

generated species in solution, one readily reversible and one not readily reversible to molecular oxygen. Since the dibridged species is formed exclusively at high pH and the high-pH species is essentially irreversible to molecular oxygen, the μ -hydroxo- μ -peroxo species I is proposed as the species which resists deoxygenation in the buffer zone.

The formation of the μ -hydroxo bridge may be the reaction which "locks" in the oxygen and prevents reversibility. The addition of acid will destroy the chelate with the liberation of oxygen, indicating that the μ -hydroxo bridge must be destroyed before oxygen will be liberated. Formation of the second (hydroxo) bridge also explains the slow equilibrium and contributes to the increased stability of the oxygenated species. The difference between the rate of dissociation observed at high and low pH is ascribed to the considerably higher thermodynamic stabilities of the reaction product I and its oxygenated precursor(s) at high pH.

It has been pointed out by McGinney, *et al.*,¹⁵ that the closer the O-O distance in the complexed oxygen molecules is to that of molecular oxygen, the greater will be the probability that the oxygen complex will

(15) J. A. McGinney, N. C. Payne and J. A. Ibers, *J. Amer. Chem. Soc.*, **91**, 6301 (1969).

be reversible to molecular oxygen. For short O-O distances, the oxygen molecule would be only weakly perturbed by the metal ion and would dissociate readily. For long O-O distances, the binding to the metal ion will be strong and the oxygen moiety will resemble a dinegative peroxide ligand. While this situation certainly obtains for solid oxygen complexes, where the equilibrium must be with gaseous oxygen and a less-coordinated metal complex, it is not a necessary condition for reactions in solution. Thus the formation of a structure such as that indicated by I, with a peroxo bridge and the cobalt formally in the 3+ state, does not preclude another state at an accessible level energetically, consisting of a cobalt(II) complex loosely coordinated to free molecular oxygen. The relative energies of these states would be determined primarily by the nature of the ligands bound to the metal ion in the free and oxygenated complexes. The mobility of the equilibrium between these two states would be determined by the energy barrier between these states, which would be determined to some extent by the ligands, but also by the solvent.

Further studies on other polyamine and peptide complexes of cobalt(II) are being undertaken in this laboratory.

An Electron Spin Resonance Study of the Structure of the Polynuclear Copper(II) Chelates of Tetrakis(aminomethyl)methane¹

T. D. Smith and A. E. Martell

Contribution from the Department of Chemistry, Texas A & M University, College Station, Texas 77843. Received August 6, 1971

Abstract: Electron spin resonance measurements have been made on equivolume water-glycol solutions of the copper(II) chelates of the spiroamine tetrakis(aminomethyl)methane over a wide range of pH and for various mole ratios of metal ion to ligand. When the metal ion to ligand mole ratio is 2:1, the signal at room temperature is almost isotropic at pH 6.0 with little loss of intensity compared to signals observed at lower pH values. This result is notable as the first observed room-temperature spectrum of a binuclear Cu(II) chelate. At 77°K and with increasing pH, the signal becomes less intense and is replaced by a broader signal. At high concentrations of metal ion, a $\Delta M = 2$ signal is observed at low field, demonstrating the presence of the binuclear species. The broad signal centered at about 3000 G together with the low-field signal are interpreted in terms of dipole-dipole coupling of the copper(II) ions in the polynuclear chelate. Solution of a spin Hamiltonian which includes the dipole-dipole interaction makes possible the calculation of the line shapes of the signals due to polynuclear species. The calculations have led to a value of 5.0 Å as the distance between the copper(II) dipoles, which is compatible with the internuclear distance between the copper(II) ions estimated from molecular models.

Recent investigations of the electron spin resonance (esr) spectra of copper(II) chelates has provided useful information on the formation of dimeric species in the liquid phase and frozen solution. These studies have been concerned with the copper(II) chelates of hydroxycarboxylic acids in aqueous and nonaqueous solutions,^{2,3} peptides,⁴ amino acids,⁵ porphyrins,⁶

dialkyl dithiocarbamates,⁷ and copper(II) natural products.⁸ Frequently other physicochemical evidence has been available to confirm the formation of dimeric species in solution so that little doubt exists concerning the interpretation of the esr results in terms of dimer formation. The results of these studies also indicate

(1) This work was supported by a research grant, A-259, from the Robert A. Welch Foundation.

(2) R. H. Dunhill, J. R. Pilbrow, and T. D. Smith, *J. Chem. Phys.*, **45**, 1474 (1966).

(3) J. F. Boas, R. H. Dunhill, J. R. Pilbrow, R. C. Srivastava, and T. D. Smith, *J. Chem. Soc. A*, 94 (1969).

(4) J. F. Boas, J. R. Pilbrow, C. R. Hartzell, and T. D. Smith, *ibid.*, **A**, 572 (1969).

(5) J. F. Boas, J. R. Pilbrow, and T. D. Smith, *ibid.*, **A**, 723 (1969).

(6) J. F. Boas, J. R. Pilbrow, and T. D. Smith, *ibid.*, **A**, 721 (1969).

(7) J. R. Pilbrow, A. D. Toy, and T. D. Smith, *ibid.*, **A**, 1029 (1969).

(8) J. F. Boas, J. R. Pilbrow, G. J. Troup, C. Moore, and T. D. Smith, *ibid.*, **A**, 965 (1969).

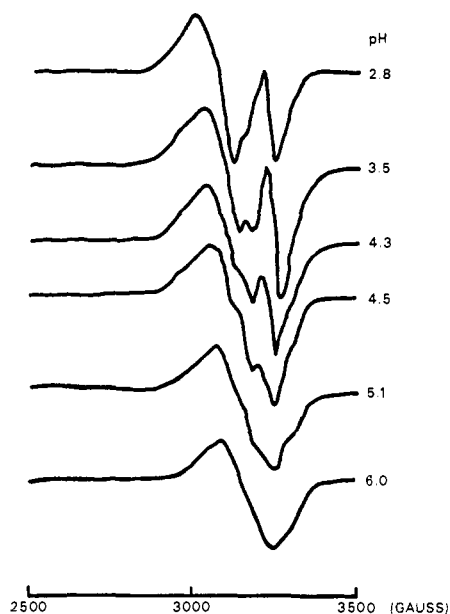


Figure 1. ESR spectra of solutions containing copper(II) chloride ($1.0 \times 10^{-2} M$) and spiroamine ($0.5 \times 10^{-2} M$) at room temperature.

that formation of dimeric species may be critically affected by solvent composition, and that frequently dimer formation takes place in frozen solution but not in the liquid phase.

A most important aspect of the information obtained from a study of the ESR spectra of the dimeric species is that the results may be treated to determine the magnetic parameters associated with the copper(II) ions in a particular chelating environment. The procedure involves a comparison of the experimental ESR line shape with one calculated on the basis that the magnetic interaction between the copper(II) ions is essentially dipolar in character. The distance between the magnetic point dipoles, which is determined from the line-simulation procedure,³ has been interpreted as being equivalent to, or close to, the internuclear distance between the copper(II) ions. An analogous model which considers the interaction between point dipoles has been used to calculate the contribution of the electrostatic dipole-dipole interaction to the energy of formation of the dimer of formic acid.⁹ More recently, the degenerate exciton interaction for dimers in solution was analyzed for a point dipole-dipole model and this approach has been applied to the determination of the geometry of the dimers of protochlorophylls and chlorophyll.^{10,11}

A knowledge of the separation of the copper(II) ions provides useful structural information on the dimeric species. In some cases where several structures arising from interactions with different functional groups provide various bridging arrangements, or where different functional groups provide various bridging arrangements, or where different conformations of a polynuclear species may be possible, information on the distance between the copper(II) ions allows a choice of structure to be made. An early investigation involving this type of decision using information gained by an X-ray determination of the crystal structure of the compound dichlorobis(tributylphosphine)- μ -oxalato-

dipalladium allowed Chatt, Mann, and Wells to distinguish between bridging by the chloride or oxalato groups.¹² To establish unequivocally the copper(II)-copper(II) separation determined by the ESR method as being the internuclear separation, the ideal situation would be to carry out ESR studies on a number of compounds containing copper(II) ions arranged in dimeric units with negligible exchange coupling and such that the internuclear distance between the copper(II) ions varies from about 3 to about 8 Å, as determined by X-ray methods. The magnitudes of the parameter r determined by ESR measurements would then be compared with the known Cu-Cu distances of the crystalline compounds.

The real situation, however, is far from ideal. In the first instance the ESR data are pertinent to frozen solutions which consist of copper(II) dimeric molecules distributed as magnetically isolated pairs throughout the host lattice presented by the frozen solvent molecules. Because of the differences in the lattice conditions, the structures of copper(II) pure crystalline complexes, and their copper(II)-copper(II) distances, may resemble or differ considerably from the structures of the binuclear complexes in the frozen solutions. Even greater structural differences may be expected for crystalline complexes and complexes in solution at room temperature. However, despite these limitations the distance between the copper(II) ions in the dimeric unit formed by the copper(II) chelate of β -alanyl-L-histidine as determined by the ESR method is similar to that determined by X-ray measurements.⁴

Any circumstances which would allow the spatial arrangements of two copper(II) ions to be closely defined by combination with the functional groups of a chelating agent of known conformation would be of particular significance in helping to establish the validity of using the magnetic dipole-dipole interaction of spin free transition metal ions as a measure of the internuclear distance between the metal ions. A suitable opportunity is presented by the 2:1 chelate formed by combination of copper(II) ions with tetrakis(amino-methyl)methane. Here the spiro conformation of the methylene groups ensures a fixed geometry of the terminal amino groups once they are part of the coordination sphere of each copper(II) ion. The convenient preparation of the spiroamine was reported by Litherland and Mann,¹³ while the preparation of some of its metal ion chelates was studied by Oehmke and Bailar.¹⁴ The nature and stability of its chelates with copper(II) ions formed in aqueous solution were investigated by Zompa and Bogucki¹⁵ using potentiometric, spectrophotometric, and polarographic techniques. Thus, when the copper to ligand ratios are 1:2 and 2:1, soluble chelates are formed at low pH values. The latter binuclear chelate undergoes a hydrolytic process to produce insoluble coordination polymers.

Experimental Section

Materials. The source of copper(II) was analytical grade copper(II) chloride dihydrate. Tetrakis(amino-methyl)methane tetra-

(12) J. Chatt, F. G. Mann and A. F. Wells, *J. Chem. Soc.*, 2086 (1938).

(13) A. Litherland and F. G. Mann, *ibid.*, 1588 (1938).

(14) R. W. Oehmke and J. C. Bailar, *J. Inorg. Nucl. Chem.*, **27**, 2199 (1965).

(15) L. J. Zompa and R. F. Bogucki, *J. Amer. Chem. Soc.*, **88**, 5186 (1966).

(9) E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1243 (1938).

(10) I. Tinoco, *Radiat. Res.*, **20**, 133 (1963).

(11) C. Housier and K. Kauer, *J. Amer. Chem. Soc.*, **92**, 779 (1970).

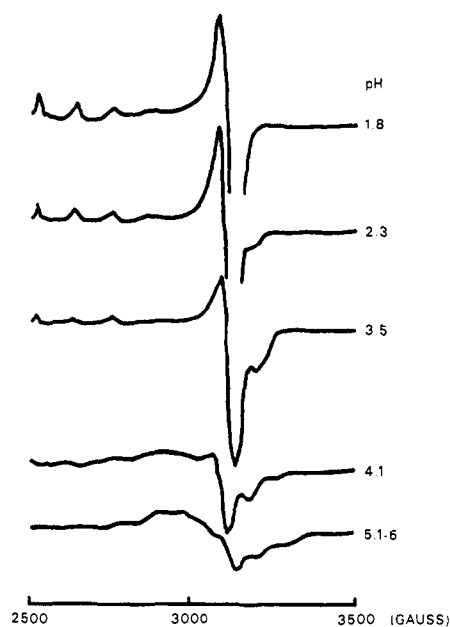


Figure 2. ESR spectra of solutions containing copper(II) chloride ($1.0 \times 10^{-1} M$) and spiroamine ($0.5 \times 10^{-2} M$) at $77^\circ K$.

hydrochloride, which had been prepared by the method of Litherland and Mann,¹³ was kindly made available by Professor I. Murase of Kyushu University, Fukuoka, Japan (presently Visiting Professor of Chemistry at Texas A&M University).

Equipment. The esr spectra were recorded at room temperature and $77^\circ K$ using the X band of a Varian 4502-15 esr spectrometer with 10⁵-hertz field modulation. For the X-band measurements at room temperature a flat quartz cell constructed to minimize dielectric loss was employed. Low-temperature measurements were made on samples contained in narrow-bore silica tubing.

Solvents. At an early stage of the investigation, it was found that using an aqueous solution containing 2:1 mole ratios of copper(II) to ligand, respectively, a precipitate formed when the solution which had been frozen was later thawed at room temperature. It was felt that this would detract from the meaning of the results obtained at $77^\circ K$. However, it was found that if ethylene glycol formed part of the solvent composition the precipitation formation could be avoided, while at the same time it was established that addition of ethylene glycol did not affect the room-temperature signals. Therefore, subsequent work was carried out using an equivolume mixture of water and ethylene glycol as the solvent for copper(II)-amine systems.

Measurements. The spectra were recorded using solutions which varied over the concentration range for copper(II) from 1.0×10^{-2} to $1.0 \times 10^{-1} M$. The more dilute solutions were used to record changes in the esr spectra in the 3000-G region at various values of pH, while the more concentrated solutions were used to measure the low-field signals observed at $77^\circ K$.

Results

The esr spectra of an equivolume water-glycol solution of copper(II) chloride ($1.2 \times 10^{-2} M$) and the spiroamine, tetrakis(aminomethyl)methane ($0.5 \times 10^{-2} M$), at room temperature and at various pH values are shown in Figure 1. The spectra at low pH clearly indicate the conversion of the aquo-metal ion complex to that of the spiroamine. The resolution of the signal is lost with increasing pH though the intensity of the signal is not markedly reduced. Similar results were obtained using the more concentrated ($1.0 \times 10^{-1} M$ in copper(II)) solutions. The corresponding spectra recorded for a sample temperature of $77^\circ K$ are shown in Figures 2 and 3. Here, the main feature is the broadening of the signal with increasing pH such that the signal changes little in the pH range 5.0-6.0. At

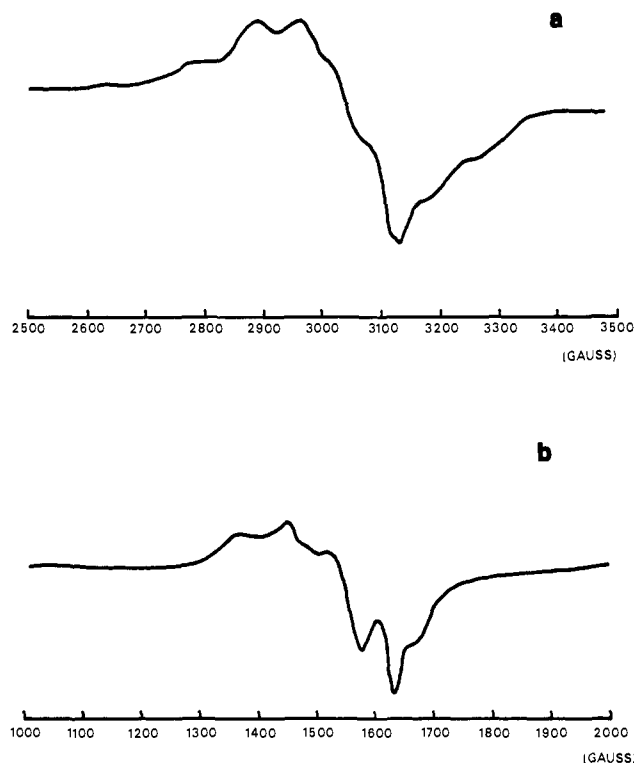


Figure 3. (a) Experimental $\Delta M = 1$ signal due to copper(II) chloride ($1.0 \times 10^{-2} M$) and spiroamine ($0.5 \times 10^{-2} M$), pH 5.5, $77^\circ K$. (b) Experimental $\Delta M = 2$ signal due to copper(II) chloride ($1.0 \times 10^{-1} M$) and spiroamine ($0.5 \times 10^{-1} M$), pH 5.5, $77^\circ K$.

higher concentrations, namely $1.0 \times 10^{-1} M$ with respect to copper(II) and $0.5 \times 10^{-1} M$ in spiroamine, a signal attributed to the $\Delta M = 2$ transitions of the triplet state due to the dipolar coupled copper(II) ions of the polynuclear species was observed and is shown in Figure 3b.

The esr spectra of solutions containing 1:1 mole ratios of metal ion to ligand are shown in Figures 4 and 5 for room temperature and $77^\circ K$, respectively. The almost isotropic signal observed at pH 5.0 to about 8.0 at room temperature is also observed at $77^\circ K$. This signal may be contrasted with those obtained using 2:1 metal ion to ligand ratios over the same pH range. Figure 5 indicates that the spectra obtained over the pH range of about 2.5 to 5.0 bear a remarkable similarity to those shown in Figure 2 and presumably indicate the presence of polynuclear species.

The influence of other chelating agents on the formation of polynuclear species was cursorily investigated by the introduction of ethylenediaminetetraacetic acid (EDTA) or *N*-methyliminodiacetic acid or citric acid into a 2:1 mole ratio solution of copper(II) and spiroamine. The intensities of the signals at $77^\circ K$ given by solutions containing the copper(II), spiroamine, and EDTA, *N*-methyliminodiacetic acid, or citric acid, typical results being shown in Figure 6, were compared with those obtained using EDTA, *N*-methyliminodiacetic acid, or citric acid alone under the same conditions. Thus copper(II) in the presence of EDTA and *N*-methyliminodiacetic acid gives closely similar well-defined signals at $77^\circ K$, while in the presence of citrate the signal cannot be detected at the concentrations of copper(II) used because of extreme line broadening which occurs as a result of the dipolar coupling of the

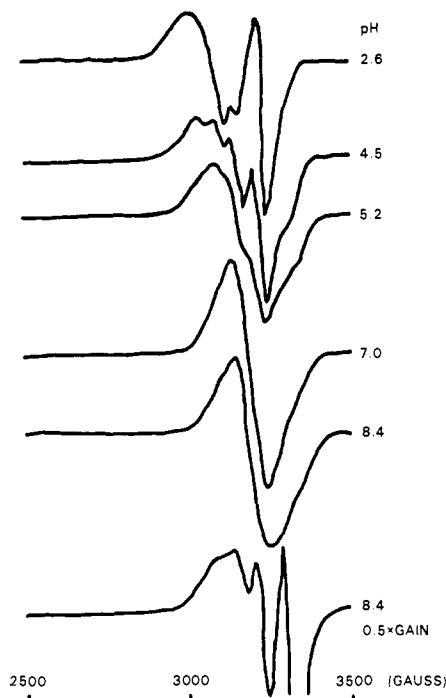


Figure 4. ESR spectra of solutions containing copper(II) chloride ($1.0 \times 10^{-2} M$) and spiroamine ($1.0 \times 10^{-2} M$) at room temperature. The bottom curve is for a solution containing $2.0 \times 10^{-2} M$ spiroamine.

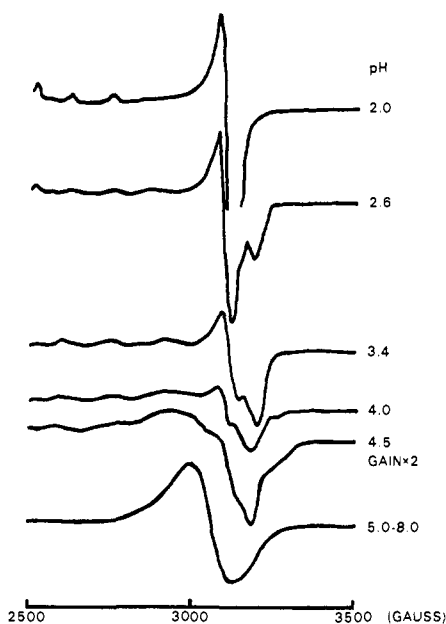


Figure 5. ESR spectra of solutions containing copper(II) chloride ($1.0 \times 10^{-2} M$) and spiroamine ($1.0 \times 10^{-2} M$) at $77^\circ K$.

copper(II) ions in the dimeric species formed under these conditions.²

The results obtained indicate that when EDTA is present in the equilibrium mixture polynuclear formation by the copper(II) and spiroamines does not take place and the copper(II) is completely converted to the EDTA chelate. However, when *N*-methyliminodiacetic acid is used even in excess, complete conversion to the copper(II) aminocarboxylate chelates does not take place. The signal obtained in the presence of citrate is due to monomeric copper(II) citrate spiro-

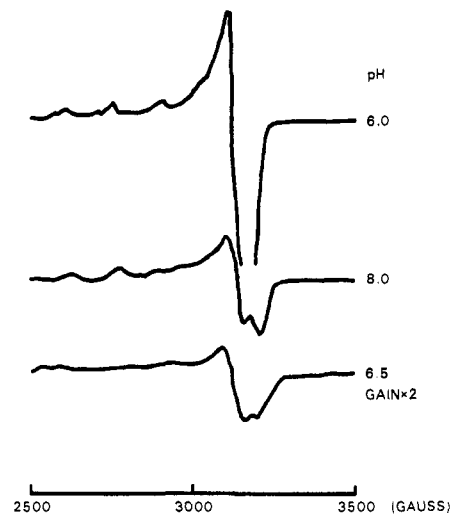
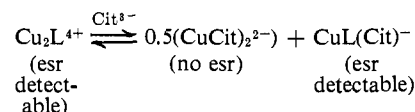


Figure 6. ESR spectra of solutions containing copper(II) chloride ($1.0 \times 10^{-2} M$), spiroamine ($0.5 \times 10^{-2} M$), and $0.02 M$ EDTA (top), $0.1 M$ *N*-methyliminodiacetic acid (middle), $0.1 M$ citric acid (bottom) at $77^\circ K$.

amine mixed ligand chelate, there being enough spiroamine present to accommodate up to one-half of the copper(II) present in this form. Thus, the equilibrium in this system seems to be



where Cit^{3-} = citrate anion and L = tetramine (spiroamine)

Discussion

The Theory of ESR Spectra Due to Copper(II)–Copper(II) Pairs. The theory relevant to the interpretation of the results discussed in this work has been described in detail previously.³ More briefly, it may be stated that when two copper(II) ions ($S = 1/2$) are coupled by a dipolar interaction, a singlet ($S = 0$) and a triplet ($S = 1$) state are formed, the dipolar interaction causing a separation of the $M_s = 1$ and $M_s = 0$ levels in zero magnetic field. Electron spin resonance transitions are observed within the triplet. These will be the normal $\Delta M = 1$ type centered about a resonance position, H_0 , but in addition the forbidden or $\Delta M = 2$ transitions may be observed at about $H_0/2$. The inclusion of the copper(II) hyperfine interactions causes a slight breakdown of the "pure" singlet and triplet character. The dipolar interaction between the two copper(II) ions may be represented as follows

$$\mathcal{H}_d = \frac{1}{R^3} [\mu_1 \mu_2 - 3(\mu_1 R^0)(\mu_2 R^0)]$$

where R^0 is a unit vector along the line joining the centers of the two ions and μ_1 and μ_2 are the magnetic dipoles of each ion. The μ 's have the form $\beta g S$, where g is the Zeeman g tensor and S the effective spin. Where both ions occupy identical sites of axial symmetry, the dipolar interaction may be represented as follows

$$\mathcal{H}_d = \beta^2 [g_{\perp}^2 (S_{1x} S_{2x} + S_{1y} S_{2y}) - 2g_{\parallel}^2 S_{1z} S_{2z}] / R^3$$

which is equivalent to the inclusion in the Hamil-

tonian of a term of the form

$$D \left[S_z^2 - \frac{1}{3} S(S+1) \right]$$

where

$$D = -\beta^2 \left(g_{\parallel} + \frac{1}{2} g_{\perp}^2 \right) / R^3$$

However, in the binuclear copper(II) spiroamine complex this is not the case and some modification of the model is required. The two ions are still in identical sites of axial symmetry, but the y axes of both ions are now parallel to the internuclear vector, R , and the z axis of one ion parallel to the x axis of the other ion as shown in Figure 7. Because the magnetic axes of the two ions are not parallel, it is necessary to choose a frame of reference, in this case that of ion 1, to describe the coordinate system of ion 2. This leads to the following spin Hamiltonians

$$\mathcal{H}_1 = \beta [g_{\parallel} H_{1z} S_{1z} + g_{\perp} (H_{1x} S_{1x} + H_{1y} S_{1y})] + A I_{1z} S_{1z} + B (I_{1y} S_{1y} + I_{1x} S_{1x})$$

and

$$\mathcal{H}_2 = \beta [g_{\perp} H_{1z} S_{2z} + g_{\perp} H_{1y} S_{2y} + g_{\parallel} H_{1x} S_{2x}] + A I_{2z} S_{2z} + B (I_{2y} S_{2y} + I_{2x} S_{2x})$$

and the dipolar interaction becomes

$$\mathcal{H}_d = \beta^2 [g_{\parallel} g_{\perp} (S_{1x} S_{2x} + S_{1z} S_{2z}) - 2g_{\perp}^2 S_{1y} S_{2y}] / R^3$$

The dipolar term is equivalent to a term of the form

$$D \left[S_y^2 - \frac{1}{3} S(S+1) \right]$$

where

$$D = -\beta^2 \left[G_{\parallel}^2 + \frac{1}{2} G_{\perp}^2 \right] / R^3$$

$$G_{\parallel} = g_{\perp}$$

$$G_{\perp} = \sqrt{g_{\parallel} g_{\perp}}$$

which represents an axial pair with the principal axis parallel to the y axis. The spin Hamiltonian can be solved using nondegenerate second-order perturbation theory by treating \mathcal{H}_d and hyperfine terms as a perturbation on the Zeeman interaction.³ Thus, transforming to the Zeeman representation and evaluating matrix elements of the Hamiltonian as before,³ neglecting nonsecular terms (*i.e.*, $B \ll A$) we obtain Matrix I,

Matrix I

	$\left \frac{1}{2}, \frac{1}{2} m_1 m_2 \right\rangle$	$\left \frac{1}{2}, -\frac{1}{2} m_1 m_2 \right\rangle$	$\left -\frac{1}{2}, \frac{1}{2} m_1 m_2 \right\rangle$	$\left -\frac{1}{2}, -\frac{1}{2} m_1 m_2 \right\rangle$
$\left\langle \frac{1}{2}, \frac{1}{2} m_1 m_2 \right $	$(g_1 + g_2)\beta H/2 + (K_1 m_1 + K_2 m_2)/2 + D_{zz}/4$	$(D_{zz} + iD_{yz})/4 + \frac{1}{2} R M_2$	$(D_{zz} + iD_{yz})/4 + \frac{1}{2} R M_1$	$(D_{xx} - D_{yy} + iD_{xy})/4$
$\left\langle \frac{1}{2}, -\frac{1}{2} m_1 m_2 \right $	$(D_{zz} - iD_{yz})/4 + \frac{1}{2} R M_2$	$(g_1 - g_2)\beta H/1 + (K_2 m_2 - K_1 m_1)/2 - D_{zz}/4$	$(D_{xx} + D_{yy})/4$	$(-D_{zz} - iD_{yz})/4 + \frac{1}{2} R M_1$
$\left\langle -\frac{1}{2}, \frac{1}{2} m_1 m_2 \right $	$(D_{zz} - iD_{yz})/4 + \frac{1}{2} R M_1$	$(D_{xx} + D_{yy})/4$	$(g_2 - g_1)\beta H/2 + (K_1 m_1 - K_2 m_2)/2 - D_{zz}/4$	$(-D_{zz} - iD_{yz})/4 + \frac{1}{2} R M_2$
$\left\langle -\frac{1}{2}, -\frac{1}{2} m_1 m_2 \right $	$[D_{xx} - D_{yy} - 2iD_{xy}]/4$	$(-D_{zz} + iD_{yz})/4 + \frac{1}{2} R M_1$	$(-D_{zz} + iD_{yz})/4 + \frac{1}{2} R M_2$	$-(g_1 + g_2)\beta H/2 - (K_1 m_1 + K_2 m_2)/2 + D_{zz}/4$

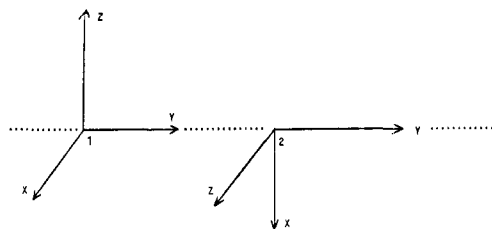


Figure 7. Coordinate axes showing average orientations of coordination spheres of two Cu(II) ions, centered at (1) and (2) coordinated to a single molecule of tetrakis(aminomethyl)methane in binuclear complex Cu_2L^{4+} ; Y axes oriented along the line of centers of the Cu(II) ions.

where

$$g_1 = (g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{1/2}$$

$$g_2 = (g_{\perp}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta \sin^2 \phi + g_{\parallel}^2 \sin^2 \theta \cos^2 \phi)^{1/2}$$

$$K_1^2 g_1^2 = A^2 g_{\parallel}^2 \cos^2 \theta + B^2 g_{\perp}^2 \sin^2 \theta$$

$$K_2^2 g_2^2 = A^2 g_{\parallel}^2 \sin^2 \theta \cos^2 \phi + B^2 g_{\perp}^2 [\cos^2 \theta + \sin^2 \theta \sin^2 \phi]$$

$$R_1 = (B^2 - A^2) g_{\parallel} g_{\perp} \cos \theta \sin \theta / K g^2$$

$$R_2 = \cos^2 \theta \cos \phi \sin \phi g_{\parallel}^2 (A^2 + AB) + B^2 g_{\perp}^2 \sin^2 \theta / K g^2$$

and the D_{ij} terms ($i, j = x, y, z$) are functions of the components of the zero-field splitting tensor and appropriate direction cosines.³ In this case both θ and ϕ are required because of the noncoincidence of the zero-field splitting tensor and the magnetic axes of the individual ions. The inner matrix involving the states $|1/2, -1/2\rangle$ and $|-1/2, 1/2\rangle$ now involve Zeeman terms on the diagonal. Previous calculations eliminated the near degeneracy of these states by diagonalization of the inner matrix and expressing in terms of new states of the form $a|1/2, -1/2\rangle$ and $b|-1/2, 1/2\rangle$. In this case it can be seen that the coefficients will depend on the values of the magnetic field, and this will lead to terms quadratic in field using the perturbation method of solution. Thus solution of allowed $\Delta M = 1$ transitions is considerably more complicated than in the case

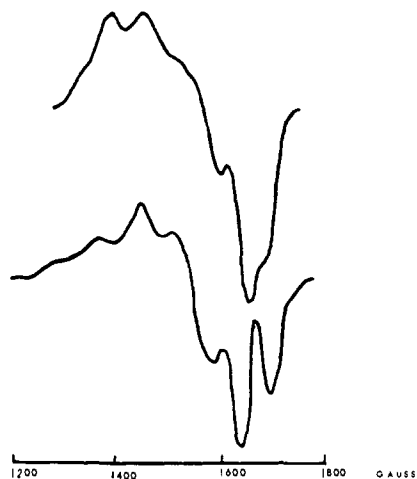


Figure 8. Computer simulation of the $\Delta M = 2$ spectrum of the binuclear copper(II) complex using the parameters $g_{\parallel} = 2.28$, $g_{\perp} = 2.04$, $A = 170 \times 10^{-4} \text{ cm}^{-1}$, $B = 15 \times 10^{-4} \text{ cm}^{-1}$, $R = 5.0 \text{ \AA}$: upper curve, nonparallel axis symmetry; lower curve, axial symmetry.

of axial symmetry of the pair of copper(II) ions. For the $\Delta M = 2$ transition between states $|1/2, 1/2 m_1 m_2\rangle$ and $|-1/2, -1/2 m_1 m_2\rangle$, these complications do not arise even if the inner matrix was diagonalized, since the transition fields and probabilities are independent of the coefficients of the new states involving $|1/2, -1/2\rangle$ and $|-1/2, 1/2\rangle$. For randomly oriented complexes, the energy levels and hence field positions are found as a function of orientation with respect to the magnetic field. The $\Delta M = 2$ transition resonant fields occur at

$$H = W/(g_1 + g_2)\beta - (K_1 m_1 + K_2 m_2)/(g_1 + g_2)\beta - \\ D[D_{yz}^2/4 + D_{xz}^2/4 + D_{yz}^2/4 + \\ (D_{zz} - D_{yy})^2/16]/(W(g_1 + g_2)\beta) - \\ \frac{1}{2}(R_1^2 m_1^2 + R_2^2 m_2^2)/(W(g_1 + g_2)\beta)$$

where $W = h\nu$ and the corresponding transition probabilities are proportional to

$$\left| \left\langle \frac{1}{2}, \frac{1}{2} m_1 m_2 \left| S_x \right| -\frac{1}{2}, -\frac{1}{2} m_1 m_2 \right\rangle \right|^2$$

where

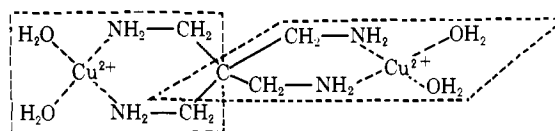
$$\left| \frac{1}{2}, \frac{1}{2} m_1 m_2 \right\rangle \quad \text{and} \quad \left| -\frac{1}{2}, -\frac{1}{2} m_1 m_2 \right\rangle$$

are the perturbed states.

A simulation of the esr spectrum of such a pair is then obtained by dividing space into a sufficiently large number of solid angle segments. The contributing esr transitions, assumed to be Gaussian in shape, are summed by computer, making allowance for angular weighting factors and Zeeman anisotropy.

Esr Parameters. The Copper(II)-Copper(II) Separation. The parameter of chief interest in this study is R , the copper(II)-copper(II) separation. The reliability of its determination is assessed by finding the range over which comparable fits of the esr spectra are obtained subject to suitable variations of magnetic and structural parameters. Using the procedures outlined above, simulation of the line shape for the $\Delta M = 2$ transition of the binuclear copper(II) spiroamine chelate leads to the following values for the relevant parameters: $g_{\parallel} = 2.28 \pm 0.01$, $g_{\perp} = 2.04 \pm 0.02$, $A = 170 \pm 5 \text{ cm}^{-1}$, $B = 15 \pm 10 \text{ cm}^{-1}$, $R = 5.0 \pm 0.5 \text{ \AA}$. The

distance of 5 \AA between the magnetic point dipoles is compatible with the internuclear distance estimated from molecular models of structure I.



I, binuclear Cu(II) complex Cu_2L^{4+} ,
L = tetrakis(aminomethyl)methane

It is of interest to compare the simulated spectrum using the present theoretical approach with that which would be obtained using the parameters for an axial pair of copper(II) ions. Figure 8 shows such a comparison of the simulation of the $\Delta M = 2$ transition. The spectrum for the copper(II) spiroamine chelate, while bearing a formal resemblance to that of an axial dimer, differs in the various intensities found in the various parts of the spectrum and is more symmetric than that due to the axial pair.

Conclusions

In studies of the triplet state of vanadyl tartrate binuclear complexes spectra have been reported which are due to triplet state phenomena at room temperature, and the circumstances in which such spectra are observed at room temperature in other systems have been reviewed by Belford, *et al.*^{16,17} In the case of binuclear copper(II) compounds, the esr spectra arising from triplet states in which the coupling is essentially dipolar in character have been observed at 77°K . The corresponding spectra of binuclear complexes at room temperature have not been observed previously. In cases where there is a more or less complete conversion in solution to dimeric species, this means that such systems do not possess esr spectra at room temperature. An example of such behavior is the copper(II)-bipyridyl system at a 1:1 molar ratio, which is about 95% converted to the μ -dihydroxo binuclear chelate in the pH range 7-9.¹⁸ Because of the absence of an esr signal for the dimer in this system, the change in intensity of the spectra obtained can be used to follow the conversion of mononuclear to polynuclear chelate species in solution.¹⁹

In the systems studied in this investigation, the potentiometric data¹⁵ indicate that at a pH of 5-6 the copper(II) is converted to the spiroamine complexes and in the case of the 2:1 metal to ligand mole ratio solutions, the copper(II) is entirely in the form of the binuclear complex. The spectra reported in this investigation therefore represent the first case where the triplet state of copper(II) is observed at room temperature.

Acknowledgment. We are grateful to Mr. P. D. W. Boyde of the Chemistry Department, Monash University, Australia, for valuable discussions on the results obtained in this investigation. The authors also express their thanks and appreciation to Professor R. L. Belford for many helpful suggestions made during the review of this manuscript.

(16) R. L. Belford, N. D. Chasteen, H. So, and R. E. Tapscott, *J. Amer. Chem. Soc.*, **91**, 4675 (1969).

(17) R. E. Tapscott and R. L. Belford, *Inorg. Chem.*, **6**, 735 (1967).

(18) R. L. Gustafson and A. E. Martell, *J. Amer. Chem. Soc.*, **81**, 525 (1959).

(19) F. J. Smentowski, D. W. Kingston, and A. E. Martell, submitted for publication.