An Electron Spin Resonance Study of the Structure of Certain Polynuclear Copper(II) Polyaminocarboxylate Chelates and the Dimeric Copper Chelates of *N,N'*-Diglycylethylenediamine[1]

T. D. Smith and A. E. Martell*

Contribution from the Department of Chemistry, Texas A & M University, College Station, Texas 77843. *Received January 22, 1971*

Abstract: Electron spin resonance measurements have been made on 80% water-ethylene glycol solutions containing the copper(II) chelates of diethylenetriaminepentaacetic acid (DTPA), triethylenetetraminehexaacetic acid (TTHA), and *N,N'*-diglycylethylenediamine (DGEN). Copper(II) forms 2:1 and 1:1 chelates with DTPA and TTHA which are stable over a wide pH range. Esr measurements at 77°K on solutions containing the polynuclear 2:1 copper(II) DTPA or TTHA chelates reveal the presence of $\Delta M = 1$ and $\Delta M = 2$ transitions arising from a triplet state involving an essentially magnetic dipolar interaction between the two copper(II) ions in the polynuclear chelates. Similar measurements show that signals are also obtained at room temperature for these systems which again are presumably due to the triplet state. Esr measurements on solutions containing copper(II) and DTPA or TTHA in 1:1 mole ratio show that $\Delta M = 2$ transitions can be observed at pH values of about 2.0 and 4.0 indicating that under these conditions some polynuclear chelate formation takes place. Solutions containing copper(II) and DGEN give rise to $\Delta M = 1$ and $\Delta M = 2$ signals at 77°K at a pH of about 6.0 providing unequivocal evidence for the formation of dimeric species in frozen solution. 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 and dimeric species at 77°K. In each case calculations have led to a value for the distance between the copper(II) ions and these data have been used to suggest possible structures for the polynuclear and dimeric species.

Recent studies of the interactions of metal ions with multidentate ligands have brought forth new ligands and have revived interest on the part of those involved with earlier investigations. In some cases the aims of these studies have been the development of ligands with increased affinity and selectivity for metal ions. Much attention has been paid to the higher homologs of EDTA such as diethylenetriaminepentaacetic acid (DTPA)[2] and more recently triethylenetetraminehexaacetic acid (TTHA) where evidence has been presented for the formation of mononuclear chelates, protonated mononuclear chelates, and binuclear chelate compounds.[3-6] Among recent studies on ligands containing peptide linkages it was found that the synthetic ligand *N,N'*-diglycylethylenediamine (DGEN) forms coordination compounds with copper(II) and nickel(II) by displacement of the protons from the amide linkages. A polynuclear copper(II) chelate which is formed at low pH depolymerizes to a mononuclear chelate in alkaline solution. The copper(II) chelate CuL^{2+} releases amide protons in two distinct steps to give the species $Cu_2(H_{-1}L)_2{}^{2+}$ and $CuH_{-2}L$.[7]

The structures of metal ion-polyaminocarboxylate chelates in the solution and in the crystalline state have been the subject of a number of investigations. A recent summary by Wilkins and Yelin[8] dealing with the nature and number of bonding sites in multidentate ligands reveals general lack of information on the structures and conformations of metal complexes of multidentate ligands in solution. Contemporary developments in the esr theory of dipolar coupled copper(II) ions has made possible the determination of the distance between the copper(II) ions in dimeric or polynuclear species.[9,10] Such knowledge of the separation between the copper(II) ions in dimeric or polynuclear species provides useful information on the structure of the chelate and in favorable cases allows a choice of structure to be made where several possibilities may exist.[11-15] This is the present situation in the case of the polynuclear or dimeric chelates formed by DGEN, DTPA, or TTHA where binding by the many sites available in these multidentate ligands provides an unusually large range of structural possibilities. In these systems some firm knowledge of the internuclear separation of the metal ions would be very useful for narrowing down the choice of possible structures in solution.

Experimental Section

Materials. The source of copper(II) was analytical grade copper(II) chloride dihydrate. *N,N'*-Diglycylethylenediamine dihydrochloride, which has been prepared by the method of Cottrell and Gill,[16] was kindly made available by Dr. J. R. Motekaitis of this laboratory. DTPA was obtained from J. T. Baker Chemical Co., and TTHA was obtained from the Dojindo Pharmaceutical Laboratories, Kumamoto, Japan. Both compounds were of the highest purity available.

Equipment. The esr spectra were recorded at room temperature and at 77°K using the X-band of a Varian 4502-15 esr spectrometer

---

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

[2] E. J. Durham and D. P. Ryskiewick, *J. Amer. Chem. Soc.*, **80**, 4812 (1958).

[3] J. H. Grimes, A. J. Huggard, and S. P. Wilford, *J. Inorg. Nucl. Chem.*, **25**, 1225 (1963).

[4] T. A. Bohigian and A. E. Martell, *Inorg. Chem.*, **4**, 1264 (1965).

[5] T. A. Bohigian and A. E. Martell, *J. Amer. Chem. Soc.*, **89**, 832 (1967).

[6] A. Yingst and A. E. Martell, *ibid.*, **91**, 6927 (1969).

[7] K. Sun Bai and A. E. Martell, *ibid.*, **91**, 4412 (1969).

[8] R. G. Wilkins and R. E. Yelin, *ibid.*, **92**, 1191 (1970).

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

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

[11] J. F. Boas, J. R. Pilbrow, C. R. Hartzell, and T. D. Smith, *ibid.*, 572 (1969).

[12] J. F. Boas, J. R. Pilbrow, and T. D. Smith, *ibid.*, 722 (1969).

[13] J. F. Boas, J. R. Pilbrow, and T. D. Smith, *ibid.*, 723 (1969).

[14] J. F. Boas, J. R. Pilbrow, G. J. Group, C. Moore, and T. D. Smith, *ibid.*, 965 (1969).

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

[16] T. L. Cottrell and J. E. Gill, *J. Chem. Soc.*, 129 (1947).

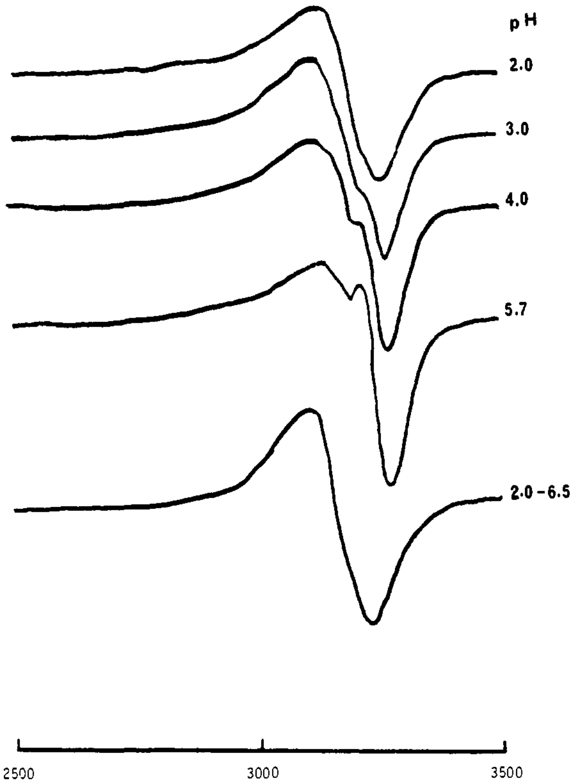


Figure 1. Esr spectra of solutions containing copper(II) chloride ($1.0 \times 10^{-1} M$) and TTHA (1.0×10^{-1} M) at room temperature. The bottom curve is for a solution containing 0.05 M TTHA and 0.1 M copper(II) chloride.

with 10^5-hertz field modulation. Low temperature measurements were made in a solution cell consisting of narrow bore silica tubing. A flat quartz cell constructed to minimize dielectric loss was employed for X-band measurements at room temperature.

Measurements. The spectral measurements were made on solutions containing copper(II) concentrations that varied from 1.0×10^{-2} M to 1.0×10^{-1} M. The more dilute solutions were used to record changes in the esr spectra in the 3000-G region as a function of pH. The more concentrated solutions were employed for measurements of low-field signals at 77°K. In this research, pH is defined as $-\log [H^+]$ (*i.e.*, $-$log hydrogen ion concentration), rather than the usual activity function, $\sim -\log a_{H^+}$. The potentiometric apparatus, consisting of a Beckman Research Model pH meter fitted with extension glass and calomel electrodes, was calibrated in the usual way by careful titration of standard strong acid with strong base in an ionic medium regulated at 0.10 M by the addition of the appropriate amount of potassium nitrate. For the low temperature measurements of frozen solutions, 25% ethylene glycol (by weight) was employed. It was found that under these conditions the metal complexes employed do not precipitate out on cooling, and this amount of ethylene glycol does not affect the room temperature spectra.

Results

TTHA. Addition of base to a water–glycol solution containing 0.1 M copper(II) chloride and 0.1 M or 0.05 M TTHA results in the formation of water soluble 1:1 and 2:1 metal chelates. Typical esr spectra of the solutions recorded at room temperature are shown by Figure 1, which includes the spectrum due to solutions containing the metal and ligand in 2:1 ratio. In the latter solution the fact that the copper(II) remains in solution even under alkaline conditions clearly indicates the capacity of the ligand to form polynuclear chelates. The spectrum obtained at room temperature at pH 6.5 is therefore due to polynuclear species. The corresponding spectra obtained at 77°K are shown by Figure 2 which indicates that well-resolved spectra are obtained at and above pH 4.0. The spectra obtained at 77°K for a solution containing 0.1 M copper(II) and 0.050 M TTHA at pH 6.5 are shown by Figure 3A and show little resolved structure. At higher instrumental gain a low-field transition depicted by Figure 3B and attributed to a $\Delta M = 2$ transition arising from the magnetic dipolar coupling of the copper(II) ions in the polynuclear chelate was observed. At this stage it may be noted that the spectra shown by Figure 2 indicate a broadening of the signal in the 3000-G region in the pH range 2–4. The low-field spectra of these solutions were investigated and at pH 2–3.5, $\Delta M =$

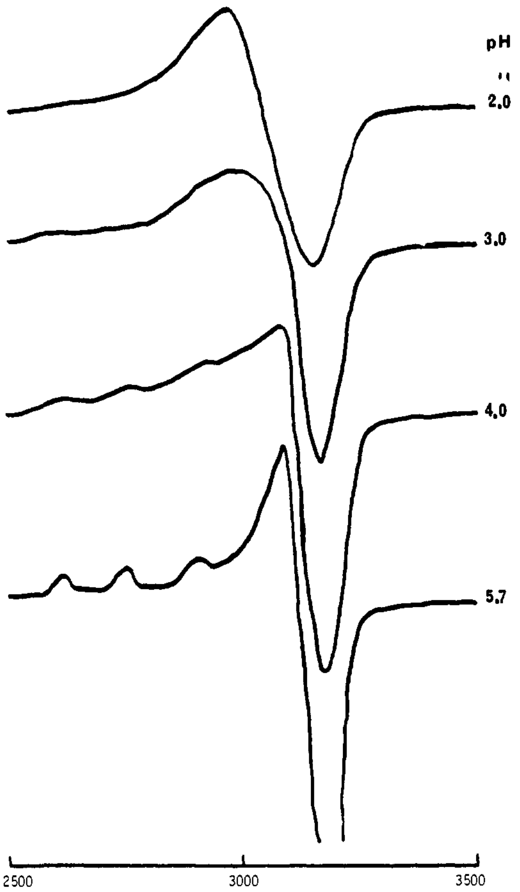


Figure 2. Esr spectra of solutions containing 0.1 M copper chloride and 0.1 M TTHA at 77°K.

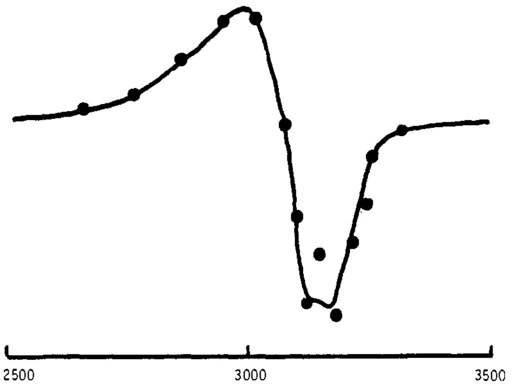


Figure 3A. Experimental $\Delta M = 1$ signal due to 0.1 M copper(II) and 0.05 M TTHA at 77°K, pH 6.5. Points represent the computed spectra using parameters listed in Table I.

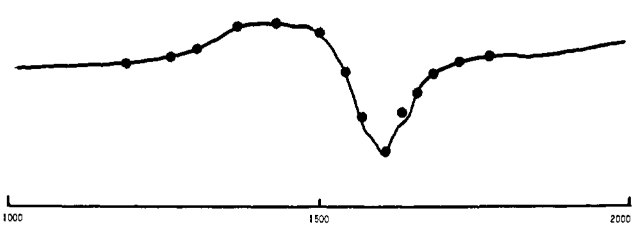


Figure 3B. Experimental $\Delta M = 2$ signal due to 0.1 M copper(II) and 0.05 M TTHA, at 77°K, pH 6.5. Points represent the computed spectra using parameters listed in Table I.

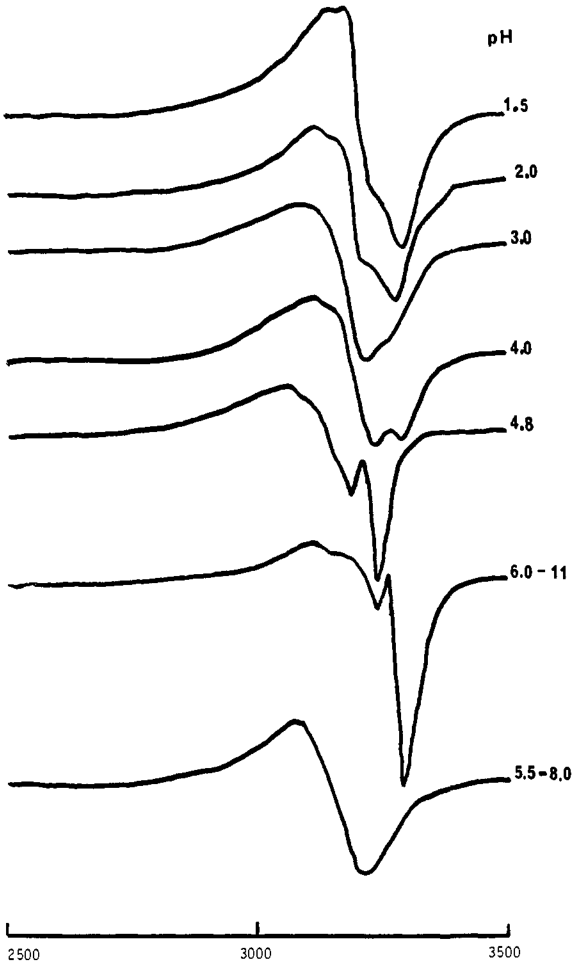


Figure 4. Esr spectra of solutions containing 0.1 M copper(II) chloride and 0.1 M DTPA at room temperature. The bottom curve is for a solution containing 0.05 M DTPA and 0.1 M copper(II) chloride.

2 signals were observed in the 1:1 mixture. These signals became difficult to detect at about pH 4.0 and disappeared at still higher pH. Thus even with 1:1 metal to ligand mole ratios evidence is provided for the formation of polynuclear chelates in the low pH range.

DTPA. DTPA also possesses the capacity to form polynuclear chelates. Thus a solution containing 0.10 M copper(II) and 0.10 M DTPA or 0.050 M DTPA gave rise to water-soluble stable chelates over the pH range 2.0–11.0. Typical room temperature esr spectra of solutions containing 0.10 M copper(II) and 0.10 M DTPA are shown by Figure 4 which also includes the spectra of a solution containing 0.10 M copper(II) and 0.050 M DTPA. This spectrum is unchanged over the pH range 5.5–8.0, a pH range where the copper(II) is involved in polynuclear chelate formation. The corresponding spectra at 77°K for the 1:1 mole ratio solutions are shown by Figure 5 where once more it may be noted that at low values of pH the signals show a broadening in the 3000-G region. A search at low field revealed the presence of $\Delta M = 2$ signals which persisted up to a pH of about 4.5. This provides evidence for the formation of polynuclear species in the 1:1 mole ratio solutions. Polynuclear formation would of course be favored in the 2:1 metal ion to ligand mole ratios and the signals at 77°K for a solution containing 0.10 M copper(II) and 0.050 M DTPA at pH 7.0 are shown by Figure 6A, which shows the broadened $\Delta M = 1$ spectra to be expected in these circumstances. Figure 6B depicts the relevant low-field $\Delta M = 2$ component of the spectra observed at higher gain.

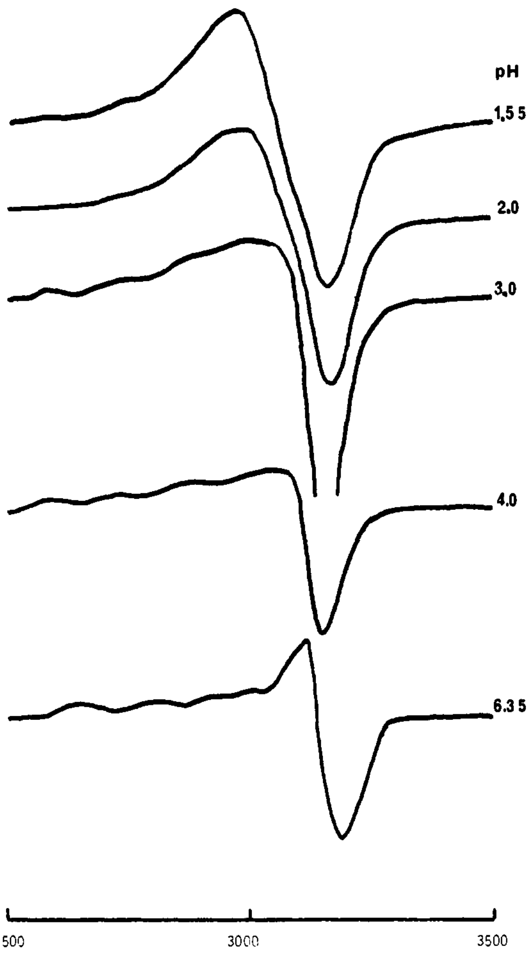


Figure 5. Esr spectra of solutions containing 0.1 M copper(II) chloride and 0.1 M DTPA at 77°K.

DGEN. When present in 1:1 mole ratio copper(II) forms a stable water-soluble chelate with DGEN which is blue up to a pH of about 9, the color changing to a crimson color at a pH of about 11. The ligand, however, is unable to form chelates having a 2:1 molar ratio of metal ion to ligand, since if the metal is present in excess of that of the ligand the excess copper(II) simply precipitates out as the hydroxide when the pH is raised. The esr spectra at room temperature of water–glycol solution containing 0.10 M copper(II) chloride and 0.10 M DGEN are shown by Figure 7. At a pH of about 4 a signal with some degree of resolu-

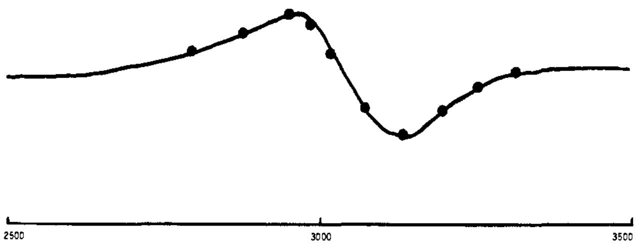


Figure 6A. Experimental $\Delta M = 1$ signal due to 0.1 M copper(II) and 0.05 M DTPA at 77°K, pH 7.0. Points represent the computed spectra using parameters listed in Table I.

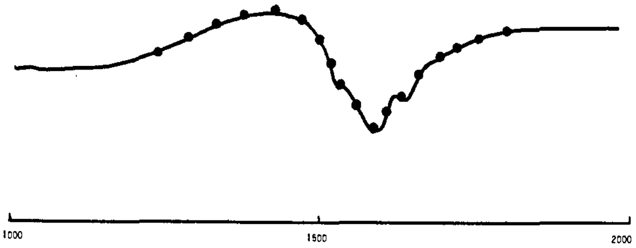


Figure 6B. Experimental $\Delta M = 2$ signal due to 0.1 M copper(II) and 0.05 M DTPA at 77°K, pH 7.0. Points represent the computed spectra using parameters listed in Table I.

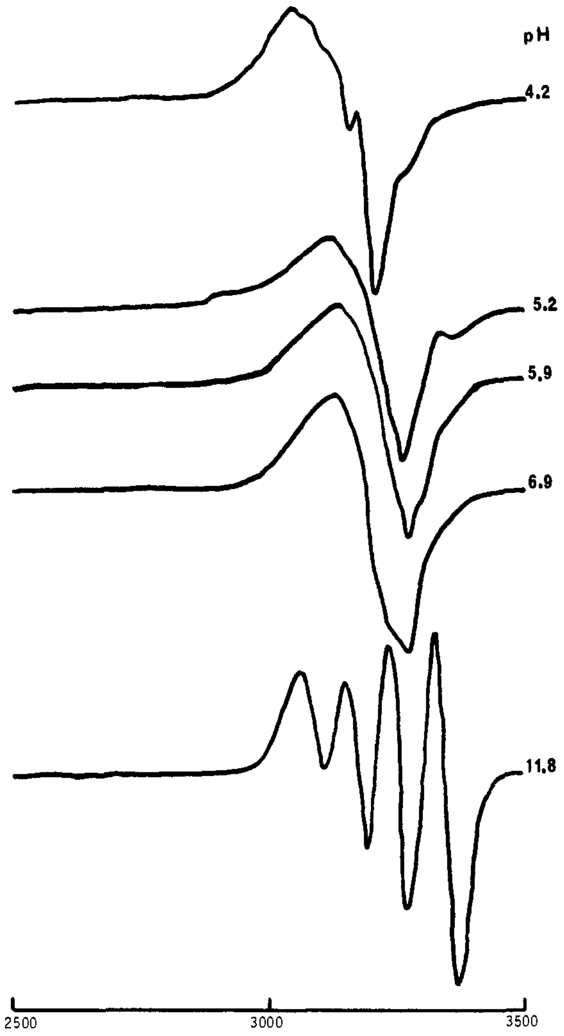


Figure 7. Esr spectra of solutions containing 0.10 M copper(II) and 0.10 M DGEN at room temperature.

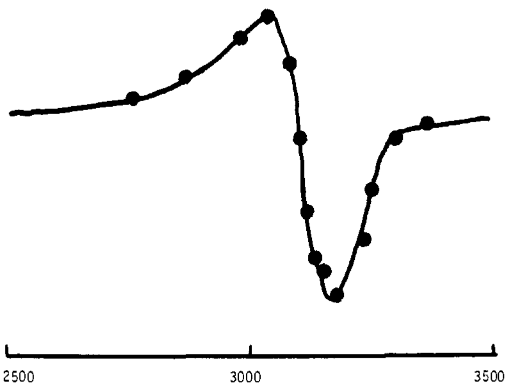


Figure 8A. Experimental $\Delta M = 1$ signal due to 0.1 M copper(II) chloride and 0.1 M DGEN at 77°K, pH 7.0. Points represent the computed spectra using parameters listed in Table I.

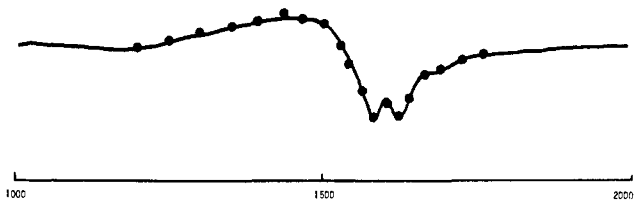


Figure 8B. Experimental $\Delta M = 2$ signal due to 0.1 M copper(II) chloride and 0.1 M DGEN at 77°K, pH 7.0. Points represent the computed spectra using parameters listed in Table I.

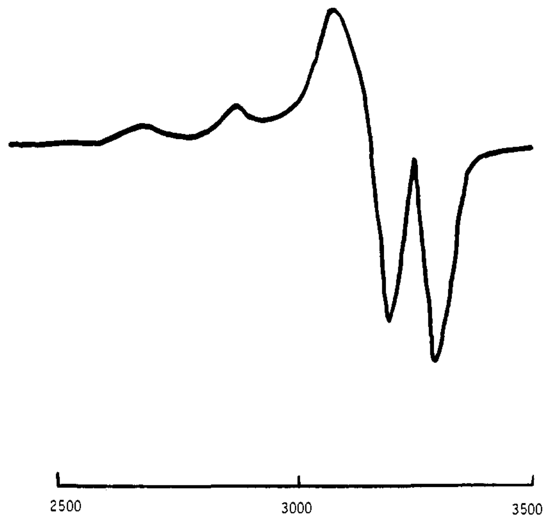


Figure 9. Esr spectrum of solution containing 0.1 M copper(II) and 0.1 M DGEN at 77°K, pH 11.8.

tion is observed. With increase of pH there is little change in the intensity of the signal though there is a loss of resolution between 6.0–7.0. At higher pH values where a color change is clearly observed the esr spectra changes dramatically and becomes quite well resolved. In frozen solution at 77°K the spectra of the 1:1 mole ratio solution at pH 7.0 consists of a broadened signal as shown by Figure 8A. Such a signal is similar to that due to the $\Delta M = 1$ transitions previously described for the polynuclear copper(II) DTPA and copper(II) TTHA chelates. Indeed at low field the relevant $\Delta M = 2$ component was observed as shown by Figure 8B. The observation of the low-field line provides unequivocal evidence for the formation of dimeric species in

Table I

System	Transition	r, Å	Line width parameters, G	$A \times 10^{-4}$ cm^{-1}	$B \times 10^{-4}$ cm^{-1}	$g_{\|}$	$g_{\perp}$
Cu_2DTPA	$\Delta M = 1$	5.5 ± 0.5	60 ± 10	140 ± 30	10 ± 5	2.30 ± 0.02	2.10 ± 0.02
	$\Delta M = 2$	5.5 ± 0.5	20 ± 5	150 ± 10	10 ± 5	2.29 ± 0.01	2.10 ± 0.02
Cu_2TTHA	$\Delta M = 1$	5.5 ± 0.5	60 ± 20	150 ± 20	10 ± 5	2.42 ± 0.03	2.09 ± 0.01
	$\Delta M = 2$	5.5 ± 0.5	25 ± 5	120 ± 30	10 ± 5	2.42 ± 0.02	2.09 ± 0.01
$(CuDGEN)_2$	$\Delta M = 1$	6.0 ± 0.5	60 ± 10	120 ± 30	15 ± 5	2.45 ± 0.03	2.10 ± 0.02
	$\Delta M = 2$	6.0 ± 0.5	15 ± 5	150 ± 20	15 ± 5	2.42 ± 0.03	2.10 ± 0.01

frozen solution. At higher pH the low-field line is not observed and the $\Delta M = 1$ signal is replaced by a species which possesses the highly resolved esr spectra shown by Figure 9. The magnetic parameters obtained from this spectrum are as follows: $g_{\|} = 2.21 \pm 0.01$, $g_{\perp} = 2.08 \pm 0.02$, $A = 180 \pm 20 \times 10^{-4}$ cm^{-1}, $B = 15 \pm 10 \times 10^{-4}$ cm^{-1}.

Discussion

Theory of Esr Spectra Due to Copper(II)–Copper(II) Pairs. The theory relevant to the interpretation of results obtained in this investigation has been described in detail previously.[10] More succinctly it may be stated that the coupling of two copper(II) ions ($S = {}^1/_2$) by a magnetic dipolar interaction brings about a singlet ($S = 0$) and a triplet ($S = 1$) state in which the dipolar interaction causes a separation of the $M_s = 1$ and $M_s = 0$ levels at zero magnetic field. Esr transitions are observed within the triplet. These will be the spin-allowed $\Delta M = 1$ type centered about a resonance position H_0. In addition, the spin-forbidden or $\Delta M = 2$ transitions may be observed. The inclusion of the copper(II) hyperfine interactions cause a breakdown of the pure singlet and triplet character. Perturbation theory allows for the inclusion of weakly allowed transitions between the singlet and triplet states, as well as for the observed copper(II) hyperfine structure on the $\Delta M = 2$ transitions. It is also possible to allow for a small exchange interaction, the effect of which is to separate the singlet and triplet states but insufficient to effect a second-order contribution to the zero field splitting within the triplet state. The appropriate Hamiltonian for a pair of copper(II) ions labeled 1 and 2 has the form

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{ex} + \mathcal{H}_d \quad (1)$$

$\mathcal{H}_1$ and $\mathcal{H}_2$ are assumed to be of the same form

$$\mathcal{H} = g_{\|}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + AS_z I_z + B(S_x I_x + S_y I_y) \quad (2)$$

where β is the Bohr magneton, H is the dc magnetic field, S ($= {}^1/_2$) is the effective electronic spin, I ($= {}^3/_2$) is the nuclear spin, $g_{\|}$ and $g_{\perp}$ are the electronic g factors parallel and perpendicular to the z axis, and A and B are the hyperfine interaction parameters parallel and perpendicular to the z axis. The g factors differ from the free-electron value because of spin–orbit coupling.

Exchange between a pair of paramagnetic ions may be represented as a cosine coupling between the effective spins, S_1 and S_2, and in the simplest case when J_{12} is a scalar

$$\mathcal{H}_{ex} = -JS_1S_2 \quad (3)$$

The interaction between two magnetic dipoles a distance r apart with moment μ_1 and μ_2 is

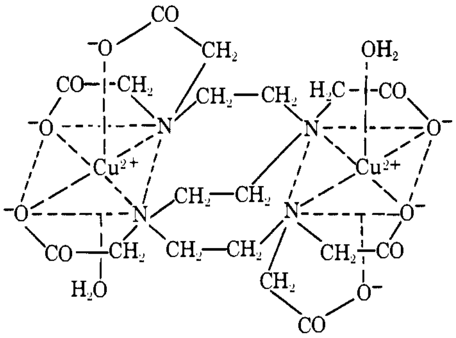
$$\mathcal{H}_d = (1/r^3)[\mu_1\mu_2 - 3(\mu_1 r^0)(\mu_2 r^0)] \quad (4)$$

where r^0 is a unit vector along the line joining the dipoles. The μ's have the form $\beta g S$ where g is the Zeeman g tensor and S the effective spin. The procedure for the simplification of eq 4 has been dealt with previously.[10] Where the interaction between the copper(II) ions is essentially dipolar in character, second-order perturbation theory may be used to solve eq 1 by treating $\mathcal{H}_d$ and the hyperfine tensor as perturbations of the electron Zeeman interaction. The value of J does not influence the validity of the perturbation results but serves to influence the simplicity of the singlet and triplet states. Since the system consists of randomly orientated complexes involving anisotropy, we find the energy levels of the system and hence the esr field positions as a function of the orientation of the complexes with respect to the dc magnetic field. Since the simulated curve cannot be obtained analytically, we divide space into a sufficiently large number of solid angle segments to ensure smoothness in the final curve. The contributing esr transitions, assumed to be Gaussian in shape, are then added by the computer making proper allowance for angular weighting factors and Zeeman anistropy corrections.[10] The resulting theoretical curve is drawn out by the computer line plotter and compared with the experimental esr curves for both $\Delta M = 1$ and $\Delta M = 2$ curves. The parameter of chief interest in these studies is r, the copper(II)–copper(II) separation. Its reliability is assessed by finding the range over which compatible fits are obtained subject to suitable variations of the parameters. Convergence of parameters when both $\Delta M = 1$ and $\Delta M = 2$ curves can be fitted independently is helpful in justifying the simple model assumed. Table I contains the results of the curve-fitting procedure and summarizes the best values of the parameters concerned which give an adequate fit to the observed line shape. The computer programs used to obtain these results were the same as those used in the previous studies.[10–15]

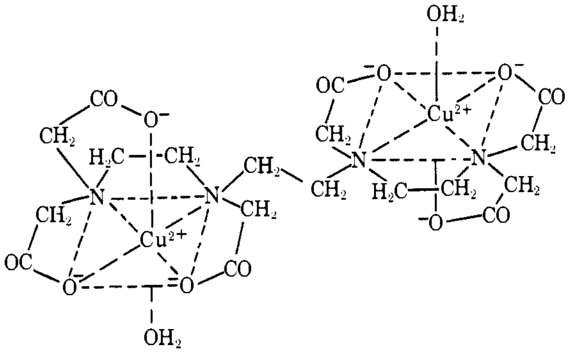
By variation of the magnetic parameters used in the simulation of the spectra, a unique set was obtained for each experimental spectrum. Thus the main spectral features of the experimental result were fitted within ±5 G. The range of values of each magnetic parameter used to achieve the fitting of the experimental curves to within these tolerances is outlined in Table I. The parameters listed in Table I were employed to compute the spectra. The excellent fits thus obtained are seen as points on the spectral curves in Figures 3, 6, and 8 for the binuclear copper(II) complexes of TTHA, DTPA, and DGEN, respectively.

It may be pointed out that the results have been collected over wide ranges of pH for each equilibrium mixture of reagents but that the spectra selected for quantitative treatment correspond to conditions where other physicochemical information indicates that most of the copper(II) is in one particular chelate form. Furthermore, though the results obtained in the $g \cong 2$ region could consist of signals due to the copper(II) present in a variety of forms, the spectrum observed at low field ($\sim$1500 G) is attributable exclusively to dipolar coupling in the binuclear chelate.

The two major structural possibilities presented by the binding sites of TTHA when forming a polynuclear complex are shown by structures Ia and Ib. In structure Ib the terminal groups bind the copper(II) ions and the ligand is in an extended form with free rotation about the center ethylene group. Molecular models indicate that the average copper(II)–copper(II) separation of this type of polynuclear complex would be larger than that found experimentally. Structure Ia on the other hand involves the bonding of each of the two central nitrogens to a Cu(II) ion different from the one bound to the adjacent terminal nitrogen, leading to a closed form of the ligand, the more rigid framework giving rise to a separation of the copper(II) ions which is compatible with the experimentally determined distance.

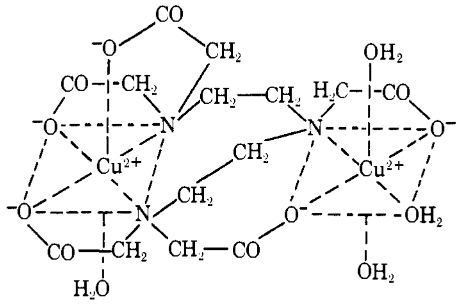


Ia Binuclear Cu-TTHA Chelate, Cu_2L^{2-} (closed form)



Ib Binuclear Cu(II)-TTHA Chelate, Cu_2L^{2-} (open form)

In a similar manner the sharing of the terminal group of DTPA by each copper(II) ion as shown by structure II again places the copper(II) ions at a distance compatible with the experimental result. Here the arrangement suggested indicates that possibly the central nitrogen and carboxyl groups are involved in bonding the copper(II) ions.

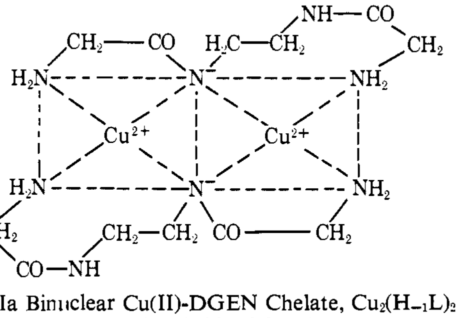


II Binuclear Cu(II)-DTPA Chelate, Cu_2L^-

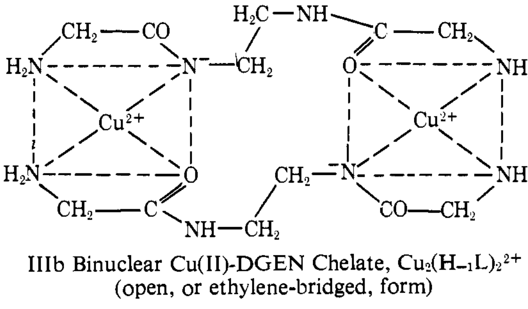
In a similar manner the sharing of the terminal group of DTPA by each copper(II) ion as shown by structure II again places the copper(II) ions at a distance compatible with the experimental result. Here the arrangement suggested indicates that possibly two ethylene bridges and an acetate group are involved in bridging the two copper(II) ions in the binuclear complex. Alternatively, a similar compact structure would be possible in which the metal ions are bound by one ethylene bridge and two acetate groups. In this case esr data allow a decision between these compact arrangements and an open structure analogous to Ib.

Evidence for the formation of dimeric copper(II) DGEN chelates in solution has been presented by Bai and Martell.[7] In the present investigation it has been found that under conditions which would favor dimer formation a signal can be easily observed at room temperature. In the light of previous investigations[10–15] where it was found that dimer formation could be followed by the disappearance of the room temperature signal this would be evidence against the formation of dimers in solution. However, evidence has been obtained here to the effect that a room temperature signal may be observed when two copper(II) ions are present together in a polynuclear chelate such as that formed by DTPA or TTHA. The situation which gives rise to the possibility of observing such spectra is not clear at present. All that can be said at the moment is the observation of the room temperature signal cannot be taken as evidence that dimers are not formed in solution.

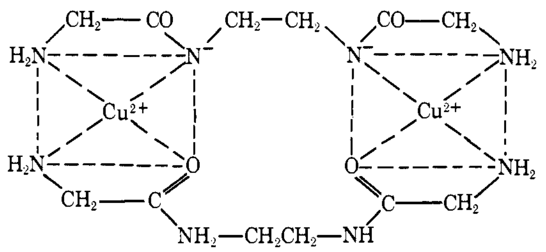
The observation of a $\Delta M = 2$ transition at 77 °K provides unequivocal evidence for the formation of dimers in frozen solution and such has been the case in the copper(II) DGEN system. The structural possibilities offered by DGEN when forming dimeric



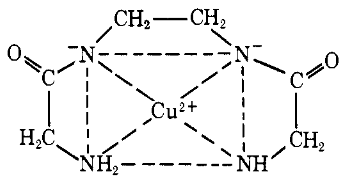
IIIa Binuclear Cu(II)-DGEN Chelate, $Cu_2(H_{-1}L)_2^{2+}$ (N^--bridged form)



IIIb Binuclear Cu(II)-DGEN Chelate, $Cu_2(H_{-1}L)_2^{2+}$ (open, or ethylene-bridged, form) copper(II) chelates has been discussed by Bai and Martell[7] and some of the possibilities are shown by structures IIIa, IIIb, and IIIc. Previously structure IIIa was the preferred possibility, involving bridging of the two copper(II) ions by the strongly binding N^- groups. Since this gives a Cu(II)–Cu(II) distance that is considerably shorter than the experimental distance determined by esr, this arrangement may now be ruled out as a possible structure. Structures IIIb and IIIc on the other hand lead to separations of the copper(II) ions which would be comparable with the experimental distance. The data, of course, do not allow any further distinction to be made but one can speculate that structure IIIb is the stronger proposition since it provides equal distribution of the strongly coordinated negative deprotonated, amidic nitrogens between the two Cu(II) ions, and since the completely deprotonated ligand, $H_{-2}L^{2-}$, indicated in IIIc has been found[7] to form a very stable 1 : 1 chelate, IV, which does not react further with additional ligand.



IIIc Binuclear Cu(II)-DGEN Chelate, $CuL(H_{-2}L)^{2+}$
(open, or ethylene-bridged, form)



IV Cu(II)-DGEN Chelate, $Cu(H_{-2}L)$

Dipolar Shifts and Structure in Aqueous Solutions of 3 : 1 Lanthanide Complexes of 2,6-Dipicolinate[1]

Henry Donato, Jr., and R. Bruce Martin*

Contribution from the Chemistry Department, University of Virginia, Charlottesville, Virginia 22901. *Received October 27, 1971*

Abstract: Tris tridentate chelate complexes of 2,6-dipicolinate (dpa) and tripositive lanthanides yield isotropic proton magnetic resonance shifts that increase upfield for Eu < Yb < Er < Tm and downfield for Sm < Nd < Pr < Ho < Tb < Dy. Shifts in the last half of the lanthanide series are all greater than any of those in the first half. For the last three complexes in each list the para and meta hydrogens are sufficiently shifted so that their resonances appear separately. The pair of meta hydrogens is always shifted more than the para, and for the last half of the lanthanide series, the ratio of chemical shifts is 1.14 ± 0.02. This ratio may be accommodated by an exclusively dipolar origin for the isotropic shift consistent with a proposed structure. The tris tridentate complexes possess D_3 symmetry with the three nitrogen donors in a plane normal to the C_3 axis. Each planar ligand makes an angle of about 49° with the plane containing the three nitrogen donors. The nine donor atoms describe the surface of a prolate ellipsoid of revolution with the long axis the C_3 axis. For the Eu and Pr complexes a small upfield contact contribution is required if the structure and the dipolar shift ratio of 1.14 are to be retained. Excess dpa and other ligands undergo shifts in the opposite directions from the first three more strongly bound dpa ligands.

Most of the numerous applications of lanthanide shift reagents have been made on adducts of neutral complexes in nonaqueous solvents. Despite widespread interest in the use of Eu^{3+}, Pr^{3+}, and other paramagnetic lanthanide complexes as shift reagents in structural analysis, few studies have been conducted on the chemical shifts occurring in more strongly bound ligands. When the extent of complex formation is known more definite statements may be made about the origin of isotropic shifts in the proton magnetic resonance spectrum. In this paper we report chemical shifts experienced by water-soluble tris complexes of the tridentate ligand 2,6-dipicolinate (dpa).

For an investigation of proton magnetic resonance (pmr) spectra of lanthanide complexes in aqueous solutions 2,6-dipicolinate offers the advantages of a chelatable ligand with two meta for each para hydrogen so that pmr peaks for the two kinds of protons are readily identifiable. Formation constants and thermodynamic properties of lanthanide complexes indicate that relatively strong complexes are formed with 3 mol of ligand for one lanthanide.[2] The rigid geometry of the aromatic ligand with two coplanar oxygen donors offers an excellent opportunity for assessing the relative importance of contact and dipolar (pseudocontact) interactions induced by paramagnetic lanthanides. Contact interactions are weak in lanthanide complexes, and dpa should provide a favorable case for their observation if they do occur.

---

(1) This research was supported by a grant from the National Science Foundation.

(2) I. Grenthe, *Acta Chem. Scand.*, **17**, 2487 (1963); *J. Amer. Chem. Soc.*, **83**, 360 (1961).