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Single Crystal EPR Spectra of $K_{12}[As_2W_{18}O_{66}Cu_3(H_2O)_2]\cdot 11H_2O$, a Copper(II) Trimer

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Received November 24, 1994

Single crystal EPR spectra of $K_{12}[As_2W_{18}O_{66}Cu_3(H_2O)_2]\cdot 11H_2O$ exhibit an orientation-dependent fine structure of an $S=3/2$ system which is accounted for by the exchange and magnetic dipole interactions among the three Cu^{2+} ions. The hyperfine structure and the lines from the $S=1/2$ manifolds have not been observed. The isotropic exchange parameters determined from the magnetic susceptibility data at 5-300 K are $J_1=J_2=-7.8$ cm^{-1}. The magnitude of J values suggests that the unpaired electrons on three Cu^{2+} ions interact through a sequence of six bonds involving two tungsten atoms and three oxygen atoms. The Cu-Cu distance, 4.37 Å, determined from the EPR spectra is considerably smaller than the value from the X-ray crystal structure determination, 4.76± 0.03 Å, indicating that the point-dipole model underestimates the dipolar interaction.

Introduction

Although EPR spectra of monomeric transition metal complexes are well understood, a detailed description of the EPR spectra for oligomeric metal ion clusters is still in a developing stage. The EPR spectrum of the binuclear copper(II) acetate, first studied by Bleaney and Bowers in 1952,[1] has revealed that both exchange and dipole-dipole interactions are important for this complex, in which the Cu-Cu separation is 2.6 Å. When the metal-metal separation is large and the exchange interaction is small, the metal separation may be determined from the dipolar splitting in the EPR spectra.[2] This technique has been used to deduce the metal ion separations for a number of dimers of copper(II), oxovanadium (IV), and titanium(III) which have unknown structure. The accuracy of the metal separations determined by this technique has not been tested with sufficient number of compounds whose structures are known. In addition, when the principal axes of the two metal ions are not parallel, a perturbation expression can be derived only for zero exchange interaction.[2] Recently we have found that both analysis of the EPR spectra and determination of the metal separation are not very reliable, if a small exchange interaction is neglected for this type of compound.[14]

As the number of paramagnetic transition metal ions increases, the EPR spectrum gets more complicated. In order to understand their EPR spectra, we need to study compounds with known structures. Some polyoxometalates were suggested as good systems for studying magnetic interactions among the metal ions, and some powder EPR spectra have been reported.[6] We have been studying single crystal EPR spectra of some polyoxometalates containing more than one paramagnetic transition metal ion. This paper reports the single crystal EPR spectra of a copper trimer, $[As_2W_{18}O_{66}Cu_3(H_2O)_2]^{12-}$ (hereafter denoted as As_2Cu_3). The X-ray crystal structure of this anion (Figure 1) shows three Cu(II) ions sandwiched between two AsW_9O_{33} subunits.[4] There are two types of copper ions, arranged in an isosceles triangle; Cu(1) is in a square planar environment and Cu(2) and Cu(3), related by a mirror plane, are in square pyramidal environments.

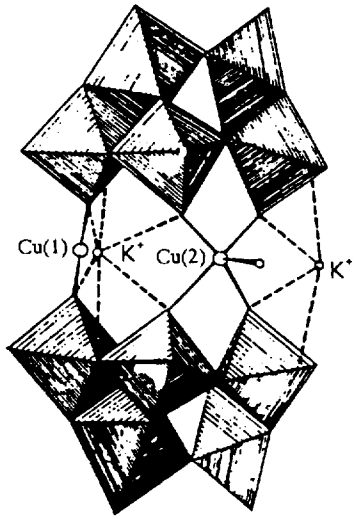


Figure 1. The structure of $[As_2W_{18}O_{66}Cu_3(H_2O)_2]^{12-}$ (reproduced from ref 4).

The structure of the heteropolyanion is slightly distorted from D_{3h} symmetry. The powder EPR spectrum of this compound was reported before, and the EPR parameters were determined by analyzing the $\Delta M=2$ and $\Delta M=3$ transitions.[5,6]

Experimental

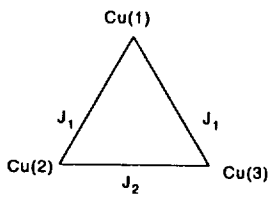
$K_{12}[As_2W_{18}O_{66}Cu_3(H_2O)_2]\cdot 11H_2O$ (I) and the corresponding sodium salt (II) were prepared according to the literature method.[4] Large single crystals were grown by slowly evaporating saturated solutions. Their powder EPR spectra agreed with the reported one.[5,6] A single crystal of I was mounted on a quartz rod attached to a goniometer, and EPR spectra were recorded every 5° with the magnetic field in three mutually perpendicular planes. The microwave frequency was measured by an Anritsu frequency counter and DPPH was used as a g marker. The magnetic susceptibility measurements at 5-300 K were performed using a SQUID magnetometer.

Results and Discussion

Magnetic Susceptibility. The magnetic susceptibility data of II at 5-300 K are shown in Figure 2. Since there are two kinds of Cu^{2+} ions in As_2Cu_3, the spin Hamiltonian appropriate to describe the exchange interactions has the following form.

$$\hat{H}=-J_1(S_1\cdot S_2+S_1\cdot S_3)-J_2S_2\cdot S_3 \quad (1)$$

Here J_1 represents the exchange interaction between Cu(1) and Cu(2) or Cu(3), and J_2 the interaction between Cu(2) and Cu(3).



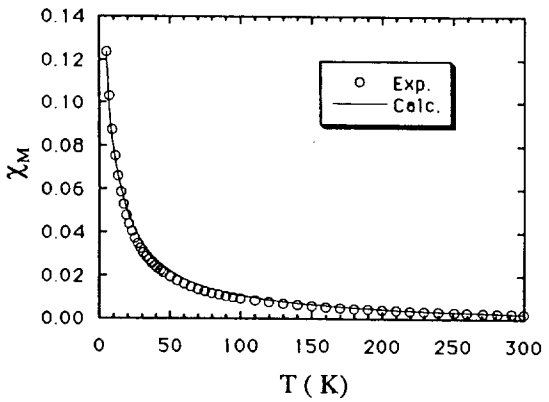


Figure 2. Temperature dependence of the molar magnetic susceptibility of $Na_{12}[As_2W_{18}O_{66}Cu_3(H_2O)_2]\cdot nH_2O$. The line represents the calculated values, and the circles the experimental values.

Energy		Spin |S,S*>
$-J_1 - 1/2\ J_2$	———	|3/2,1>
$3/2\ J_2$	———	|1/2,0>
$2\ J_1 - 1/2\ J_2$	———	|1/2,1>

Figure 3. Energies of the spin states for isosceles three ($S=1/2$) spin-coupled systems. $S=S_1+S_2+S_3$ and $S^*=S_2+S_3$.

The spin states can be represented by $S=S_1+S_2+S_3$, and $S^*=S_2+S_3$. The resulting spin states are two doublets ($S=1/2$) and one quartet ($S=3/2$); their energies are shown in Figure 3. The molar magnetic susceptibility for this system can be expressed as[7,8]

$$\chi_M=\frac{Ng^2\beta^2}{k(T-\theta)}\times\frac{X}{Y}+\chi_{dia}\ M_w$$

$$X=10\ \exp\{(1/2\ J_1+1/4\ J_2)/kT\}+\exp\{(-J_1+1/4\ J_2)/kT\}+\exp\{-3J_2/4kT\}$$

$$Y=4\ \exp\{(1/2\ J_1+1/4\ J_2)/kT\}+2\ \exp\{(-J_1+1/4\ J_2)/kT\}+2\ \exp\{-3J_2/4kT\} \quad (2)$$

where M_w is the molecular weight and χ_{dia} is the diamagnetic susceptibility. The g value was determined from the EPR spectra. The experimental susceptibility values at 5-300 K have been fit to this equation by treating J_1, J_2, θ, and χ_{dia} as adjustable parameters. The best least square fit is achieved with $J_1=J_2=-7.8\ cm^{-1}$, $\theta=1.0$ K, and $\chi_{dia}=-3.6\times10^{-7}$ emu/g (Figure 2). Since the Cu(1)-Cu(2) and Cu(2)-Cu(3) separations are slightly different (4.736 *vs.* 4.782 Å), J_1 and J_2 need not be the same. However, it was not possible to determine them separately, because using different values for J_1 and J_2 did not improve the fit.

The J values are considerably larger than the previously reported value,[9] $-3.4\ cm^{-1}$. The diamagnetic susceptibility is also larger than $\chi_{dia}=-0.12\times10^{-6}$ emu/g of a diamagnetic heteropoly compound,[10] $(CN_3H_6)_4V_2W_4O_{19}$. Since the maximum susceptibility is expected to be found below 5 K, measurements at 0-5 K would give more accurate J values.

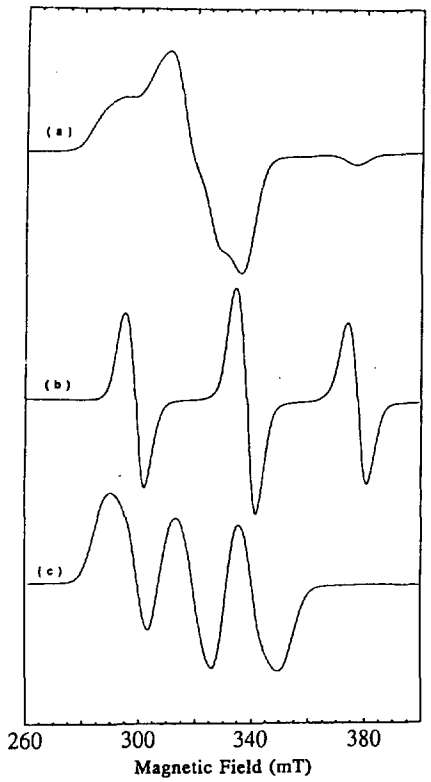


Figure 4. (a) The full-field region of the polycrystalline EPR spectrum of $K_{12}[As_2W_{18}O_{66}Cu_3(H_2O)_2]\cdot 11H_2O$. (b) The single crystal spectrum with the smallest g value and the largest dipolar splitting, (c) The single crystal spectrum with the largest g value.

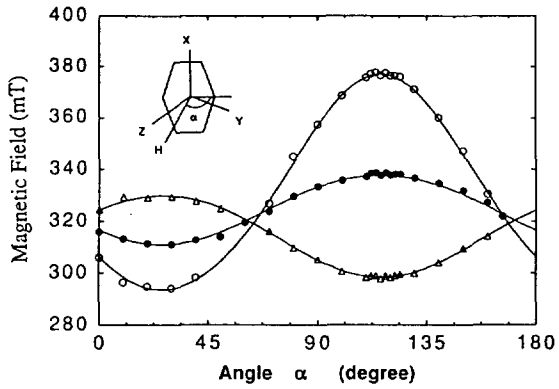


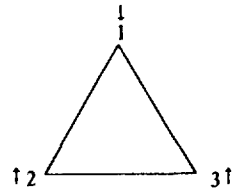
Figure 5. Angular dependence of the EPR spectrum of $K_{12}[As_2W_{18}O_{66}Cu_3(H_2O)_2]\cdot 11H_2O$ with the magnetic field in the yz plane. Symbols represent the observed values (○, M = −1/2; ●, $M=1/2$; △, $M=3/2$) and the lines the calculated values. See Eq. (4) for the meaning of M.

The magnitude of J values indicates that there is significant magnetic interactions among the Cu^{2+} ions. The unpaired electron occupies the $3d_{x2-y2}$ orbital in the Cu^{2+} ion, and a direct through-space overlap between two $3d_{x2-y2}$ orbitals can be ruled out. The isotropic exchange interaction must therefore occur through six bonds involving two tungsten atoms and three oxygen atoms.

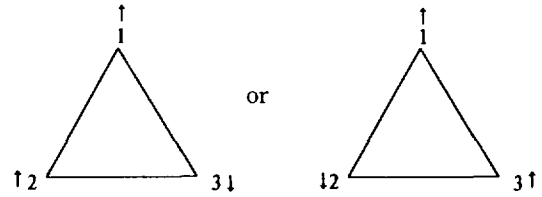
EPR Spectra. Single crystal EPR spectra were measured at room temperature with the magnetic field in three mutually perpendicular planes. Each spectrum consists of three lines at the full field region and a weak line at the half-field region. The one third-field line was too weak to be observed in the single crystal spectrum. The full-field spectra for two different directions of the magnetic field are shown in Figures 4b and 4c.

The three-line spectra may be attributed to the fine structure of the $S=3/2$ manifold (Figure 3). The hyperfine structure and the lines from the $S=1/2$ manifolds have not been observed. Since each fine line is expected to be split into up to 64 lines by three copper nuclei ($I=3/2$), the hyperfine lines will not be resolved in the spectra of concentrated single crystals.

The absence of the $S=1/2$ lines may be associated with relaxation processes within the two $S=1/2$ manifolds. If $|J_1| > |J_2|$, the ground state is $|1/2, 1>$, and it may be represented schematically as[11]



If $|J_1| < |J_2|$, the ground state is $|1/2, 0>$, and it may be represented as



If $J_1=J_2$, the two doublet states are degenerate. In this situation the system hesitates as for the nature of its ground state: the system is frustrated. Spin frustration seems to cause rapid relaxation of the spins, which explains the absence of the $S=1/2$ lines in the EPR spectra. For linearly arranged trinuclear copper systems, the EPR transition within the $S=1/2$ manifold was observed.[7]

The EPR spectra for an $S=3/2$ system can be interpreted by the following spin Hamiltonian:

$$\hat{H}=\beta S\cdot g\cdot H+D\{S_z^2-S(S+1)/3\}+E(S_x^2-S_y^2) \quad (3)$$

The EPR transitions derived from this Hamiltonian are given by the following equation:[12]

$$\begin{aligned} h\nu=E_M-E_{M-1}=g\beta H_o+(M-1/2)\ &[D(3g_z^2\cos^2\theta/g^2-1) \\ &+3E\cos 2\phi(1-g_z^2\cos^2\theta/g^2)] \\ &-(Dg_z g_\perp\cos\theta\sin\theta/g^2)^2\,[4S(S+1)-24M(M-1)-9]/2g\beta H_o \\ &+(Dg_\perp^2\sin^2\theta/g^2)^2\ [2S(S+1)-6M(M-1)-3]/8g\beta H_o \quad (4) \end{aligned}$$

where

$$H_o=h\nu/g\beta$$
$$g^2=g_\perp^2\sin^2\theta+g_z^2\cos^2\theta$$
$$g_\perp^2=g_x^2\cos^2\phi+g_y^2\sin^2\phi$$

The spectrum in Figure 4b has the smallest g value and

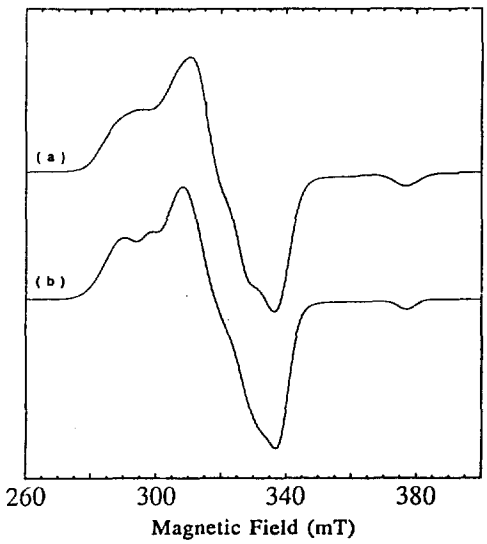


Figure 6. (a) Experimental and (b) calculated powder EPR spectrum of $K_{12}[As_2W_{18}O_{66}Cu_3(H_2O)_2]\cdot 11H_2O$ at room temperature.

the largest dipolar splitting, and its highest field line coincides with the highest-field line in the polycrystalline spectrum (Figure 4), indicating that the magnetic field is parallel to the 'C_3' (z) axis of the heteropolyanion. This spectrum was best simulated using $g_z=2.060$, $D=0.0189$ cm^{-1}, w (linewidth)$=4.0$ mT, and the Gaussian line shape. The single crystal spectrum with the largest g value is shown in Figure 4c. This spectrum, which is expected when the magnetic field is perpendicular to the z axis, was best simulated using $g_{max}=2.238$, $D=0.0189$, $E=0.0$ cm^{-1}, and $w=7.5$ mT. g_{max} was identified to be g_x by simulating the powder spectrum (see below). Then $g_y=2.231$ was determined from the single crystal spectrum with the magnetic field perpendicular to both the z and x axes. The angular dependence of the spectrum with the magnetic field in the yz plane is shown in Figure 5.

In order to simulate the powder spectrum, we use the following expression for the linewidth, for it originates mainly from the unresolved hyperfine splitting:

$$w^2=w_z^2\ \cos^2\theta+w_\perp^2\ \sin^2\theta \qquad (5)$$

The EPR parameters obtained from the single crystal spectra were used to simulate the powder spectrum measured at room temperature (Figure 6). A perfect fit to the experimental spectrum could not be obtained using one set of linewidths because the line shape, which is determined by the hyperfine structure, deviates significantly from the Gaussian line shape. For example, $w_z=4.0$ and $w_\perp=7.5$ mT produce a good fit near 300 mT, but a poor resolution near 340 mT. The spectrum shown in Figure 6b was calculated using $g_x=2.238$, $g_y=2.231$, $g_z=2.060$, $D=0.0189$, $E=0.0$ cm^{-1}, $w_z=3.0$ and $w_\perp=7.5$ mT. The EPR parameters agree reasonably with those determined from $\Delta M=2$ and $\Delta M=3$ transitions of a powder spectrum.[5] Since the g anisotropy is quite small and $E=0.0$, this system has essentially axial symmetry. It is noted that two lines attributable to the spectrum with the magnetic field along the z axis are clearly seen in the powder spectrum. Two parameters g_z and D can be determined from these two lines, even when single crystal spectrum is not available.

The D value, containing both direct and pseudo dipolar contributions, does not give the metal-metal distance directly.[1] In order to get the metal-metal distance and the exchange interaction (when it is comparable to the dipolar interaction), we may use an alternative spin Hamiltonian containing the exchange and dipolar interactions among the Cu^{2+} ions. If it is assumed that the exchange and dipolar interactions between two Cu^{2+} ions are the same for all three pairs, the spin Hamiltonian has the following form:

$$\hat{H}=\beta\sum_{i=1}^{3} S_i\cdot g_i(m)\cdot H-J(S_1\cdot S_2+S_2\cdot S_3+S_3\cdot S_1)+\hat{H}_{dipol} \qquad (6)$$

$$\hat{H}_{dipol}=\sum_{i,j,k=x_1,y_1,z_1}(J_{ij}^{1}\ S_{1i}S_{2j}+J_{ik}^{2}\ S_{1i}S_{3k}+J_{jk}^{3}\ S_{2j}S_{3k})$$

where

$$J_{ij}^{1}=g_{1i}\{\sum_{l=x_2,y_2,z_2} g_{2l}d_{jl}(d_{il}-3\sigma_i\sum_{m=x_1,y_1,z_1} d_{ml}\sigma_m^{1})\}\ \beta^2/r^3$$

$$J_{ik}^{2}=g_{1i}\{\sum_{l=x_3,y_3,z_3} g_{3l}d_{kl}(d_{il}-3\sigma_i\sum_{m=x_1,y_1,z_1} d_{ml}\sigma_m^{2})\}\ \beta^2/r^3$$

$$J_{jk}^{3}=[\sum_{l=x_2,y_2,z_2} g_{2l}d_{jl}\sum_{n=x_3,y_3,z_3} g_{3n}d_{kn}$$
$$\{d_{ln}-3\sum_{m=x_1,y_1,z_1} d_{ml}\sigma_m^{3}\sum_{p=x_1,y_1,z_1} d_{pn}\sigma_p^{3}\}]\ \beta^2/r^3$$

The expression for J_{ij}^{k} based on the point-dipole model was given previously for the binuclear systems.[2] Here $g(m)$ represents the g matrix for a CuO_4 group, while g in Eq. 3 represents the molecular g matrix. And r is the Cu-Cu distance, d_{ji}'s are direction cosines connecting the 1 and 2 (or 3) coordinate frames, and σ_i's are direction cosines of the Cu-Cu vectors with respect to x_1, y_1, and z_1. Each Cu^{2+} ion was assumed to have axial symmetry with the same $g_\parallel(m)$ and $g_\perp(m)$ values, and the three $g_\parallel(m)$ axes were assumed to be perpendicular to the 'C_3' axis.

The advantage of this Hamiltonian is that it can be used for any value of J. 8×8 energy matrices were set up and solved numerically to obtain the line positions and the transition probabilities for various orientations of the magnetic field. Although this spin Hamiltonian gives the transitions from both the $S=3/2$ and $S=1/2$ manifolds, only those from the $S=3/2$ manifold were used for simulating the spectra. Since the J value has little effect on the EPR spectra when $|J|\gg0.3$ cm^{-1} (the microwave frequency), J cannot be determined from the EPR spectra. $J=-7.8$ cm^{-1} determined from the magnetic susceptibility data was used. Other parameters determined by simulating the spectra are $g_\parallel(m)=2.410$, $g_\perp(m)=2.060$, and $r=4.37$ Å.

Because of the geometrical arrangements of the CuO_4 groups, their perpendicular directions agree with the z axis of the heteropolyanion, and thus $g_\perp(m)=g_z$. When the magnetic field is in the plane perpendicular to the z axis, the average g value of the three CuO_4 groups calculated from $g_\parallel(m)=2.410$ and $g_\perp(m)=2.060$ is 2.239, which agrees with g_x. The r value is considerably smaller than the values from the X-ray crystal structure determination, 4.736 Å for Cu(1)-Cu(2) and 4.782 Å for Cu(2)-Cu(3). This indicates that the point-dipole model underestimates the dipolar interaction for this system. It was shown that delocalization of the unpaired

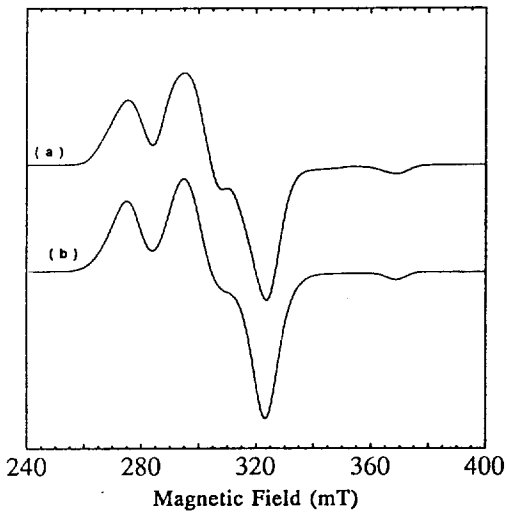


Figure 7. (a) Experimental and (b) calculated powder EPR spectrum of $K_{12}[As_2W_{18}O_{66}Cu_3(H_2O)_2]\cdot 11H_2O$ at 77 K.

electrons onto the ligands could increase the dipolar interaction and thus decrease the estimated value of r for VF_6.[13]

The powder spectrum measured at 77 K was also simulated using the Hamiltonian in Eq. (4); see Figure 7. The resulting parameters are $g_x=g_y=2.226$, $g_z=2.062$, $D=0.0223$ cm^{-1}, $E=0.0$, $w_z=4.0$, and $w_\perp=8.0$ mT. The D value is considerably larger than the room temperature value (0.0189 cm^{-1}). The dipolar splitting at 77 K corresponds to a metal-metal separation of 4.20 Å, which is about 0.2 Å smaller than the room temperature value. This probably reflects the contraction of the heteropolyanion at 77 K.

We have shown that both single crystal and powder EPR spectra of a Cu(II) trimer could be interpreted using two different spin Hamiltonians. Although the Hamiltonian containing the exchange and dipolar interactions among three copper ions is more complex, it gives the metal-metal separation directly. However, the metal-metal distance determined by using the point-dipole model is considerably smaller than the value from the X-ray crystal structure determination.

Acknowledgment. Financial assistance from the Ministry of Education is gratefully acknowledged. We thank Dr. Namhwi Hur of the Korea Standards Research Institute for the magnetic susceptibility measurements.

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