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A PHENOLATE-BRIDGED BINUCLEAR COPPER(II) COMPLEX WITH SQUARE PYRAMIDAL STRUCTURE

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Two molecules of the copper(II) complex chelated with a tripod-like ligand, tris(2-benz[d]imidazolylmethyl)amine are bridged by p-chlorophenolate in acetone to form a binuclear copper(II) complex, in which two copper(II)'s varied from trigonal bipyramidal structure to square pyramidal one, losing anisotropic feature on ESR spectrum and exhibiting lowered magnetic moment of 1.7 B. M. (B. M. = 9.274 x 10^{-24} A m^2)

Although type III coppers in hemocyanin, tyrosinase, and multi-copper oxidases such as ceruloplasmin, laccase, ascorbate oxidase are known to be antiferromagnetically coupled, the inherent bridging group has not been disclosed hithereto. Oxide, hydroxide or phenolate group of a tyrosine residue is now considered to be most probable as the intervening group.[1)] However, the answer to this question seems to await further approach both from copper proteins and various model compounds. We present here an example of an antiferromagnetically coupled binuclear copper(II) complex bridged only by an extra phenolate group.

The starting material used in this study was a copper(II) complex of a tripod-like ligand, tris(2-benz[d]imidazolylmethyl)amine(tba), with an additional water molecule, [Cu(tba)(H_2O)]-(ClO_4)$_2$, which is in the d_{z^2} ground state and bears a trigonal bipyramidal structure in acetone.[2)] Upon gradual addition of sodium p-chlorophenolate(pcp) to an acetone solution of Cu-(tba), the original green solution turned intense green. The absorption spectral change of d-d band region during this process indicated that the trigonal bipyramidal structure of the parent copper(II) complex varied almost stoichiometrically to the square pyramidal structure[3)] at 2 : 1 Cu(tba) : pcp ratio as illustrated in Fig. 1. Charge transfer band between phenolate and copper(II) has not been identified, although absorption intensity in ultra-violet region prominently increased corresponding to the increase of the amount of pcp. Synchro-

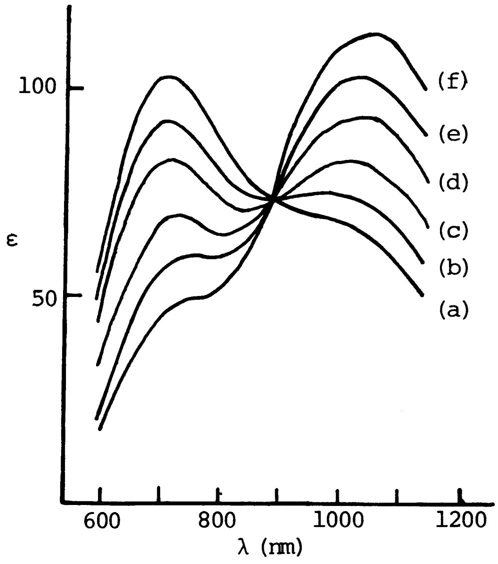


Fig. 1. Electronic spectra of Cu(tba)-pcp system in acetone at ratios of (a) 2 : 1, (b) 2 : 0.8, (c) 2 : 0.6, (d) 2 : 0.4, (e) 2 : 0.2, (f) 2 : 0.

nously, ESR spectra of copper(II) in acetone glass gradually lost its anisotropic feature and exhibited an additional signal due to $\Delta M_s = 2$ transition, indicating that copper(II)'s are interacting with each other(Fig. 2). In line with this, magnetic moment as determined by NMR method$^{4)}$ through measurements of the paramagnetic shift of methyl signal of t-butylalcohol in acetone-d_6 at room temperature was 1.9 and 1.7 B. M. for Cu(tba) and Cu(tba)-pcp complexes, respectively. Isolation of the present ternary complex has not been succeeded yet.

Taking the above experimental results in consideration, the structure as depicted below right is proposed for the binuclear complex, although a half moiety of the binuclear complex might be arranged in the reverse side. The rather strong copper-copper interaction may be realized when the copper(II)'s are in the $d_{x^2-y^2}$ ground state and the phenolate occupies an equatorial position,$^{5)}$ contrary to the case of Calderazzo et al.$^{6)}$ The combination of such ligand groups as aromatic amines and phenolate oxygen in equatorial position may favor the formation of a binuclear copper(II) complex.$^{7)}$ On the other hand, tris(2-aminoethyl)amine(tren) with only aliphatic amines did not afford a corresponding binuclear copper complex.

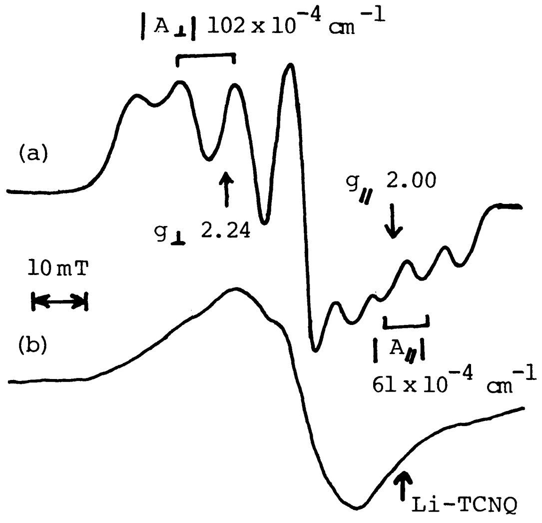
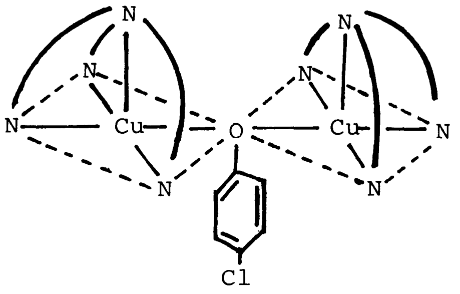


Fig. 2. X-band ESR spectra of (a) Cu(tba) and (b) Cu(tba)-pcp(2 : 1) at 77 K and 9.27 GHz.



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