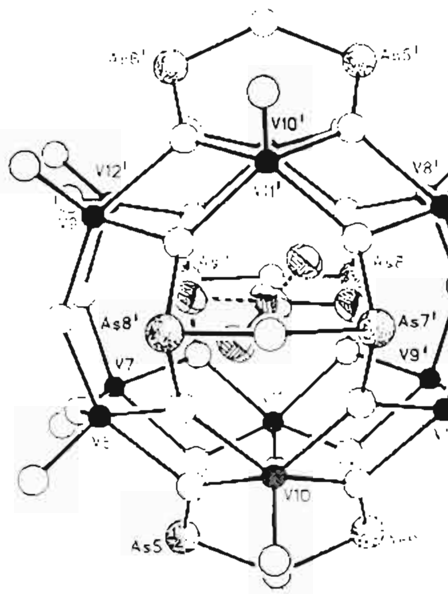

Figure 1. Structure of $[V_{12}As_8O_{40}(HCO_2)]^{3-}$.

identical to each other, being related by an inversion center, and different from the internal one.

The four vanadium atoms in the two external squares are connected by four μ_2-oxo bridges, and they are connected to the metal atoms of the internal square through four diarsenite $(As_2O_5)^{4-}$ groups. A vanadium atom in the external square is connected to a nearest neighbor in the internal square by two oxygen atoms of two different diarsenites and to two next-nearest neighbors through two O–As–O bridges. The four vanadium atoms in the internal square are also connected by four O–As–O bridges.

Charge compensation considerations suggest that in I there are six vanadium(IV) and six vanadium(V) ions, while in II, there are eight vanadium(IV) and four vanadium(V) ions. The standard analysis of the valence bond summations[14] around the vanadium atoms suggests that those of the internal square correspond to vanadium(IV), while those in the external squares are intermediate between vanadium(IV) and vanadium(V). In the following we will assume that one over four atoms in the external squares of I and two over four in II are vanadium(IV). According to this model, we expect valence localization in the internal square and complete valence delocalization in the external squares.

The clusters have approximately tetragonal symmetry, the pseudo-C_4 axis making an angle of ca. 8° with the crystallographic *c* axis in the case of compound I.

Magnetic Properties. The temperature dependence of the χT product of I and II in the range 4.2–300 K is shown in Figure 2. It is apparent that the behaviors are very different for the two compounds. For I, χT at room temperature is 2.05 emu mol^{-1} K, which is close to the value expected for six uncoupled electrons. With decreasing temperature, χT increases to a maximum of 2.5 emu mol^{-1} K at ca. 25 K and then decreases, reaching 2.2 emu mol^{-1} K at 6 K. On the other hand, χT for II is almost constant at the value of 1.2 emu mol^{-1} K from room temperature to ca. 60 K. This value is close to that expected for four uncoupled electrons. Below this temperature, χT decreases rapidly, reaching 0.06 emu mol^{-1} K at 4.2 K. The susceptibility passes through a maximum at ca. 13 K.

EPR Spectra. The EPR spectra of I at 9 GHz are practically unchanged in the range 4.2–200 K. They show one feature at g = 1.96 typical of exchange-narrowed lines, with a Lorentzian shape.[17] A single-crystal analysis showed that the **g** tensor is axial; g_1 = 1.97 and g_2 = g_3 = 1.95. The highest g value, 1.97, is observed, within error, parallel to the pseudotetragonal axis of the cluster, while g_3 is parallel to the *b* crystal axis. Although in the monoclinic cell two magnetically nonequivalent molecules are expected, only one signal was observed in all the crystal orientations. Since the pseudotetragonal axes of the two molecules are practically parallel to each other and to the *c* crystal axis, the expected difference in the resonance field is so small that it cannot be detected.

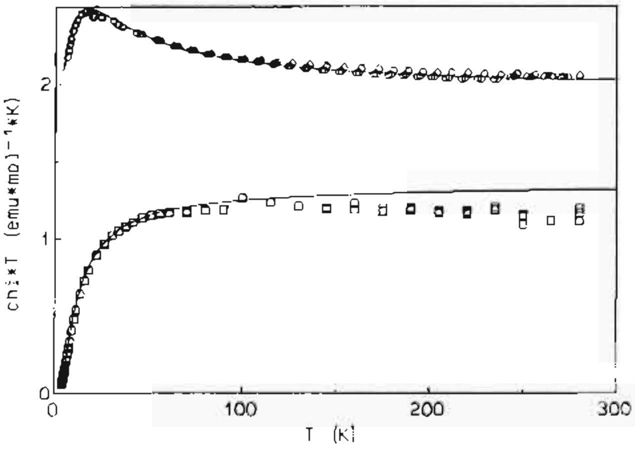

Figure 2. Temperature dependence of χT for $[V_{12}As_8O_{40}(HCO_2)]^{3-}$ (upper curve) and for $[V_{12}As_8O_{40}(HCO_2)]^{5-}$ (lower curve): points, experimental values; Continuous curves, best fits (see text).

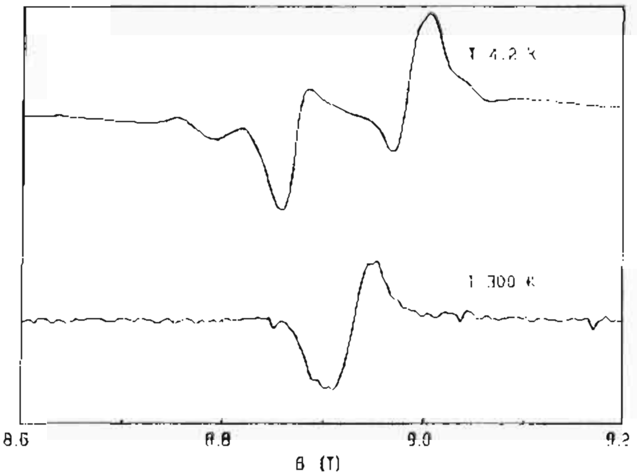

Figure 3. Polycrystalline powder EPR spectra of $[V_{12}As_8O_{40}(HCO_2)]^{3-}$ at various temperatures. The exciting frequency is 240 GHz.

This pattern of **g** tensor values is that expected as a result of an averaging process among the tensors of the four localized and two delocalized vanadium(IV) ions. In fact, assuming that each vanadium(IV) is in an axial crystal field with the V═O direction corresponding to $g_{\parallel}$ = 1.93, and with $g_{\perp}$ = 1.98, as usually observed in VO_5 chromophores,[18] the average of the **g** tensors of the four localized and the two delocalized vanadium(IV) ions is g_1 = 1.97 and g_2 = g_3 = 1.95, in good agreement with the experimental data.

Polycrystalline powder EPR spectra of I were also recorded at low temperature with a high-field spectrometer operating at 255 GHz. The spectra down to ca. 20 K are substantially similar to those of X-band frequency, with a quasi-isotropic feature at g = 1.96. However, on cooling, the spectrum becomes markedly asymmetric, as shown in Figure 3. It shows at least six well-resolved features centered at g = 1.97. The two central features are separated by ca. 0.1 T, and the two external features are separated by approximately the same fine structure. The shape

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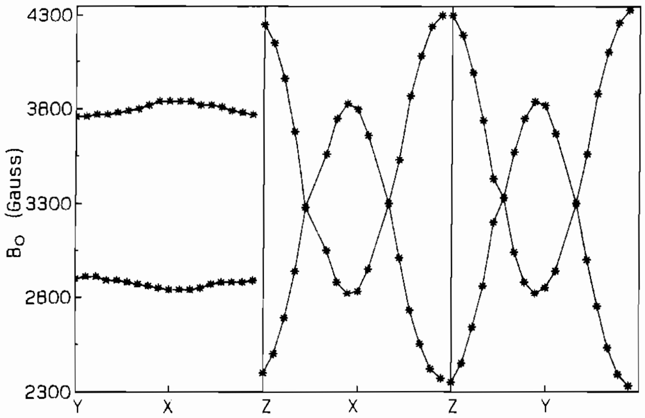

Figure 4. Angular dependence of the transition fields of a monocrystal of $[V_{12}As_8O_{40}(HCO_2)]^{5-}$, at X-band frequency and 4.2 K. The *x*, *y*, and *z* axes refer to the laboratory frame.

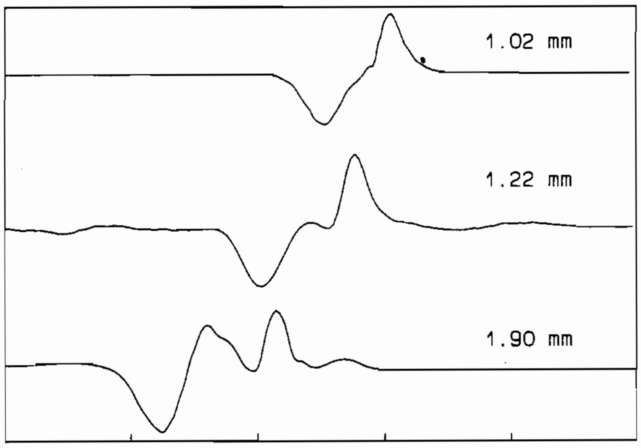

Figure 5. Polycrystalline powder EPR spectra of $[V_{12}As_8O_{40}(HCO_2)]^{5-}$ at various exciting frequencies. The entire width is 5000 G.

suggests that they are perpendicular transitions, and since there are four lines in the structure, the spectra can be interpreted with $g_\perp = 1.97$ and $D = 0.09$ cm^{-1} for an $S = 2$ state. The parallel transitions are presumably weaker and are not observed.

The two intermediate features, also centered at $g_\perp = 1.97$, are separated by ca. 0.2 T. We tentatively assign them to perpendicular transitions of an $S = 1$ state, with $g = 1.97$ and $D \sim 0.2$ cm^{-1}.

The ESR spectra of II at 9 GHz and room temperature are again typical of exchange-narrowed species, with Lorentzian line shapes. The principal *g* values and directions are analogous to those of I.

At 4.2 K, the spectra are typical of a triplet, as shown by the angular dependence of the resonance fields in Figure 4. As the temperature increases, the lines of the triplet tend to merge into a unique central line. The polycrystalline powder spectra provide $g_\perp = 1.95$, $g_\parallel = 1.98$, and $D = 0.093$ cm^{-1}. A single-crystal analysis confirmed these values, showing also that the parallel direction coincides with the pseudo-C_4 axis. Beyond the transitions typical of a triplet, there is an additional feature at a field corresponding to the average of the two fine-structure components. The relative intensities of the two sets of signals are temperature dependent, the intensity of the average signal increasing with increasing temperature.

Variable-frequency EPR measurement at 4.2 K showed that the spectra become progressively averaged with increasing frequency, as shown in Figure 5. At a frequency of 294 GHz, a quasi-isotropic signal centered at $g = 1.96$ is observed, while at 159 GHz the spectra shown several features resembling a fine structure with asymmetry due to thermal depopulation effects. Analysis of the spectra is not possible at this stage.

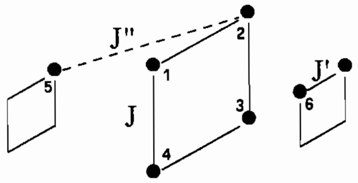

Figure 6. Scheme of the exchange pathways within the V_{12} clusters.

Discussion

The magnetic measurements of I and II provide immediately some qualitative information on the mechanism of exchange and the interplay of exchange and delocalization effects. In fact, the magnetic data for II show that, at high temperature, at least four electrons are completely coupled, while the remaining four are largely uncorrelated. The low-temperature data, with a maximum in the susceptibility at ca. 13 K, indicate an antiferromagnetic coupling of the order of 7 cm^{-1} between the remaining electrons.

The magnetic data for I, on the other hand, show that, at high temperature, all six electrons are essentially uncorrelated. It is apparent that the strong interaction which completely couples four electrons in II has disappeared. Since the structures of the two compounds are almost identical, the only difference being the number of delocalized vanadium(IV) ions, which increases from 2 to 4 on passing from I to II, it is tempting to assume that the strong coupling observed in II is associted with the delocalized vanadium(IV) ions. In this hypothesis it is possible to fit the experimental susceptibility of II with a model in which the four delocalized vanadium(IV) ions are completely coupled and the temperature dependence of the susceptibility is given by the exchange interaction between the four localized vanadium(IV) ions in the internal square. The expression of the susceptibility is straightforward, and the best fit, corresponding to $g = 1.9$ and $J = 10$ cm^{-1}, is shown in Figure 2. These values compare well with those previously reported for analogous bridges.[13,19-21] The ground state is a singlet, with an excited triplet at 10 cm^{-1} and two other degenerate ones at 20 cm^{-1}.

The fact that the electrons on the external squares appear to be completely paired already at room temperature does not necessarily mean that the Heisenberg exchange interaction between the two vanadium(IV) ions is strong. In fact, a theoretical treatment, which takes parametrically into account Coulomb and electron-transfer effects, showed that it is the latter which very effectively couples the electrons.[16]

We assume that in I the interaction within the four localized vanadium(IV) ions is similar to that observed in II. If the electron delocalization over the four external sites is fast, the exchange interaction between the ions of the internal square and the delocalized vanadium(IV) is averaged, so that the spin levels can be approximated by the effective Hamiltonian:[16]

$$H = J(S_1{\cdot}S_2 + S_2{\cdot}S_3 + S_3{\cdot}S_4 + S_1{\cdot}S_4) + J''(S_1 + S_2 + S_3 + S_4){\cdot}(S_5 + S_6) \quad (1)$$

This Hamiltonian is equivalent to

$$H = J''S_q{\cdot}S_d + J/2[S_q(S_q + 1) - 2(S_1{\cdot}S_3 + S_2{\cdot}S_4) - 3] \quad (2)$$

$S_q = S_1 + S_2 + S_3 + S_4$, $S_d = S_5 + S_6$, and the coupling constants are indicated in Figure 6. The energy levels and the magnetic susceptibility are easily calculated.

Since the experimental magnetic data for I clearly show that, with decreasing temperature, χT initially increases, it is apparent

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that the first levels to be thermally depopulated are low-spin ones. Therefore, since the antiferromagnetic interaction within the internal square leaves high-spin states as the highest in energy, the experimental data can be reproduced only if J'' is assumed to be ferromagnetic.

The fit of the temperature dependence of χT for I was made by fixing $g = 1.9$ and $J = 10$ cm^{-1} as obtained in the fit of the magnetic properties of II. The best fit parameter is $J'' = -12$ cm^{-1}, and the corresponding calculated χT values are shown in Figure 2. The ground state is calculated to be $S = 2$, with an excited triplet at 1.4 cm^{-1}.

As expected, no reasonable fit could be obtained for positive J'' values. Whether this has a physical meaning or is just an artifact of the simplified model used is an open question. It is certainly surprising that a ferromagnetic coupling is operative, since up to now only antiferromagnetic couplings ranging from weak to very strong have been observed for vanadium(IV) pairs.[13,19–23]

A theoretical treatment[16] showed that, in the limit of strong delocalization, electron transfer in I does not give rise to any stabilization of high-spin states akin to double-exchange effects[24,25] observed in d^n–d^{n+1} pairs, $n > 0$. In fact, in this case, an electron jumping from vanadium(IV) to a nearby vanadium(V) does not find any other unpaired electron which can influence its spin orientation; therefore no spin polarization is observed.

The need for a ferromagnetic J'' may be an indication of intermediate electron delocalization effects or of tunneling of the electrons between the two external squares.

Another remarkable feature of I and II is provided by their EPR spectra. They are very similar at high temperature, where both show one signal at $g \sim 1.96$ with no evidence of zero-field splitting, independent of the frequency of the exciting radiation. This can be taken as evidence of fast relaxation between the different thermally populated multiplets, which effectively averages to zero the fine structure, or alternatively of intercluster exchange interactions.

The spectra of I are essentially unchanged upon cooling to 4.2 K at X-band frequency, showing that, at that temperature, there is still fast relaxation among the multiplets which are populated. However when the EPR frequency is increased, the spectrum shows evidence of a fine structure, belonging to both $S = 2$ and S = 1 states, in good agreement with the levels obtained by the best fit of the magnetic susceptibility.

The spectra of II, on the other hand, are typical of a triplet at 4.2 K and X-band frequency, suggesting that, at low temperature, relaxation is effectively quenched. Energy considerations suggest that it corresponds to the first excited triplet. The zero-field splitting is however roughly 1 order of magnitude larger than expected for dipolar interactions. Since the next excited triplet is degenerate, antisymmetric exchange can effectively mix these states, producing a higher zero-field splitting than expected on the basis of simple isotropic exchange and dipolar interactions.[26] An increase of the external magnetic field produces a stabilization of the levels of the degenerate triplet which then admix more efficiently with the lower triplet, thus resulting in fast relaxation and averaging of the signals.

On the other hand, for I the high field stabilizes the levels of the ground $S = 2$ state, thus making the admixture with the levels of the excited triplet more difficult, leading to localization of the multiplets.

Conclusions

The analysis of the magnetic properties of I and II showed that the behavior of these large spin clusters is rather complex. The data confirm that high-nuclearity spin clusters provide many novel magnetic behaviors and nicely correlate with the geometry and/or the topology of the cluster. Even the magnetic structures of fragments are comparable in different species. It can be assumed that the results have general model character for spin organization in materials of biological metal clusters.

Although reasonable fits of the experimental susceptibilities were obtained, it is surprising that a ferromagnetic coupling is required for I. We have tried several models in order to avoid a ferromagnetic coupling, but we did not succeed. Whether this is an artifact or a true result is still an open question. Our feeling is that it is simply an indication of the necessity of elaborating sophisticated models taking into account exchange and electron delocalization effects.

The second puzzling feature is the opposite behaviors observed in the EPR spectra of I and II at low temperature for measurements at low and high fields, respectively. Clearly, relaxation effects are involved, which deserve a deeper theoretical treatment, taking into account anisotropic and antisymmetric exchange components, as well as the interplay of exchange and delocalization effects.

Acknowledgment. The financial support of MURST, CNR Progetto Finalizzato Chimica Fine, Bundesminisrerium für Forschung und Technologie, and Fonds der Chemischen Industrie is gratefully acknowledged.

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