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EPR Investigation of the Binuclear Copper(II) Complexes with 3,12-Bis(carboxymethyl)-6,9-dioxa-3,12-diazatetradecanedioic Acid

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Binuclear copper(II) complexes of 3,12-bis(carboxymethyl)-6,9-dioxa-3,12-diazatetradecanedioic acid have been investigated by EPR. It has been confirmed that three different binuclear complexes are formed, depending on the pH of the solution. The complex formed in the low pH region has a copper–copper distance of 5.5 Å and a weak magnetic dipolar interaction. The other two are of olated forms with strong magnetic interactions between the copper atoms through oxygen bridges. One of them has an antiferromagnetic interaction; though the other has a weak antiferromagnetic interaction, it shows a large zero-field splitting. Such differences between the magnetic properties of the two olated complexes are attributed to a difference in the bridged style, i.e., the former is a mono-μ-hydroxo-bridged complex and the latter is a double-μ-hydroxo-bridged complex.

The metal complexes of polyamine-*N*-polycarboxylic acids are widely used not only in analytical chemistry, but also in research in the fields of pharmacy, medicine, and foodstuffs.[1] Their usefulness arises from their high stability due to the strong chelating ability of such polydentate ligands.[2,3] In all these fields, ethylenediaminetetraacetic acid (H_4edta) has been the most fundamental key ligand reagent, and many related reagents, such as 3,12-bis(carboxymethyl)-6,9-dioxa-3,12-diazatetradecanedioic acid (H_4egta), which is widely used as a biochemical reagent for the sake of high Ca^{2+} binding selectivity, have been derived under the guide of H_4edta.[4,5] The crystal structures recently investigated for the egta^{4-} complexes of alkaline earth metals indicate considerable diversity regarding the coordination number of the metal ions and in the formation of polynuclear complexes.[1d,5] On the other hand, though potentiometrical studies of the chelate complexes of transition metals have often been carried out, structural studies have been quite limited.[6–8]

A potentiometric titration study concerning the interaction between the copper(II) ion and egta^{4-} revealed that there exist three kinds of binuclear complexes, expressed as Cu_2L, $Cu_2L(OH)$, and $Cu_2L(OH)_2$ (charges and H_2O ligands are omitted for simplicity, L=egta^{4-}), in aqueous solutions.[7] Carr et al. obtained only one structural datum by EPR, which shows that the Cu_2L species has a non-paralell axis alignment of the g and A tensors for the two copper(II) ions at a separation of about 4.0 Å.[8] However, there has been no structural information concerning the $Cu_2L(OH)$ and $Cu_2L(OH)_2$ species. One of the purposes of this work was to investigate the complex formation between copper(II) ions and egta^{4-} in aqueous solution and to clarify the structures of the copper(II) complexes formed there by EPR spectroscopy.

On the other hand, numerous studies are now available concerning the magnetic properties of copper(II) binuclear complexes in a solid, in which the nature and the magnitudes of the copper–copper interactions are related to their molecular structures. Despite intensive investigations of the copper(II) binuclear complexes, there still remains much uncertainty about the structures as well as magnetic properties in solution. In this paper we also discuss the magneto-structural correlations of binuclear complexes observed for the Cu(II)–egta system.

Experimental

EPR spectra were recorded with a JEOL JES-FE2XG EPR spectrometer over the temperature range 77 K to room temperature, and with a Varian E112 over the range 6 K to 60 K. All of the sample solutions were prepared by dissolving H_4egta and copper(II) perchlorate hexahydrate, and the ionic strength was adjusted by addition of sodium perchlorate. The concentrations of the copper(II) ion and the ligand in solutions for EPR measurements were determined by titrations. The intensities of the EPR spectra were obtained by double integration of the observed first-derivative spectra. The intra-molecular spin-exchange interaction energy, J, was evaluated from the temperature dependence of the spectral intensity.[9]

The magnetic susceptibility of Cu_2(egta) was determined by the Evans method,[10] by using a 50 mM solution of Cu_2(egta) containing 2% *t*-butyl alcohol as an indicator and by recording the NMR spectra with a JEOL JNM-FX90QFT NMR spectrometer at 25 °C.

H_4egta from Dojindo Laboratories Co. and copper(II) perchlorate hexahydrate from Nakarai Chemicals, Ltd. were recrystallized from hot water. All other reagents were of reagent grade, or higher, and were used without further purification. Cu_2(egta) used for the magnetic susceptibility measurements was synthesized as follows. Copper(II) sulfate pentahydrate (2.5 g) was added to an aqueous slurry (30 ml) of H_4egta at 90 °C, the solution was well stirred at this temperature until all the compounds were dissolved. The resultant solution was cooled and left standing overnight.

A dark-blue crystalline compound which appeared was washed with water and recrystallized from hot water. (Calcd for $Cu_2C_{14}H_{20}N_2O_{10}\cdot 4.5\ H_2O$: C, 28.77; H, 5.00; N, 4.79%. Found: C, 28.70; H, 5.06; N, 4.65%). The pH adjustment was done without any buffer throughout this work.

Results and Discussion

Solution EPR Spectra. Figure 1 shows the EPR spectra for aqueous 2 : 1 and 1 : 1 Cu(II)-egta solutions at pH 4.7. The EPR spectrum of the 1 : 1 Cu(II)-egta solution does not depend on the pH in the range pH 2 to 10. From the spectral pattern showing equally spaced four hyperfine lines, as well as the stoichiometry of copper(II) ion and the ligand in solution, the spectrum obtained for the 1 : 1 Cu(II)-egta solution can be assigned to the 1 : 1 mononuclear copper(II) complex.

By contrast, the EPR spectrum of the 2 : 1 Cu(II)-egta solution depends on the pH. As Fig. 2 shows, the EPR intensities of the 2 : 1 Cu(II)-egta solution gradually decrease upon changing the pH from 5 to 9 and is reduced to almost zero at pH 10. In this pH range there is no possibility of a reduction of Cu(II) to Cu(I). On the other hand, from a comparison with Fig. 3 (which shows species distribution analysis calculated by the formation constants reported by Schrøder[7]) one can see that the pH range revealing the decrease of the EPR intensity corresponds well to that for an increase in the $Cu_2L(OH)$ and $Cu_2(OH)_2$ concentrations. The decrease in the EPR intensity, therefore, can be attributed to the formation of two binuclear complexes which are EPR silent in a fluid solution, owing to a line-broadening effect of strong spin-exchange interactions. The formation of such binuclear species is supported by the magnetic susceptibility data and by the frozen solution EPR spectra shown later.

According to the species-distribution analysis in Fig. 3, Cu_2L exists in the pH range from 3 to 9, where

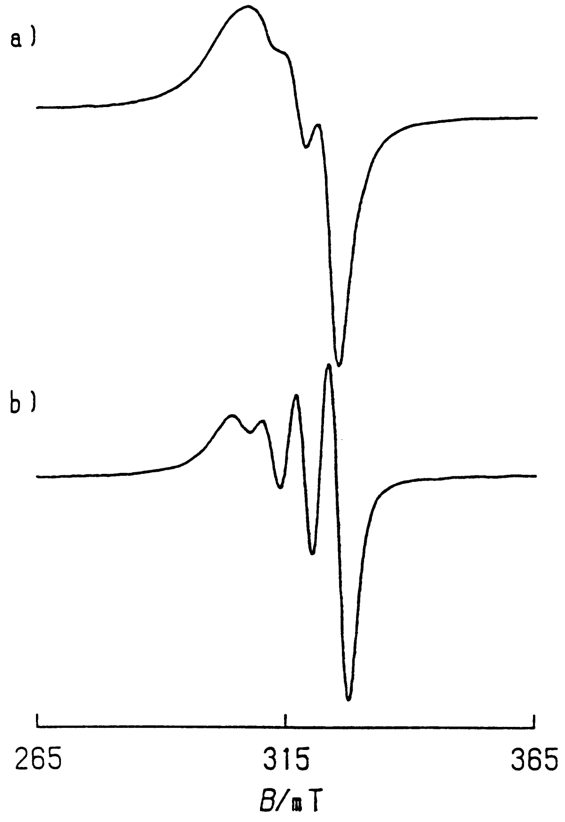

Fig. 1. EPR spectra of Cu^{2+}-egta complexes in fluid aqueous solutions at pH 4.70. $[Cu^{2+}]=5.00\times10^{-3}$ M, $[NaClO_4]=0.50$ M, $\nu=9.4378$ GHz; a, $[Cu^{2+}]/[H_4egta]=2$; b, $[Cu^{2+}]/[H_4egta]=1$.

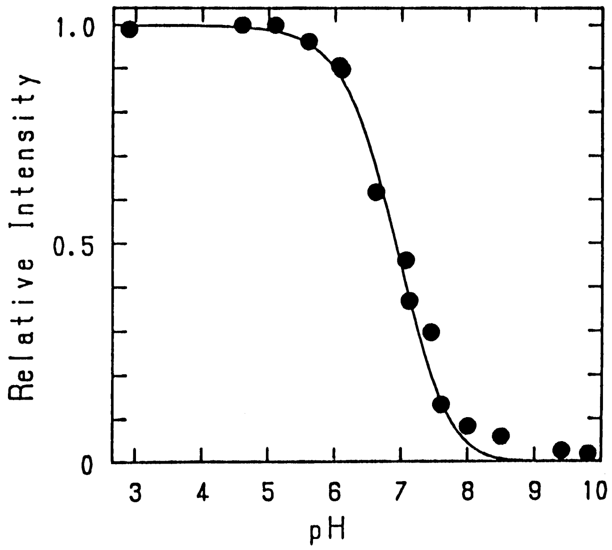

Fig. 2. pH Dependence of the intensities of EPR spectra for the 2 : 1 Cu^{2+}-egta aqueous solution at 25 °C. Solid line indicates the calculated spectral intensity changes (see text).

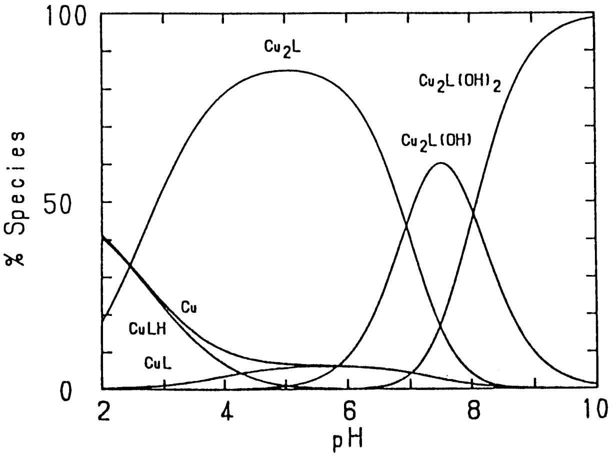

Fig. 3. Species distributions for the 2 : 1 Cu^{2+}-egta solution as a function of pH. $[Cu^{2+}]=5.00\times10^{-3}$ M. Charges and H_2O ligands are omitted for simplicity.

the EPR spectrum is clearly observed; hence, the observed spectrum is attributed to Cu_2L. Based on this assignment, the EPR intensity changes with pH were calculated[11] by

$$1/I=A[K_1K_2/[H^+]^2+K_1/[H^+]+1], \quad (1)$$

where

$$K_1=[Cu_2L(OH)][H^+]/[Cu_2L], \quad (2)$$

and

$$K_2=[Cu_2L(OH)_2][H^+]/[Cu_2L(OH)]. \quad (3)$$

In Eq. 1, A is a proportionality constant and K_1 andK_2 are the formation constants (expressed by Eqs. 2 and 3). The calculated result shown by the solid line in Fig. 2 satisfactorily fits the experimental data, giving strong evidence to the above assignment. The spectral pattern (Fig. 1-a), however, do not comprise the equally spaced seven hyperfine lines which are usually observed in copper(II) dimers.[11] Similar quasi-mononuclear spectral patterns have been observed for some dimers with large copper-copper distances, such as Cu_2(edta), which has a copper-copper distance of 5.6 Å in a crystal.[12] The Cu_2L observed here must be a binuclear complex of such type.

Inspection of Table 1 and Fig. 3 shows that μ_{eff} is small in the pH range where $Cu_2L(OH)$ is a dominant species and becomes large in the pH range where $Cu_2L(OH)_2$ is mainly formed. This indicates that coppers in $Cu_2L(OH)$ have an antiferromagnetic interaction and those in $Cu_2L(OH)_2$ have a ferromagnetic or a weak antiferromagnetic interaction. In consideration of the species distribution shown in Fig. 3, the μ_{eff} value for $Cu_2L(OH)$ was evaluated to be about 1.5 B.M. Shrøder considered that egta^{4-} binds two copper(II) ions by working as two tridentate ligands, and hydroxide ions coordinate successively to the two copper(II) ions.[7] These coordination forms, however, seem to be unreasonable, since these forms would not have strong spin exchange interactions. Spin exchange interactions in binuclear copper complexes have been extensively studied.[13] Hatfield and Hodgson have shown that hydroxo-bridged binuclear complexes have strong spin exchange interactions through the bridges.[14] By an analogy, it is more likely to consider that the $Cu_2L(OH)$ and $Cu_2L(OH)_2$ have olated structures.

Frozen Solution EPR Spectra. The frozen solution EPR spectra of binuclear copper(II) complexes are useful for finding species which exist in solution and to obtain structural information.[13,15] The EPR spectra for a 2 : 1 Cu(II)-egta solution at 77 K are shown in Figs. 4 and 5. The EPR signals were observed at all pH ranges studied, in contrast to the fluid solution. The spectrum at pH 4, which has a better resolution than that reported by Carr et al., is attributed to the Cu_2L species (as mentioned above). This spectrum shows weak absorption at a low magnetic field of about 0.15 T, and strong absorption in the region around g=2, indicating that the spectrum apparently comes from a triplet state having a weak spin-spin interaction between the copper atoms. The low-field EPR signal corresponds to the $\Delta M_S=2$ transitions which arise from magnetic dipolar couplings between the two copper(II) ions.

In general, the $\Delta M_S=2$ spectra give information concerning the relative orientation of the nuclear hyperfine coupling tensors, and also the orientation of the inter-spin vector. Carr et al. pointed out that the Cu_2L species has a non-parallel axis alignment of the copper(II) ions with respect to the g and A tensors. Their conclusion may be reasonable, because the spectral pattern of the $\Delta M_S=2$ transition is very different from those of the usual parallel planar dimers with

Table 1. Effective Magnetic Moments for the 2 : 1 Cu^{2+}-egta Aqueous Solutions at 25 °C and Different pH's[a]

pH	μ_{eff}/BM
5.00	1.82
7.50	1.62
8.25	1.67
9.82	1.86

a) $[Cu_2(egta)]=5.00\times10^{-2}$ M, M=mol dm^{-3}.

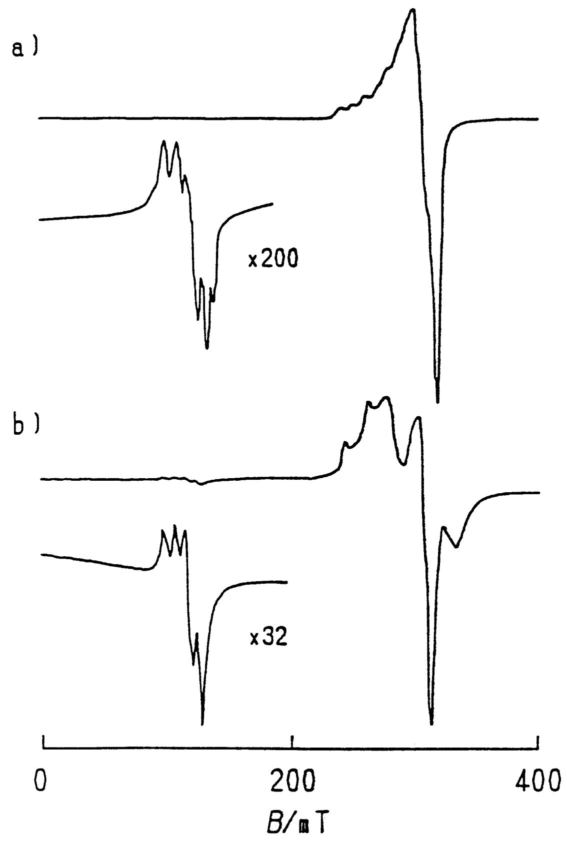

Fig. 4. EPR spectra for the 2 : 1 Cu^{2+}-egta frozen aqueous solutions at 77 K and different pH's. $[Cu^{2+}]=5.00\times10^{-2}$ M, $[NaClO_4]$=2.5 M, ν=9.1537 GHz; a, pH 4.7; b, pH 7.5.

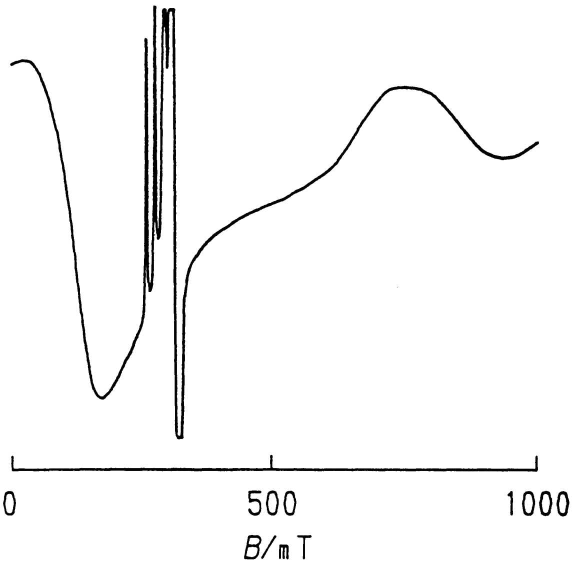

Fig. 5. EPR spectrum for the 2 : 1 Cu^{2+}-egta frozen aqueous solution at 106 K and pH 9.8. [Cu^{2+}]= 5.00×10^{-2} M, [$NaClO_4$]=2.5 M, ν=9.1819 GHz.

two identical copper ions with respect to the A and g tensors.[8,16,17] It has been shown that the intensity ratio of the forbidden $\Delta M_S=2$ transition to the allowed $\Delta M_S=1$ transition depends only on r; hence, it makes possible an estimation of the copper-copper distance.[17,18] In the present case, the ratio is 7.3×10^{-4} according to the integrated intensities of the spectra; it gives a copper-copper distance of 5.5 Å:[18a]

$$r=[(21/I)\,(9.1/\nu)^2]^{1/6}, \qquad (4)$$

where r is expressed in the unit of Å, I is the relative intensity and ν is microwave frequency in units of GHz.

The distance r obtained here is useful for estimating the correct structure from the two possible types of structures for the Cu_2L species: open configuration and compact type. The former, which has been proposed by Shrøder,[7] would have a copper-copper distance of about 16 Å, as exemplified by the Mg_2(egta) crystal.[5] On the other hand, the latter type would have a copper-copper distance of 4 to 6 Å. Carr et al. pointed out that the conformation brought about by coordination of the ether-type oxygen has a copper-copper distance of 4 Å.[8a] It seems unlikely, however, that the ether-type oxygen coordinates to copper(II) ions in an aqueous solution; if the copper-copper distance were 4 Å, the spectrum might not be observed in a fluid solution because of its large anisotropic interaction and short relaxation time. According to the CPK molecular model, even when the ether-type oxygens are far away from the copper atoms, a copper-copper distance of 4—6 Å may be possible to realize. Cu_2L, therefore, must have a compact-type conformation, as shown in Fig. 6a. This is also reasonable from the view point that the complex shows a quasi-mononuclear hyperfine pattern in a fluid solution, since Cu_2(edta) has a copper-copper distance of 5.6 Å and also shows such a hyperfine pattern. Though there may be a possibility of coordination of water molecules, even if this is the case, the coordinating water molecules must be in such a state that they do not significantly affect the magnetic properties of the complex.

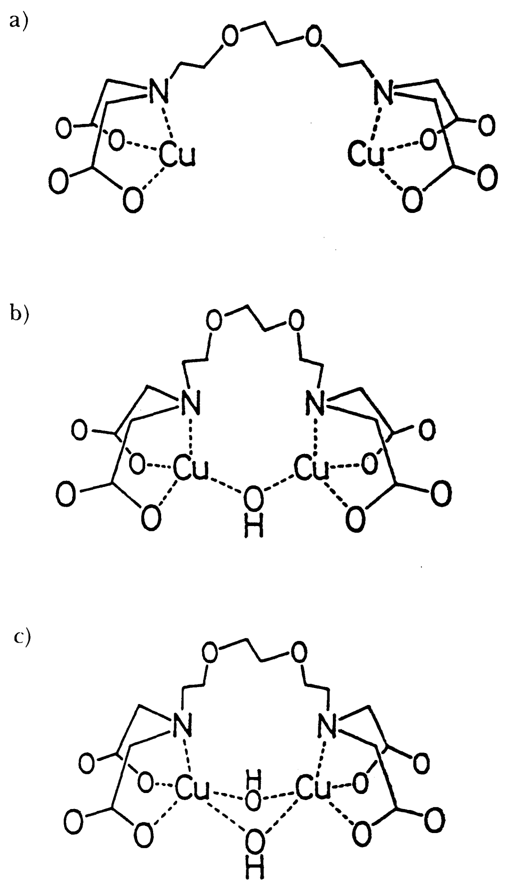

Fig. 6. Proposed complex structures. a, Cu_2L; b, $Cu_2L(OH)$; c, $Cu_2L(OH)_2$.

The EPR spectrum for the 2 : 1 Cu(II)-egta solution at pH 7.5 and at 77 K is shown in Fig. 4b. The spectral pattern at the g=2 region indicates the presence of two different binuclear copper(II) complexes. From the equilibrium analysis given in Fig. 3, one of the binuclear copper(II) complexes is assigned to Cu_2L and the other to $Cu_2L(OH)$. The $Cu_2L(OH)$ species has a relatively large $|D|$ value of about 0.05 cm^{-1}, which is estimated from the zero-field splitting pattern in the g=2 region. It was mentioned above that the species has an antiferromagnetic interaction. The $|D|$ value presented here also indicates that this complex has an appreciable spin-spin coupling and, hence, the species may have an olated form, as shown in the binuclear copper(II) complexes of polyamine-N-polycarboxylic acid reported by Martell et al.[3] (Fig. 6b).

The EPR spectrum observed for the 2 : 1 Cu(II)-egta solution at pH 9.8 and 77 K shows broad signals at magnetic field strengths of 0.05 T and 0.5—1.0 T, besides a sharp signal with a hyperfine structure at the magnetic fields of 0.25—0.35 T, which can be assigned to the residual mononuclear species (Fig. 5). From the pH dependence of the signal intensities (Fig. 2) and an equilibrium analysis (Fig. 3), the triplet state signal observed here is attributed to $Cu_2L(OH)_2$. The spectral pattern shows that $Cu_2L(OH)_2$ has a much larger $|D|$ value (about 1 cm^{-1}) than that of Cu_2L-(OH), suggesting that $Cu_2L(OH)_2$ is also a complex of an olated type (Fig. 6).

When the EPR triplet spectra do not show any microwave power saturation, the spectral intensity, I, is regarded as being proportional to the paramagnetic susceptibility of the binuclear complex, and is expressed by

$$I = C/T(3+\exp(-2J/kT))^{-1}, \qquad (5)$$

where C is a proportionality constant and J is the isotropic spin-exchange interaction energy.[9,13e] The J value is, therefore, determined from the temperature variation of the relative EPR intensities. Since the linewidths were kept constant over the entire temperature range, a relative peak height of the $\Delta M_S=2$ transition was used as a substitute for I. The temperature dependence of the signal intensities, thus obtained, for $Cu_2L(OH)_2$ is shown in Fig. 7. The solid line is the relative intensity change calculated by using Eq. 4 with $J=-5$ cm^{-1}, showing good fit with the experimental data.

There are a few μ-hydroxo-bridged binuclear copper(II) complexes which have a small J value, but a large $|D|$ value.[20] Theoretical and experimental studies show that the copper-copper distance (r) and the Cu-O-Cu bridging angle (θ) are the key factors in determining the magnitude of the exchange interactions. Hatfield and Hodgson have shown that the J value varies steadily with the θ value, and that a singlet ground state occurs for $\theta > 97.5°$ and a triplet ground state occurs for $\theta < 97.5°$.[14] On the other hand, Charlot et al. have shown that the zero-field splitting paramter $|D|$ decreases with an increase in r for the case of $\theta > 90°$.[20] They summarized J and $|D|$ values of various di-μ-hydroxo-bridged binuclear copper(II) complexes with known bridging structure. In reference to them, the r and θ values of $Cu_2L(OH)_2$ were estimated to be ca. 3 Å and ca. 99°, respectively.

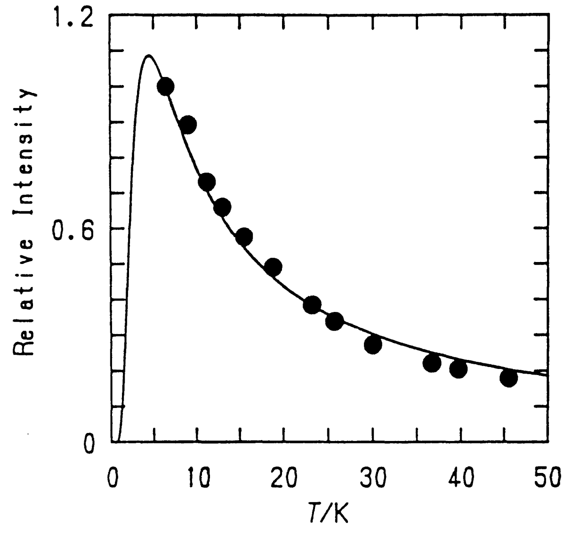

Fig. 7. Temperature dependence of the relative intensities of the low field transitions for the $Cu_2L(OH)_2$ complex. ●, experimental data; ——, calculated with $J=-0.5$ cm^{-1}.

The experimentally obtained zero-field splitting paramter, $|D|$, is given by the sum of two components: the through-space magnetic dipole interaction between the two copper ions, D_{dd}, and the spin-orbit coupling contribution, D_{so}.[13] For the $Cu_2L(OH)_2$ complex, D_{dd} was calculated, based on the copper-copper distance estimated above, to be about 0.1 cm^{-1}, which corresponds to 10% of the observed $|D|$. D_{so} contains a term for the two-electron exchange integral, j, in the excited electronic configuration; the variation of D_{so} arises mostly from j. A theoretical calculation for a model complex shows that j has a maximum for θ close to 95°.[13a,20] The fact that $Cu_2L(OH)_2$ has a large D_{so} seems, therefore, reasonable from the proposed complex structure.

In mono-μ-hydroxo-bridged complexes, the steric restriction for the structure is less than that for the double-bridged ones and the bridged angle may be nearly constant at 130°, determined by the hybridization of the oxygen's atomic orbitals.[21,22] It seems reasonable to consider that the correlations of J and j to the θ shown for the di-μ-hydroxo-bridged complexes also hold for mono-μ-hydroxo-bridged complexes, since the magnitudes of J and j are related to the overlap densities between the magnetic orbitals of the two copper centers and they depend on θ.[20] It is, therefore, expected that $Cu_2L(OH)$, which was estimated to have a large θ, has both a large J value and a small j. This expectation is consistent with the experimental observation that the $Cu_2L(OH)$ complex has an appreciable antiferromagnetic interaction and a small $|D|$. This also justifies the estimated complex structure. As was shown above, J and $|D|$ are useful for estimating the coordination geometry of hydroxide ions in such μ-hydroxo-bridged binuclear copper(II) complexes in solution.

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