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ESR Studies of an Oxo-Bridged Manganese(III, IV) Complex of 2,2′-Bipyridine

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ESR spectra were recorded on the single crystal of di-μ-oxo-tetrakis(2,2′-bipyridine)dimanganese(III,IV) perchlorate trihydrate. ESR signals attributable to the excited quartet state were observed in addition to an ESR signal due to the ground doublet state. From the temperature dependence of the signal intensities, the exchange integral was determined as $J/k=-207$ K. The spectrum of the quartet state exhibits a fine structure: $|D|$ and $|E|$ were estimated to be equal to 0.39 and 0.12 cm^{-1}, respectively. The constants are interpreted in terms of the dipole-dipole interaction and the crystal-field effect; the anisotropic part of the exchange interaction is negligibly small. The hyperfine structure in the spectrum of the doublet state indicates that odd electrons are distributed unequally on two manganese atoms in the dimer. This is due to an odd e electron (in the $t_2{}^3$-$t_2{}^3e^1$ system) localized mostly on one of the paired manganese atoms.

X-Ray crystal analysis and magnetic susceptibility measurement[1)] showed that di-μ-oxo-tetrakis(2,2′-bipyridine)dimanganese(III,IV) perchlorate trihydrate, $[(\mathrm{bipy})_2\mathrm{Mn^{III}O_2Mn^{IV}(bipy)_2}](\mathrm{ClO_4})_3\cdot3\mathrm{H_2O}$, is a good model compound for studying magnetic interaction between metal atoms in different oxidation states. As shown in Fig. 1, two manganese atoms bridged by two oxygen atoms are in different coordination fields. From the fact, it was suggested that Mnl is a high spin d^4 ion, Mn^{3+}, and Mn2 a d^3 ion, Mn^{4+}. For a 2-3/2 spin system, four spin levels are derived with the energies $E_{1/2}=0$, $E_{3/2}=-3$, $E_{5/2}=-8$, and $E_{7/2}=-15J$ on the basis of the Hamiltonian,

$$\mathscr{H} = -2J\mathbf{S}_1\cdot\mathbf{S}_2. \tag{1}$$

The magnetic susceptibility[1)] indicates that an antiferromagnetic interaction ($J/k=-147$ K) operates between the dissimilar ions. In the ESR spectrum,[2)] a weak signal attributable to the excited states was observed in a region corresponding to $g=4$, in addition to a strong signal due to the ground state at a field of $g=2$. An ESR study of the excited states is expected to provide valuable information on the magnetic interaction. However, no detailed investigation has been undertaken. In the present investigation, ESR experiments have been carried out on the single crystal of the novel compound.

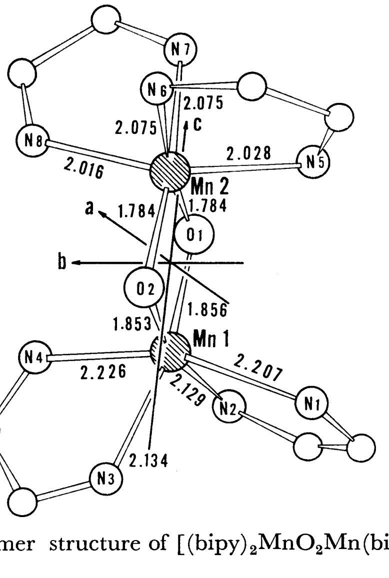

Fig. 1. Dimer structure of $[(\mathrm{bipy})_2\mathrm{MnO_2Mn(bipy)_2}]^{3+}$.

Experimental

Single crystals of the complex were prepared by the method reported by Plaksin.[2)] Deep green crystals were grown in the form of plates with well developed ab faces.

The ESR spectra were recorded by means of a JEOL ES-SCXA X-band ESR spectrometer equipped with a JEOL JM 350-MR electromagnet. Crystalline powders of MgO doped with Mn(II) ions were employed as a standard.

The crystal has a monoclinic space group P2$_1$/c with four molecules per unit cell.[1,2)] The Mn–Mn axis lies almost parallel to the bc plane and makes an angle of about 20° with the c axis. In a magnetic field applied along the ac plane, all molecules are magnetically equivalent. The ESR spectra were first recorded by rotating the crystal about its b axis, which coincides with one of the principal magnetic axes. An ESR signal exhibiting a hyperfine structure was observed at a field of $g=2$ (Fig. 2). Although the exact g factor was difficult to determine owing to the composite and asymmetric ESR curve, the anisotropy of the g factor was estimated to be 0.01 at most. The hyperfine structure showed no appreciable angular dependence. In addition to the main signal, weak signals were observed in regions of 1—2 and 5—11 kG (the unit G corresponds to 10^{-4} T in the SI unit system). Figure 2 shows an ESR spectrum for crystal orientation with the a axis perpendicular to magnetic field H_0. The positions of the weak signals exhibited marked angular dependence (Fig. 3). The maximum separation between the two signals was observed for $H_0\perp$a. The axis

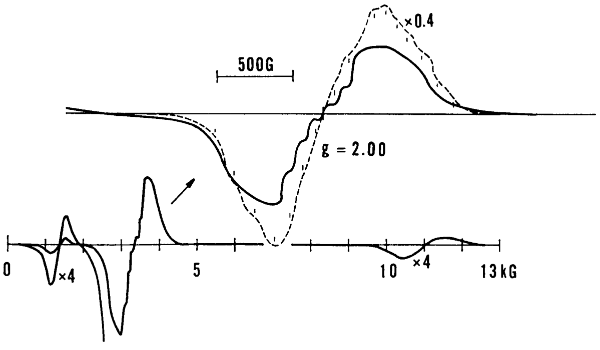

Fig. 2. ESR spectrum observed for H_0 applied along the K_m axis at 300 K. The broken curve displays the main signal ($g=2$) recorded at 183 K.

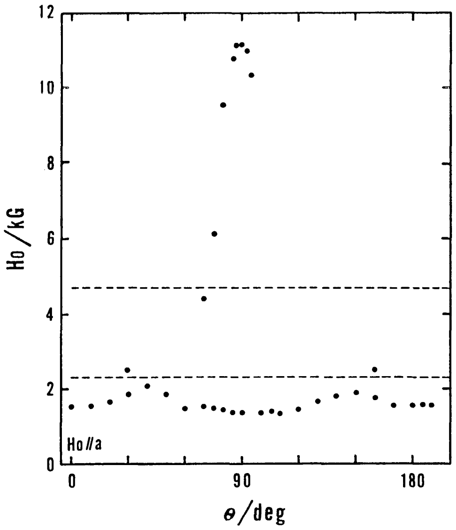

Fig. 3. Angular dependence of the positions of weak signals attributed to the quartet state for H_0 perpendicular to the b axis. The main signal ($g=2$) masks weak signals at fields between the broken lines.

K_m related to the maximum separation can be defined as one of the principal magnetic axes. Hence, the third axis coincides with the a axis. The ESR spectra were recorded by rotating the crystal about the K_m and a axes.

The temperature dependence of signal intensity was determined for the crystal orientations $K_m//H_0$ and $b//H_0$ (H_0 was applied along the bK_m plane) in a temperature range of 100—300 K.

Results

Temperature Dependence of Signal Intensity. The relative reciprocal intensity $I(293)/I(T)$ of the main signal observed at the field of $g=2$ is plotted against the temperature in Fig. 4. The intensity increases with decreasing temperature. On the other hand, the intensities of the weak signals decrease with decreasing temperature. The relative intensity $I(T)/I(293)$ of the signal at the lower field is shown in Fig. 4.

In a spin system having an exchange integral much larger than energies due to the zero-field splitting and the Zeeman term, the intensity $I_s(T)$ of an ESR signal attributed to the level S is proportional to $1/T$ and the unpaired-electron population $P_s(T)$ in the level:

$$I_S(T) \propto \frac{P_S(T)}{T} = \frac{(2S+1)\exp(-E_S/kT)}{T\sum_S (2S+1)\exp(-E_S/kT)}. \tag{2}$$

The population in each level is estimated as $P_{1/2}=0.66$, $P_{3/2}=0.30$, $P_{5/2}=0.04$, and $P_{7/2}=0.002$ at 300 K with the exchange integral determined from the magnetic susceptibility. The main signal is attributable to the ground doublet state, while the weak signals are attributable to the quartet state because contributions from the sextet and octet states are negligibly small. The intensity ratio of the weak signal to the main signal is expected to be proportional to $\exp(-3J/kT)$. The semilogarithmic plot of the ratio against $1/T$ yields a straight line over the temperature range investigated. From the slope, the exchange integral is determined to be -204 K (-142 cm^{-1}) for $H_0//b$ and -210 K (-146 cm^{-1}) for $H_0//K_m$. The difference between the values cannot directly lead to the conclusion that the exchange interaction has an anisotropy, because the error of the integrated intensity amounts to about ± 10 % and the uncertainty of temperature is estimated to be about 4°. Relative intensities calculated with the averaged value -207 K reproduce well the corresponding data (Fig. 4). Usually, magnetic susceptibility experiments give more accurate exchange integrals than ESR experiments. For the complex, however, the signal intensities can be determined separately for the two spin levels, and so the exchange integral determined by the present experiment seems to be highly reliable.

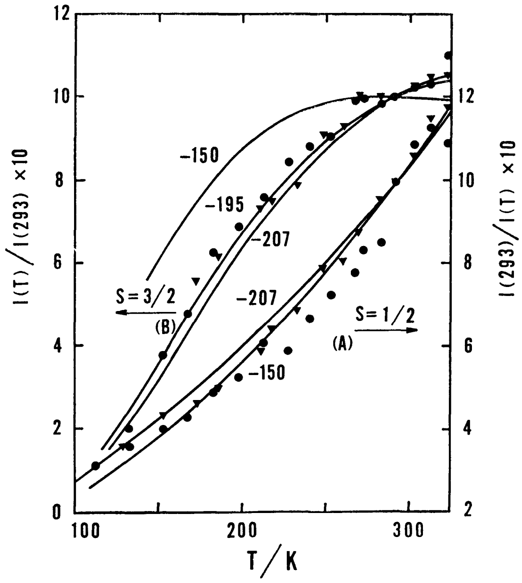

Fig. 4. Temperature dependence of signal intensities observed for $H_0//K_m$ (●) and $H_0 \perp K_m$ (▼). The main signal (A) at $g=2$ and the weak signal (B) at the lower field are attributable to $S=1/2$ and $S=3/2$, respectively. The curves display relative intensities calculated with various J/k values.

Spectrum of the Doublet State. The main signal attributed to the doublet state exhibits a hyperfine structure due to manganese nucleus-electron coupling. At low temperatures, the structure appears clearly on either side of the derivative curve as seen in Fig. 2. At least 16 lines can be found with spacings equal to 70—100 G: the structure consists of more than 11 lines expected for a pair of equivalent manganese atoms. This suggests that two manganese atoms in the dimer are not equivalent with each other, in line with the X-ray result showing that the two manganese atoms are in different oxidation states.

For H_0 along the aK_m plane, the g factor is approximately estimated to be equal to 2.00, the anisotropy being 0.01 at most. For crystal orientation in the ab plane, the g anisotropy is estimated to be less than 0.01.

Spectrum of the Quartet State. The shape and the resonance field of the signals depend markedly on the crystal orientation, but show no appreciable temperature dependence. The angular dependence of the position is shown in Fig. 3 for the crystal orientation in

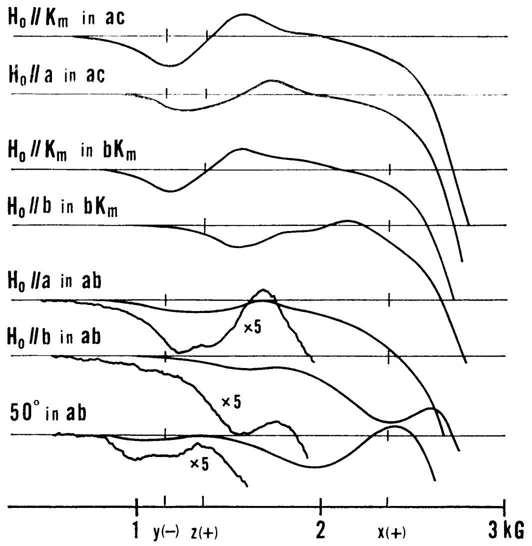

Fig. 5. Some spectra of the weak signal in the lower-field region.

H_0 along the ac plane. The intensity of the signals also depends on the crystal orientation. Especially, the signal in the higher field region is markedly angular dependent: no resonance line is observed above 100° of angle. An ESR pattern for H_0 along the bK_m plane resembles that for H_0 along the ac plane. When H_0 is applied along the ab plane, the crystal shows no ESR signal in the high field region. Figure 5 shows some spectra at the lower fields. The crystal oriented with its b axis parallel to H_0 shows different signals according to the direction of the microwave field H_1.

Because the exchange interaction energy is much larger than the Zeeman energy, the rate of mutual spin flipping is so high that only an average of two dissimilar spins is significant. In this case, the spin Hamiltonian for a pair of similar ions is applicable to the quartet state:

$$\mathscr{H} = g\mu_B \mathbf{S}\cdot\mathbf{H}_0 + D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2), \tag{3}$$

where x, y, and z axes are defined as local or molecular magnetic axes. The zero-field splitting constants D and E arise from the dipole-dipole interaction between two manganese atoms in the dimer, the anisotropic part of the exchange interaction, and the crystal field effect. When magnetic field is applied along the z axis, the following states and energy levels are derived.[3]

$$\theta_{\pm 3/2} = \cos\alpha_{\pm} |\pm\frac{3}{2}> + \sin\alpha_{\pm} |\mp\frac{1}{2}>, \tag{4}$$

$$\theta_{\mp 1/2} = -\sin\alpha_{\pm} |\pm\frac{3}{2}> + \cos\alpha_{\pm} |\mp\frac{1}{2}>, \tag{5}$$

$$W_{\pm 3/2} = \pm g_z\mu_B H_0/2 + [(D \pm g_z\mu_B H_0)^2 + 3E^2]^{1/2}, \tag{6}$$

$$W_{\mp 1/2} = \pm g_z\mu_B H_0/2 - [(D \pm g_z\mu_B H_0)^2 + 3E^2]^{1/2}. \tag{7}$$

In these expressions, $\tan 2\alpha_{\pm} = \sqrt{2}E/(g_z\mu_B H_0 \pm D)$. The energy levels for $H_0//x$ are derived as

$$W_{\pm 3/2} = \pm g_x\mu_B H_0/2 \pm [(g_x\mu_B H_0)^2 \mp (D-3E) g_x\mu_B H_0 + D^2 + 3E^2]^{1/2}, \tag{8}$$

$$W_{\pm 1/2} = \mp g_x\mu_B H_0/2 \pm [(g_x\mu_B H_0)^2 \pm (D-3E) g_x\mu_B H_0 + D^2 + 3E^2]^{1/2}. \tag{9}$$

The energy levels for $H_0//y$ are obtained by replacing $(D-3E)$ by $(D+3E)$. The transitions $\theta_{+3/2} \leftrightarrow \theta_{+1/2}$, $\theta_{+1/2} \leftrightarrow \theta_{-1/2}$, and $\theta_{-1/2} \leftrightarrow \theta_{-3/2}$ in H_0 directed to the i (x, y, or z) axis are abbreviated as i(+), i(0), and i(−), respectively. The transition probability depends on the $\alpha_{\pm}$ values and the direction of H_1 as well as H_0,[3] giving rise to the angular dependence of the signal intensity.

Four molecules in the unit cell are divided into two magnetically different groups: the Mn–Mn axes, which lie almost parallel to the ac plane, are inclined at +20 and −20°, respectively, with respect to the c axis, and the O–O axes are inclined at +40 and −40°, respectively, with the a axis. Thus, the principal zero-field splitting constants of the molecule cannot be determined definitely from the principal values of the crystal, since D and E in Eq. 3 are difficult to express as functions of angle. The following tentative analysis has been carried out. The Mn–Mn axis can be defined as one of the local principal axes, showing small deviation from the c axis approximately parallel to the K_m axis. Thus, the magnetic fields of z(+) and z(−) can be assumed to be equal to a set of the resonance fields observed for H_0 along K_m. The g values of the quartet state are presumed to be equal to those of the doublet state. On the basis of the assumptions, $|D|$ and $|E|$ are evaluated as 0.39 and 0.21 cm^{-1}, respectively. By use of the values, the transitions for H_0 directed to other principal axes are expected to take place at the fields $H_{y(+)} = 14.2$, $H_{y(-)} = 1.15$, $H_{x(+)} = 2.38$, and $H_{x(-)} = 5.09$ kG. The $|D|$ and $|E|$ values are so large that no i(0) transitions are allowed. The positions of the transitions in a magnetic field applied along the ab plane vary with crystal orientation in regions of $H_{x(+)}$–$H_{y(+)}$ and $H_{x(-)}$–$H_{y(-)}$. When H_0 makes 40 or 50° with the a axis, the spectrum shows resonance peaks at 1.36 and 2.27 kG (Fig. 5). A clear hump is observed at the high field side of the main signal, showing the presence of a signal at about 4 kG. The three transitions can be explained by $H_{y(-)}$, $H_{x(+)}$, and $H_{x(-)}$ fairly well, indicating that the tentative $|D|$ and $|E|$ values do not differ much from the inherent values. One of the principal axes is normal to the Mn–O$_2$–Mn plane, and the third axis is parallel to the O–O axis. It is noteworthy that $|E/D|$ of the complex is very large compared with the ratio ($\lesssim 1/3$) normally observed for metal complexes.

Discussion

The zero-field splitting constant arising from the dipole-dipole interaction between manganese atoms is evaluated as $D_{dip} \approx -3g^2\mu_B^2 r^{-3} = -0.26$ cm^{-1}, with the Mn–Mn distance 2.716 Å. The anisotropy of the exchange interaction is of the order of the magnitude $|D_{ex}| \approx |J(2-g)^2|$. Because the g factor is very close to 2.00, $|D_{ex}|$ is estimated to be less than 0.01 cm^{-1}. The value is negligibly small compared with $|D_{dip}|$. An additional contribution comes from the crystal field effect. Usually, the zero-field splitting constants of d^4 ions are much larger than those of d^3 ions.[4] Hence, MnI makes a dominant contribution. The constants of d^4 complexes are given by[3)]

$$D_{\mathrm{cf}} = -3\left(\rho+\frac{\lambda^2}{\Delta}\right)\left[\frac{2\Delta}{8\lambda}(2-g_{z'})-1\right], \tag{10}$$

$$E_{\mathrm{cf}} = -\frac{1}{4}\left(\rho+\frac{\lambda^2}{\Delta}\right)\left(\frac{\Delta}{\lambda}\right)(g_{x'}-g_{y'}), \tag{11}$$

where x′, y′, and z′ are defined as the local axes of the crystal field, λ is the spin-orbit coupling constant, Δ is the energy separation between Γ_3 and Γ_5 levels, and ρ is the constant of the spin-spin interaction. The values of λ and ρ are estimated to be equal to 88 and 0.18 cm^{-1}, respectively.[3)] Usual manganese(III) complexes have Δ equal to 20 000 cm^{-1}. When $|g_{z'}-2| \approx 0.01$ and $|g_{x'}-g_{y'}|<0.01$, $|D_{\mathrm{cf}}|$ is approximated to be equal to 0.7 cm^{-1}, and $|E_{\mathrm{cf}}|$ is less than 0.3 cm^{-1}. The $|D_{\mathrm{cf}}|$ and $|E_{\mathrm{cf}}|$ values of Mn^{3+} in TiO_2 amount to 3.4 and 1.2 cm^{-1}, respectively.[3)] This is the only example reported for Mn^{3+}, indicating that the aforementioned values of the complex are not overestimated. This suggests that the contribution from the crystal-field effect may be comparable to that from the dipole-dipole interaction. The octahedron of MnI is elongated along N1 and N4 directions, which are practically normal to the Mn–O_2–Mn plane. Because the z′ axis is defined as a direction perpendicular to the plane, it is normal to the principal z axis of D_{dip}. Hence, D arises from D_{dip} and E_{cf}, and E is due to D_{cf}. This explains the large $|E/D|$ value. Although the uncertainty of the crystal orientation amounts to ±5°, the K_{m} axis deviates from the axis of D_{dip} directed to the Mn–Mn axis. This is probably due to a slight discordance between the crystal-field axis and dipolar-interaction axis systems. The zero-field splitting constants can be interpreted in terms of the dipole-dipole interaction and the crystal-field effect. The anisotropy of the exchange interaction is so small that the Hamiltonian (Eq. 1) of ideally isotropic interaction is valid for the complex.

The hyperfine structure in the ESR spectrum of the doublet state suggests that the odd electrons are unequally distributed on the two manganese atoms in the dimer. This situation is different from that in cobalt(III,IV) complexes, $[(NH_3)_5CoO_2Co(NH_3)_5]X_5$, in which an odd electron is distributed over the Co–O–O–Co system and the two cobalt atoms are equivalent with each other.[5)] In the manganese(III,IV) complex, the spin delocalization takes place through the p orbitals of bridging oxygen atoms, giving rise to the antiferromagnetic interaction between the t_2^3 and $t_2^3e^1$ systems. The t_2 electrons forming dπ–pπ bonds can be delocalized through the π systems, while the e electron occupying mostly the d_{z^2} orbital makes little contribution to the formation of Mn–O π bonding for symmetric and steric reasons, so that the e electron is stably localized on one of the paired manganese atoms or on MnI having the more distorted coordination field. For this reason, the two manganese atoms in the dimer differ from each other despite the strong exchange interaction operating between them.

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