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Single-crystal ESR and X-Ray Crystallographical Studies of a Binuclear Copper(II) Complex with a Coaxially Stacked Square-pyramidal Geometry

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A binuclear complex of bis(μ-*N*,*N*′-dipicolinoyl-1,3-propanediamine)-bis(sulfato)dicopper(II) has been isolated as a blue single crystal tridecahydrate, $[\{Cu(SO_4)(ppda)\}_2]\cdot 13H_2O$, from an aqueous solution. The crystals are orthorhombic, $C222_1$, with $a=15.42(1)$, $b=24.92(2)$, $c=25.73(2)$ Å, and $Z=8$. Each copper(II) ion is in a square-pyramidal coordination with two pyridine nitrogen atoms, two carbonyl oxygen atoms, and a sulfate oxygen atom at the apex. The two equivalent copper(II) ions, about 3.9 Å apart from each other, are aligned coaxially. The eight Cu-Cu vectors are approximately parallel to one another along the c axis. The most important feature of the crystal structure is the presence of the bulky ligands and of many water molecules, which magnetically isolate the Cu-Cu coupled pair from one another. This facilitates the ESR study of the molecular anisotropies by using the single crystal, even at room temperature. The ESR parameters determined are as follows: $g_{//}=2.280(2)$, $g_{\perp}=2.067(1)$, $|D|=422.4(8)$, $|A_{//}|=170(2)$, and $|A_{\perp}|=14(1)$ in 10^{-4} cm^{-1}. Bleaney and Bowers treatments of the exchange coupling contribution in the *D* parameter indicated a ground singlet state about 7 cm^{-1} below a triplet state for the coupled copper(II) ions. A comparison of the ESR parameters measured for the single crystal with those in the aqueous solution enabled us to conclude that the molecular structure in the solution was very similar to that in the crystalline phase, apart from the coordination of sulfate ions.

The imidazole ring, as a histidine moiety, derives a function as a ligand towards transition-metal ions in a variety of biologically important metalloprotein and peptides.[1] As one simple model ligand, *N*,*N*′-dipicolinoyl-1,3-propanediamine (abbreviated as ppda, Fig. 1), which is a dipeptide with pyridyl groups in place of the imidazolyl groups, was employed to mimic the structure of the metal-active site involving the histidine ligand of related metalloproteins. In an aqueous solution, the coordination chemistry of ppda containing a copper(II) ion has been much altered as the solution is varied from an alkaline one to an acidic one.[2,3] The complex prepared in the alkaline solution has been isolated in the form of trihydrate, and it has been characterized by Ojima[2] by means of visible and IR spectroscopies. This complex is electrically neutral and is composed of mononuclear copper(II) ion. Its coordination geometry is to be ascribed to deprotonation from the amide groups. The acidified solution of this complex showed a sharp red-shift, implying protonation to the anionic nitrogen atoms.[2] ESR measurements in solution have given critical knowledge about the molecular structures: we ourselves have previously reported that the copper(II) complex stable in an alkaline solution takes a square-planar ligand geometry, while the one stable in an acidic solution behaves as an axially symmetric binuclear copper(II) complex ion.[3]

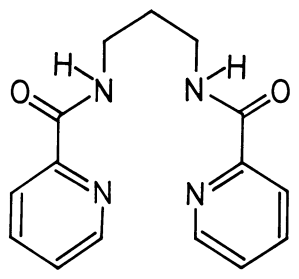

Fig. 1. The chemical structure of *N*,*N*′-dipicolinoyl-1,3-propanediamine (ppda) ligand.

The ESR studies of the binuclear complex ion in an aqueous solution have suggested that the square-planar chromophores bearing the two equivalent copper(II) ions stack so as to possess a common *Z* axis; thus, the respective unique axes of the *g* and *D* tensors of axial symmetry coincide with the molecular unique axis.[3] This structure is quite exceptional as compared with the structures reported for a great many of copper(II) binuclear complexes.[4] In many cases, the unique axes of the two square basal planes are inclined to each other, and the observed ESR parameters are usually described in terms of a spin Hamiltonian, with a rhombic symmetry. In order to reveal the absolute molecular geometry of the ppda-copper(II) binuclear complex ion, X-ray crystallographic studies have been undertaken of those of its crystals which contain sulfate or chloride ions. The former, bis(μ-*N*,*N*′-dipicolinoyl-1,3-propanediamine)-bis(sulfato)dicopper(II) tridecahydrate, $[\{Cu(SO_4)(ppda)\}_2]\cdot 13H_2O$, has been successfully obtained as a blue single crystal in a concentrated aqueous solution. However, the crystal is easily cracked as soon as it is taken from the solution or as soon as the solution is warmed beyond room temperature. Since the crystals show such disorder, the model structure has not been refined beyond an *R* factor of 17%. In so far as we have examined, the latter crystal, $[\{CuCl_x(H_2O)_y(ppda)\}_2]\text{-}Cl_{4-2x}\cdot(2-2y)H_2O$, gave no Bragg reflection.

Although the ppda-copper(II) binuclear complex has been of interest to us as a model for active sites in metalloproteins[5] and as a bimetallic catalyst,[6] the ESR feature in the aqueous solution and the crystal and molecular structure of this complex have caused us to pay much attention to its magnetic properties. The

structure around the copper(II) ions revealed by the X-ray analysis is consistent with the structure indicated by the ESR study in the aqueous solution; this is an example of an investigation in which the crystallographic study assisted by ESR study plays a decisive role in establishing the molecular structure in solution. The prominency of this example is due to the question of whether the ESR parameters for the single molecule in the crystal are the same as those for one in the solution. Even at room temperature, the ESR spectrum of the crystal has exhibited a resolved hyperfine structure as well as a fine structure similar to that in a glassy aqueous solution, which is a very rare case. In order to compare the single-crystal ESR parameters with those obtained from the solution spectrum, therefore, the results of the single-crystal ESR and crystallographic studies of $[\{Cu(SO_4)(ppda)\}_2]\cdot 13H_2O$ are reported in the present paper.

Experimental

Materials. The ppda ligand was prepared from methyl picolinate and 1,3-propanediamine by the method of Ojima.[2] The complex was isolated by the slow evaporation of an aqueous solution containing an equimolar mixture of ppda and $CuSO_4$. Recrystallization from the aqueous solution gave deep blue rhombic-plate crystals with the plate normally along the c axis and diagonals along the a and b axes. The analogous procedure gave a solid containing chloride ions.

Exactly 200 mg of the chloride, dried in the air at room temperature, was reduced to 191.86 mg by further drying in a vacuum for 12 h at 110 °C; this indicated a formula of $[\{CuCl_x(H_2O)_y(ppda)\}_2]Cl_{4-2x}\cdot(2-2y)H_2O$. Anal. calcd for this formula: C, 39.61; H, 4.33; N, 12.32%. Found: C, 39.55; H, 4.32; N, 12.31%. $\lambda_{max}(H_2O)=680$ nm with $\varepsilon=60$. Based on this ε value, $[\{Cu(SO_4)(ppda)\}_2]\cdot 13H_2O$ was assumed for the present compound. Anal. calcd for this formula: C, 32.11; H, 5.21; N, 9.99%. Found: C, 31.97; H, 5.49; N, 10.19%.

ESR Measurements. The ESR spectra from the single crystal were observed at room temperature through the rotation of the three crystallographic axes. The spectrum from the aqueous solution was recorded at 77 K by the use of a glassy solvent containing 30% ethylene glycol. All the measurements were carried out on a JES-ME-3X X-band spectrometer equipped with a 100 kHz field modulation for the first derivative. The magnetic field was calibrated by the splitting of Mn^{II} in MgO, which had previously been corrected by the splitting of Fremy's salt ($a_N=1.300$ mT and $g=2.0054$[7]). The microwave frequency was measured with a Takeda-Riken frequency counter. The resonant-field intensities were estimated based on the spacings between the respective spectral lines and the line from Li-TCNQ taken as a secondary standard.

X-Ray Analysis. Some of the crystals recrystallized a few times were coated with a manicure while the others were sealed in glass capillaries. They were all then tested on a Rigaku automated diffractometer AFC or on a Weissenberg camera. The preliminary measurements showed that the crystals belonged to the orthorhombic system, but some of them lost their orthorhombic symmetry.

After many trials, the diffraction data were obtained for the best crystal examined. Crystal data: $C_{30}H_{58}N_8O_{25}S_2Cu_2$, F.W.=1194.1, orthorhombic, space group=$C222_1$, $a=15.42(1)$, $b=24.92(2)$, $c=25.73(2)$ Å, $V=9885(13)$ Å^3, $D_x=1.51$($Z=8$), $D_m=1.52$ g cm^{-3}. The intensity data were collected on the same diffractometer up to $2\theta=40°$. The observed data numbered 910, about 40% of the possible reflections. The intensity data were corrected for the Lorentz and polarization factors.

The intensity distribution showed some special features:

(a) only $k+l=4n$ are observed for $0kl$, with a few exceptions,

(b) only $h+k=4n$ are observed for $hk0$ at lower angles, while only $h+k=4n+2$ are observed for $hk0$ at higher angles, and

(c) 008 is extraordinary strong.

Based on these feature, the reasonable positions of the heavy atoms were obtained after several attempts.

Successive Fourier syntheses revealed the planar atomic groups around the Cu atoms, and also SO_4 groups above and below the planes. R index was reduced to about 23% by the block-diagonal least-squares method. Although the R index could be further reduced by additional cycles, the molecular shape became poor. Therefore, a constrained refinement was applied in order to keep a reasonable molecular shape. The bases for the constraint were the picolinoyl and SO_4 groups. Many residual peaks corresponding to the crystalline water molecules were added from the difference Fourier syntheses. Without the constraint, the R index could be reduced to 17%, but it was about 21% with the constraint. The atomic scattering factors were taken from the "International Tables for X-Ray Crystallography."[8]

Results and Discussion

Crystal Structure. In the asymmetric unit there are two crystallographically independent molecules, each with a two-fold axis through the central methylene carbon atoms in the bridging propane groups. One of them has two pairs of pyridyl rings, upper and lower, which overlap each other almost completely, while the other has two pairs in which the overlapping is partial. The other differences between the two geometries are not very great, so the sketch of only the latter molecule is shown in Fig. 2.

The copper(II) ion is ligated by two pyridine nitrogen atoms and by two carbonyl oxygen atoms to give a square-planar coordination geometry, and that ion is about 0.3 Å above the basal plane. The apical ligand is the oxygen atom of the sulfate ion as a proximal group (Cu–O≃2.3 Å) and the copper ion in the alternative moiety as a distal one (Cu···Cu≃3.9 Å). The two major planes of the pairs of the picolinamido

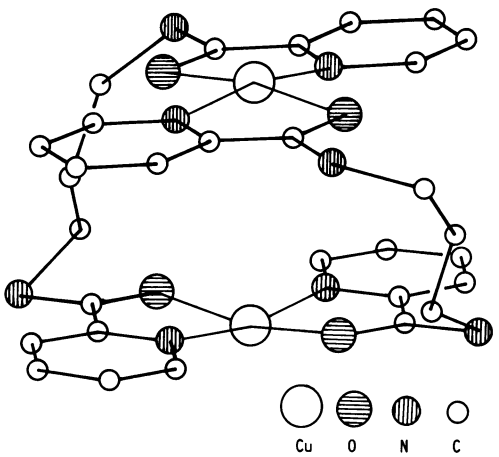

Fig. 2. The sketch of the molecular structure of $[\{Cu(ppda)\}_2]^{4+}$ moiety.

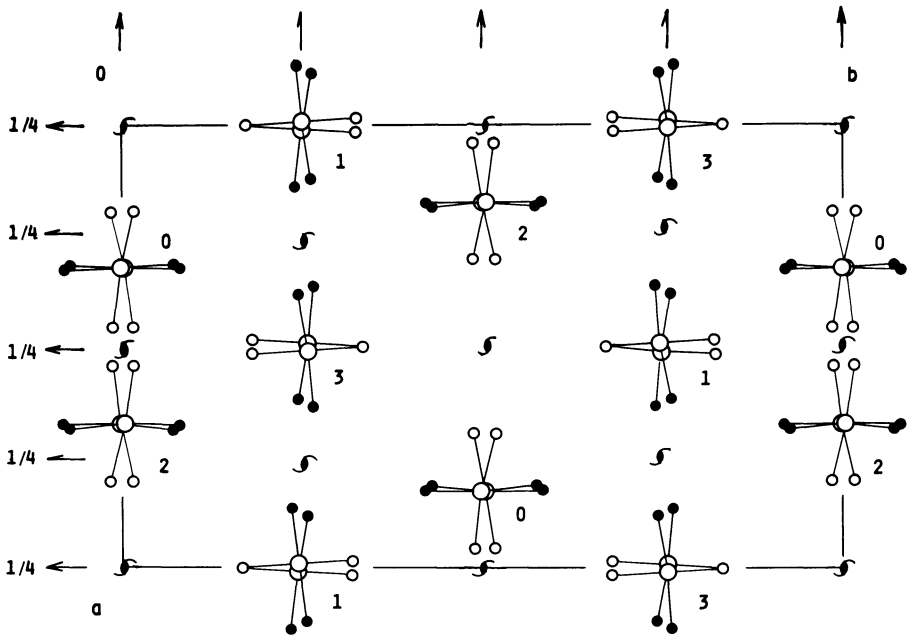

Fig. 3. The arrangement of the [{Cu(N_2O_2)}$_2$] chromophore in the unit cell viewed along the c axis.
The large open circle stands for copper atom, the small open circle oxygen atom, and the solid circle nitrogen atom. The n figure shows the z-component of $z=n/4$ for the center of indicated Cu-Cu pair.

groups are approximately perpendicular to the Cu-Cu distance vector. The two square-planar chromophores bearing two equivalent Cu(II) ions are stacked together so that their local axes approximately coincide to form two sets of x, y, and z axes; this can be seen better in Fig. 3 than for Fig. 2.

Figure 3 shows how the pairs of the copper ions and the metal-binding sites of ppda ligands are packed in the unit cell. The crystal structure consists of a parallel array of the biplanar molecules. The directions of the two-fold axes are parallel to the a and b axes respectively. Therefore, the orientations of the molecules in the c-axis projection are perpendicular to each other. This arrangement is consistent with the extra extinction (b) mentioned in the last section.

The temperature factors of some atoms, especially those at the end of the pyridine rings, are unreasonably high. Therefore, it can not be completely denied that the result might be biased by the proposed model or by the shape of the constrained base. However, the general agreement of the F_o's with the F_c's is good, and the results are at least generally satisfactory within the limits of the quality of the diffraction data.

Magnetic Aspect of the Structure. One can concisely discuss the magnetic aspect of this crystal structure by taking each copper(II) ion to be in an identical coordination geometry of an ideal square pyramid and by taking all the *intramolecular* Cu-Cu distance vectors to be parallel to the c axis.

Then, any single copper ion shows a magnetic anisotropy of a nearly axial symmetry, and the unique axis of the anisotropy is parallel to the c axis. Because the difference between the two kinds of intramolecular Cu-Cu distances can be neglected, the binuclear paramagnetic clusters occupy identical sites of the axial symmetry. On the other hand, the small overlapping between the ligands of the molecules packed discretely indicates a very weak *intermolecular* spin-spin exchange interaction. Moreover, the shortest intermolecular Cu-Cu distance is about 8.3 Å, which is sufficiently large to take the magnitude of the *intermolecular*

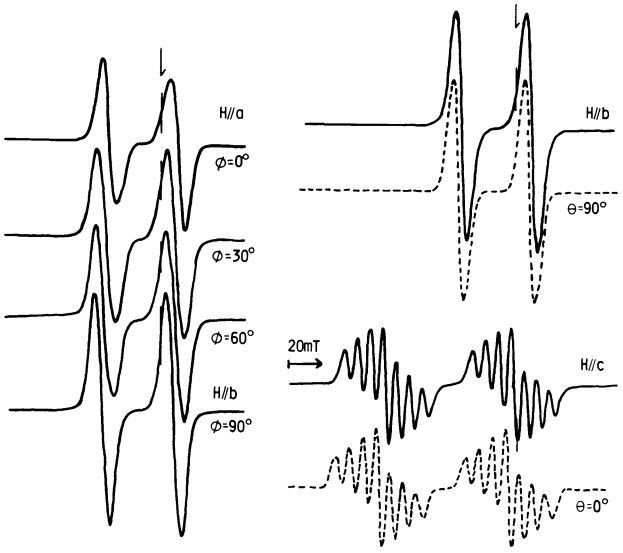

Fig 4. The ESR spectra observed (solid line) and simulated (broken line).
The spectra at left side were obtained when the applied field, $\boldsymbol{H}$, was rotated around the c axis, from $\boldsymbol{H}$//a (uppermost) to $\boldsymbol{H}$//b (lowest) at intervals of 30°. The spectra upper and below at alternative side were recorded when $\boldsymbol{H}$//b and $\boldsymbol{H}$//c, respectively. The arrow shows the resonant field of Li-TCNQ. The simulation was carried out approximating the transition probability to be $g_\perp^2(1+g_{/\!/}^2/g^2)$, where $g^2=g_{/\!/}^2\cos^2\theta+g_\perp^2\sin^2\theta$, and the line-shape function to be Gaussian, with $\sigma_{/\!/}=\sigma_\perp=4.0$ mT ($\boldsymbol{H}$//b) and $\sigma_{/\!/}=\sigma_\perp=3.2$ mT ($\boldsymbol{H}$//c).

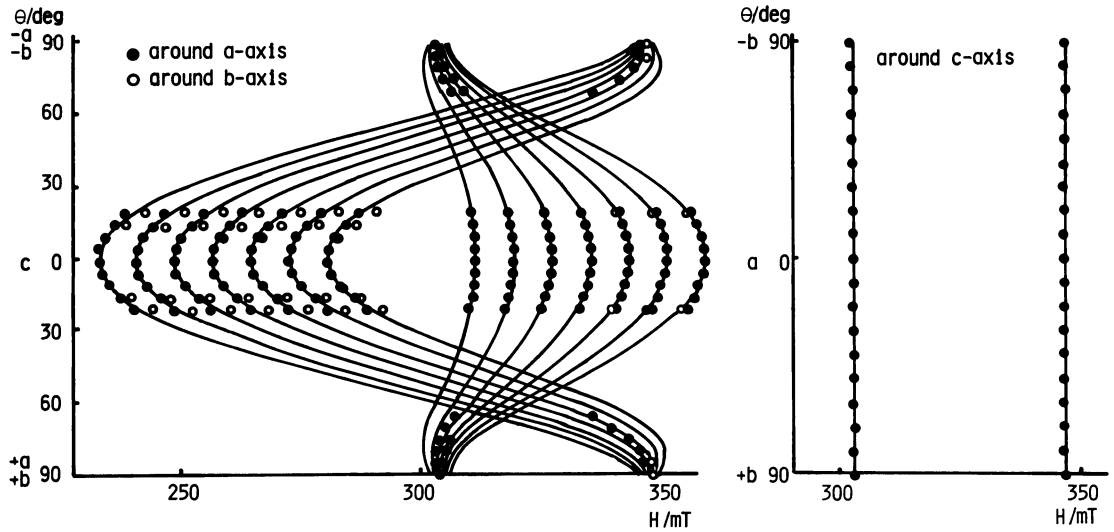

Fig. 5. The angular variation of the resonant fields observed (circles) and calculated (solid lines) when the applied field was rotated around the a and b axes (left side) and the c axis (right side).

magnetic dipolar interaction down one place from that of the *intramolecular* one. Therefore, we can take the crystal anisotropy to be the molecular anisotropy within the limits of the present approximation.

Magnetic Anisotropy. Within the limits of the approximation mentioned above, the axial symmetry of the coordination geometry places restrictions on the principal direction of the molecular coordinate system; therefore, an *a priori* deduction of the magnetic axes can be made. This contrasts with the case of the low symmetric copper binuclear complexes, for example, the $[Cu_2Cl_8]^{4-}$ anion,[9] the low symmetry of which precluded any *a priori* determination of the magnetic principal axes. Figure 4 shows the ESR spectra of the present copper binuclear complex, obtained by applying the external field parallel to the respective principal axes, which coincide with the crystallographic axes. The spectra show a fine structure from the system of $S=1$ and a hyperfine structure due to the exchange-coupled copper atoms. Some investigators have observed fine structures from authentic single crystals of copper binuclear complexes at room temperature.[10] However, they could not record any hyperfine structure from those crystals.

The angular variations of the fine and hyperfine structures are shown in Fig. 5. The error in the setting of the a, b, and c axes is believed to be less than 3°. Figure 5 indicates that the anisotropies in the g factor, the spin-spin dipolar interaction, and the hyperfine interaction are all of an axial symmetry and that the paramagnetic clusters are in equivalent sites. These results are consistent to the approximation made in this text.

In order to obtain the g tensor components ($g_{/\!/}$, $g_{\perp}$), the zero-field splitting parameter (D), and the components of the hyperfine coupling tensor ($A_{/\!/}$, $A_{\perp}$), the following spin Hamiltonian is employed:

$$\begin{aligned}\mathcal{H} &= \beta[g_{/\!/}H_zS_z+g_{\perp}(H_xS_x+H_yS_y)] \\ &+D[S_z^2-S(S+1)/3]+2J\boldsymbol{S}_1\cdot\boldsymbol{S}_2 \\ &+A_{/\!/}S_zI_z+A_{\perp}(S_xI_x+S_yI_y),\end{aligned} \quad (1)$$

where $S=S_1+S_2$, $I=I_1+I_2$, while the other symbols have their usual meanings. The simulation of the ESR spectrum from the glassy solution suggested that the exchange-coupling energy, $|J|$, is much greater than the micro-wave quantum, $W=h\nu=g\beta H_0\cong 0.3\,cm^{-1}$. Under such conditions, Lund and Hatfield[11] calculated the allowed transitions:

$$\begin{aligned}H_{1,2}/H_0 &= 1-[\pm 3D_1+K(m_1+m_2)/2]/W \\ &-[D_3^2/2+D_4^2/2+R^2(m_1+m_2)^2/8\pm 3D_4R(m_1+m_2)/2]/W^2 \\ &-(B_1\mp B_2)/W^2,\end{aligned} \quad (2)$$

where the meanings of the symbols are as given in their paper. Using this equation, the spin Hamiltonian parameters were determined by the nonlinear least-squares method for the data shown in Fig. 5. The starting parameters were obtained by the conventional method. The hamiltonian parameters thus obtained are as follows: $g_{/\!/}=2.280(2)$, $g_{\perp}=2.067(1)$, $|D|=422.4(8)$, $|A_{/\!/}|=170(2)$, and $|A_{\perp}|=14(1)$, in $10^{-4}\,cm^{-1}$. The unique principal axis, Z, of the axial symmetry is parallel to the c axis. Based on these parameters, the angular variations of the fine and hyperfine structures are calculated to be as shown by the solid lines in Fig. 5. The spectra simulated for the $\boldsymbol{H}$//a and $\boldsymbol{H}$//c cases are presented in Fig. 4 by broken lines. The agreement of the simulated spectra with those observed is good in view of the approximation employed. The observed zero-field splitting parameter, D, is the sum of the magnetic dipolar and exchange coupling contributions:

$$D=D_{ex}-(g_{/\!/}^2+g_{\perp}^2/2)\beta^2/r^3. \quad (3)$$

Here, the second term results from the dipolar interaction and is appropriate in this particular form only if both ions occupy identical sites of axial symmetry.[12,14] The observed g components and r(Cu-Cu)=3.86 Å indicate the approximate value of $-55\times 10^{-3}\,cm^{-1}$ for the dipolar contribution. On the other hand, D_{ex} depends on the sign of D. When D is negative, $D_{ex}=13\times 10^{-3}\,cm^{-1}$ is obtained; hence, the

dipolar coupling rules over the zero-field splitting. If D is regarded as positive, $D_{ex}=97\times10^{-3}\,cm^{-1}$ is derived. The negative D value can be inferred in view of the long distance between the two copper ions in the binuclear complex. When one uses the simplest expression for D_{ex} given by Bleaney and Bowers:[13]

$$D_{ex}=-2J[(g_{//}-2)^2-4(g_{\perp}-2)^2]/32, \quad (4)$$

the exchange-coupling parameter, J, or a half of the energy separation between the singlet and triplet levels can be estimated to be about $-3.5\,cm^{-1}$, based on the negative D value. If D is positive, the calculated J is $-26\,cm^{-1}$. The negative J values indicate antiferromagnetic exchange-coupling between the two copper ions. In order to determine which of the J's is adequate, we measured the magnetic susceptibility of this complex by using liquid nitrogen as a coolant; we thus obtained the Weiss constant of $\theta=-4$ K. Since the binuclear complex molecules are isolated from one another in the present crystal, the J parameter obtained from the susceptibility data can be attributed to the exchange-coupled pair of the copper ions in the binuclear complex. The Weiss constant corresponds to $J=2k\theta\simeq-5.5\,cm^{-1}$, which is much closer to the value of $-3.5\,cm^{-1}$ based on the negative D value than to that of $-26\,cm^{-1}$ estimated from the positive D value. Thus, the separation between the ground-singlet and excited-triplet energy levels is estimated from the ESR parameters to be about $-7\,cm^{-1}$. The copper hypefine interaction causes a slight breakdown of the pure singlet and triplet character.[14]

In order to know how the coordination geometry is perturbed by the dissolution of the crystal in a water medium, the ESR parameters obtained for the aqueous solution are compared with those for the single crystal. The observed spectrum, shown with a solid line in Fig. 6, has been simulated with a broken line in the same figure by means of the following parameters: $g_{//}=2.280$, $g_{\perp}=2.072$, $|D|=453$, $|A_{//}|=168$, and $|A_{\perp}|=14$, in $10^{-4}\,cm^{-1}$. The values other than D are in good agreement with those for the crystal. The disagreement between the two D parameters corresponds to the shortening of the Cu-Cu distance by 2.5%, within the limits of the point-dipole approximation.[15] Therefore, one can take it for granted that the molecular structure of the present binuclear complex is retained throughout both the crystalline and solution states, apart from the coordination of the sulfate ions. We suppose that the water molecules play an important role in bringing the molecular structure in the solution into the crystalline phase as it stands, as well as in stabilizing the binuclear complex, since the ppda and the copper(II) ion in common organic solvents do not form any binuclear complex.

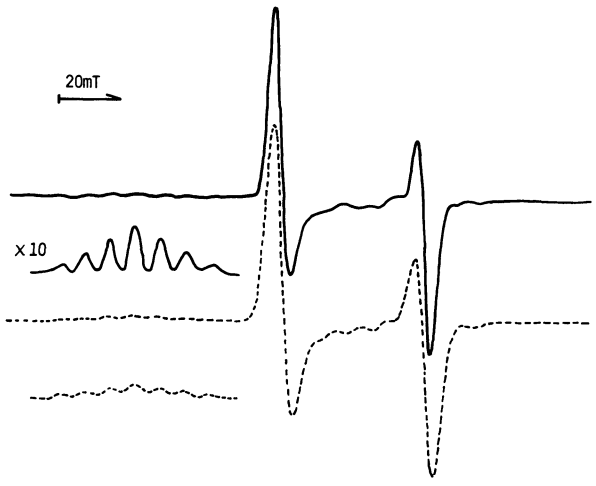

Fig. 6. The ESR spectrum of $[\{Cu(SO_4)(ppda)\}_2]\cdot13H_2O$ dissolved in 30% ethylene glycol aqueous solution at 77 K (solid line) and its simulated spectrum (broken line). The following parameters were employed in the simulation: $g_{//}=2.280$, $g_{\perp}=2.072$, $|D|=0.0453$, $|A_{//}|=0.0168$, $|A_{\perp}|=0.0014\,cm^{-1}$, and $\sigma_{//}=\sigma_{\perp}=2.5$ mT. The transition probability and the line-shape function were the same as those applied in the simulation in Fig. 4.

The authors are grateful to Professor Heijiro Ojima of Aichi Kyoiku University for his encouragement throughout this work. The crystallographic calculations were performed on a FACOM M-200 computer at this Institute using the UNICS III program system.[16] The magnetic data were processed at the Computer Center of this University.

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