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ESR STUDIES OF THE Cu(II) COMPLEXES OF N,N'-BIS(PICOLINOYL)-1,3-PROPANEDIAMINE, A PYRIDINE CONTAINING POLYPEPTIDE MODEL LIGAND

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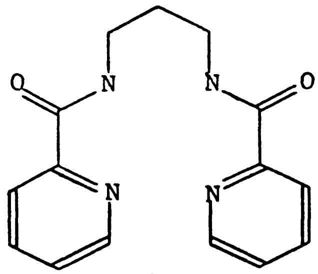
A triplet ESR spectrum (S = 1) was observed for the dimerous N,N'-bis-(picolinoyl)-1,3-prcpanediaminato Cu(II) complex formed in acidic aqueous solution (pH = 3.8). Based on the simple dipole model, internuclear copper-copper atomic distance in the stacked dimerous copper chromophore was estimated to be about 4 Å.

The Cu(II) complexes of N,N'-bis(picolinoyl)-1,3-propanediamine (1) prepared in the alkaline aqueous solution was purely isolated, and have been characterized by visible and IR spectroscopies by H. Ojima.$^{1)}$ In the case of the complex obtained in acidic media, on the other hand, no detailed informations have been obtained. We wish to report the fact that N,N'-bis(picolinoyl)-1,3-propanediaminato Cu(II) (PPDA-Cu(II)) exists as a very stable dimer in the acidic media. In order to sketch a crude structure of the complex, the ESR and IR spectroscopies were applied and the bonding scheme was investigated in the present paper.



(1)

The PPDA-Cu(II) complex revealed the well defined isosbestic point in the pH dependent visible absorption spectra. This justifies that the monomer-dimer equilibrium exists under the different pH conditions (Fig. 1).

The violet complex isolated from neutral or alkaline solutions displays the maximum visible absorption at 570 nm with molar extinction coefficient ε = 96, as was already cited in the previous study.[1] The complex was isolated as a dark blue-violet crystal; the elementary analysis, Found: C, 44.72; H, 5.12; N, 13.96. Calcd for $C_{15}H_{14}N_4O_2Cu\cdot 3H_2O$: C, 45.05; H, 5.04; N, 14.01. The ESR spectrum of the violet complex shown in Fig. 2 can be assigned to that of the mononuclear Cu(II) complex with $d_{x^2-y^2}$ ground state. The relatively large $A_{//}$ value and the observation of the nitrogen superhyperfine splitting ($A_N = 13.6 \times 10^{-4}\ cm^{-1}$) confirmed that the ligand geometry is likely to take the square planar structure.

The dimer complex with the characteristic visible absorption indices (λ_{max} = 680 nm, ε = 60) was isolated as a blue colored crystal. The potentiometric titration concludes that the amide protons are not dissociated under the relatively low pH values (pH = 1.0 ~ 4.5). The elementary analysis of the dimer complex was; Found: C, 31.97; H, 5.49; N, 10.19. Calcd for $C_{30}H_{32}N_8O_{12}S_2Cu_2\cdot 13H_2O$: C, 32.11; H, 5.21; N, 9.99.

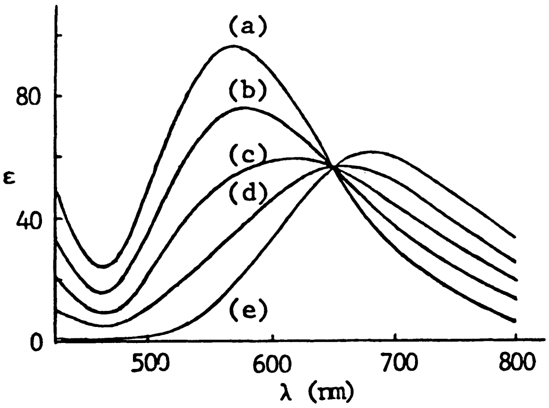


Fig. 1. pH dependence of visible absorption spectra of PPDA-Cu(II).

	(a)	(b)	(c)	(d)	(e)
pH	7.5	4.8	4.7	4.4	3.8

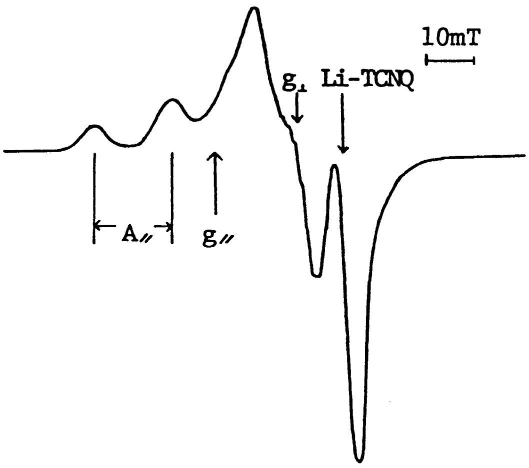


Fig. 2. ESR spectrum of PPDA-Cu(II) in water-ethyleneglycol at 77 K (pH=7.5).

The IR data of the blue and the violet complexes are shown in Table 1. In the blue complex, coordination of carbonyl oxygen to Cu(II) ion is suggested by the IR data;[2,3] both $\nu_{C=O}$ and $\nu_{C=N}$ of the blue complex showed a blue-shift as compared with that of the violet complex in which the deprotonated peptide nitrogens coordinate to the copper atom. We therefore conclude that the doner set of the mononuclear Cu(II) chromophore in the cluster is a type of N_2O_2.

The ESR spectrum of the blue complex in the water-ethyleneglycol rigid matrix at 77 K (pH = 3.8) is shown in Fig. 3. The existence of the binuclear triplet cluster can be confirmed based on the observation of the forbidden ESR transition ($\Delta M_s = \pm 2$) at ca. 150 mT. In the $\Delta M_s = \pm 1$ transition, the seven-line hyperfine

Table 1. IR data of PPDA-Cu(II)

	$\nu_{C=O}$	$\nu_{C=N}$
Violet complex	1620	1330
Blue complex	1630	1350

(cm^{-1})

Table 2. ESR parameters of PPDA-Cu(II)

	$g_{/\!/}$	$g_{\perp}$	$A_{/\!/}^{*}$	$A_{\perp}^{*}$	A_{N}^{*}
Violet complex	2.202	2.058	191	24	13.6
	$g_{/\!/}$	$g_{\perp}$	D^{*}	A_{L}^{*}	A_{H}^{*}
Blue complex	2.259	2.069	446	100	100

(* $\times 10^{-4}$ cm^{-1})

splitting due to the two equivalent copper atoms (I = 3/2) with line intensity ratio 1:2:3:4:3:2:1 can clearly be detected at the wings of the dipolar splitting. The Spin-Hamiltonian for the dimer can be written as;

$$\hat{H} = \beta\hat{S}\tilde{G}H + \tilde{D}\hat{S}_z^2 + \tilde{E}(\hat{S}_x^2 - \hat{S}_y^2)$$

The E term can be neglected, because the difference in the x, y component of the dipolar splitting is the order of ESR line width (see Fig. 3). The copper hyperfine splitting constant measured at the higher field side, A_H, was found to be nearly equal to that measured at the lower field side, A_L. Thus, one may assume that the square planar chromophores bearing the two equivalent copper atoms stacked together as to coincide the G and D tensor axes in the coordination geometry for the dimer.$^{4-6)}$ The A values were nearly equal to the half of the hyperfine splitting constant, which have been known for the Cu(II) complexes with the peptide ligand in the square planar

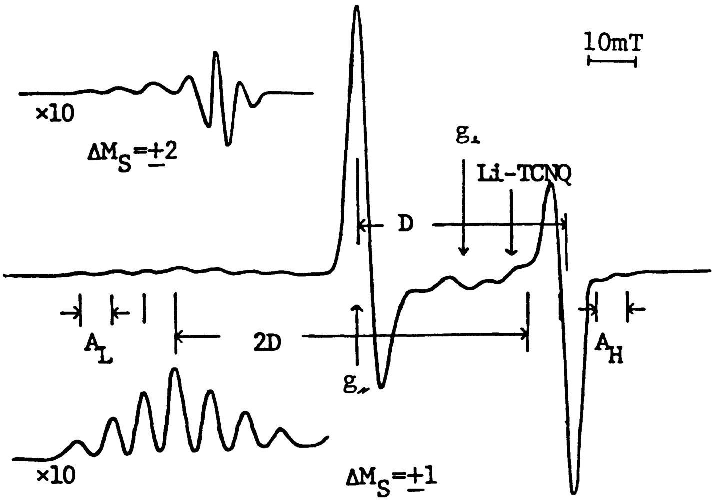


Fig. 3. ESR spectrum of PPDA-Cu(II) in water-ethyleneglycol at 77 K (pH = 3.8).

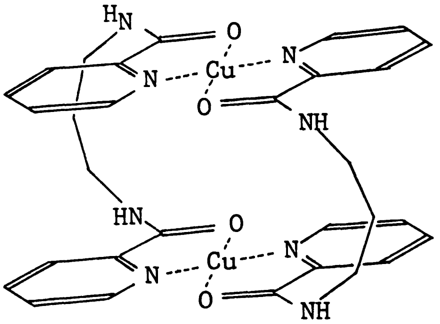


Fig. 4. One of the possible structure of the dimer.

geometry. Therefore, the spin-spin exchange interaction, J, would be larger than ca. 190 × 10^{-4} cm^{-1}. The averaged copper-copper atomic distance, R, in the cluster can be evaluated to be 4 Å using the simple point dipole approximation, written as; $R = (0.65g_{\parallel}^2/D)^{1/3}$.7)

The proposed model of the dimer as illustrated in Fig. 4 gave the excellent accordance with the structure, which has been refined by X-ray analysis.8) The internuclear copper-copper distance measured is 3.7 Å for this stacked dimer in which the two copper atoms are positioned together on the common vertical axes drawn at each paramagnetic center under the tetragonal ligand geometry. One of the interesting features of the X-ray analysis is the fact that each aromatic plane of pyridine forms the coplanar layered array in the cluster, A dominant stability as recognized in the low pH environment may be ascribed to the π-π interactions between the stacking aromatic groups. A detailed analysis of the structure and the more detailed characterization of this dimer complex are now under way.

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