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FORMATION OF THE IMIDAZOLATE-BRIDGED BINUCLEAR COPPER(II) COMPLEXES IN AQUEOUS SOLUTION AS STUDIED BY ESR

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It has been revealed by ESR spectroscopy that, when imidazole is added to the aqueous solutions of the 1:1 complexes of copper(II) with familiar tridentate ligands or aminocarboxylates by half the molarity of the complexes, imidazolate-bridged binuclear copper(II) complexes are formed almost stoichiometrically at pH $\gtrsim$ 9. Spin exchange interactions in the imidazolate-bridged complexes are sensitively and subtly dependent on environmental and structural factors.

Discrete imidazolate-bridged complexes, especially of copper(II), are of current interest to prepare and characterize,[1-4] primarily because the enzyme bovine erythrocyte superoxide dismutase has a histidine bridged copper(II)-zinc(II) active site.[5] There have been, however, few reports on simple imidazolate-bridged binuclear copper(II) complexes (μ-Im-Cu_2 complexes) in aqueous solutions. Here we show new aspects on the complex formation and properties of them by ESR spectroscopy.

The 1:1 complexes of copper(II) with *N*-glycylglycine (GG), *N*-(2-aminoethyl)-1,2-ethanediamine (Dien), and related ligands in frozen aqueous solutions show monomer ESR spectra of a so-called "tetragonal" pattern (for example, Fig. 1A). In the cases of GG and Dien, on addition of imidazole by half the molarity of the complexes to their solutions at pH $\gtrsim$9, ESR spectra drastically change into single broad absorptions superimposed by slightly remaining monomer spectra (Fig. 1B). The intensities of the remaining monomer ESR spectra are always minimized at the concentration ratio of imidazole to the copper(II) complexes of 0.5:1.0. At these spectral changes around 0.3 T (1 T = 10^4 Gauss), half-field signals around 0.15 T are too weak to be observed, despite the fact that half-field signals are characteristic of ordinary dimeric copper(II) complexes. Very weak half-field signals, however, have been found to appear even in these cases by any one of the following changes of systems: the addition of

methanol or ethanol by more than half the volume to the aqueous solutions, the substitution of *N'*-[2-(dimethylamino)ethyl]-*N'*,*N'*-dimethyl-1,2-ethanediamine (Me_4Dien) for Dien, and the addition of imidazole to the aqueous solution of a 1:1 mixture of the copper(II) complex of GG and that of Dien. We have also found that several 1:1 complexes of copper(II) with aminocarboxylates, such as *N*,*N'*-1,2-ethanediylbis-glycinate (EDDA), *N*,*N*-bis(carboxymethyl)-glycinate (NTA), *N*-(carboxymethyl)-*N*-(2-hydroxyethyl)-glycinate, *N*-[2-[(carboxymethyl)amino]ethyl]-*N*-(2-hydroxyethyl)-glycinate, and related ligands, form μ-Im-Cu_2 complexes in a similar manner as above, as exemplified by two of the μ-Im-Cu_2 complexes in Fig. 1 C–G. Half-field signals for these complexes are easily observable, in contrast to the complexes of GG and Dien. All the above results obviously indicate that similar dimeric or binuclear copper(II) complexes are formed at high concentrations in all the solutions.

An analysis of the above ESR results was attempted by the computer simulation method developed for the system of parallel planar copper(II) dimers.[6] The simulation is based on the spin Hamiltonian $H = \beta S \cdot g \cdot H - JS_1 \cdot S_2 + S \cdot A \cdot I + H_{dd} + H_{pd}$. The last two terms belong to the zero-field splitting term. H_{dd} has an usual expression of electron spin dipole-dipole interaction, which contains two structural parameters, r and ξ, where r is the Cu-Cu distance and ξ, the angle between the Cu-Cu direction and the normal to the molecular plane. On the other hand, H_{pd} is a J-dependent term called the pseudo-dipolar one, which was here taken into consideration as a generalized expression of $DS_z^2 + E(S_x^2 - S_y^2)$.[7] It has been generally accepted that H_{pd} has no remarkable effects on dimer ESR line shapes, if $|J| < 20$ cm^{-1}. The r values of some μ-Im-Cu_2 complexes in crystals are known to be $\sim$6.0 Å, while $\xi \simeq 90°$ is always true. The simulated spectra based on the parameters of r = 6.0 Å, ξ = 90°, and zero or very small D and E values show broad featureless line shapes around 0.3 T, which are in good agreement with the observed ones (for example, Fig. 1B').

The spectral intensity for forbidden $\Delta M = 2$ transitions is theoretically expected to be proportional to the zero-field splitting parameter squared, indicating that the intensity increases rapidly with increasing D and E values and with decreasing r value. For example, in the case of negligibly small D and E values ($|J| < 20$ cm^{-1}), half-field spectral intensities for the dimers of r = 6.0 Å are reduced to less than one-tenth those for ordinary dimers which mostly have $r \lesssim 4.0$ Å. This may be the reason for which some systems in this work show extremely weak half-field spectra. On the other hand, non-negligible D and E values resulting from $|J| > 20$ cm^{-1} will give rise to more intense half-field spectra. This is evidenced by the following fact: The μ-Im-Cu_2

complex of EDDA shows a fairly intense half-field spectrum (Fig. 1E), while this complex has a large spin exchange interaction of J = -(38 ± 3) cm^{-1}, which was determined as previously[6b,6c,8] from the temperature variation of the half-field spectral intensity. Interestingly, this J value is comparable to those for the μ-Im-Cu_2 complexes of GG and Me_4Dien in crystals (-38 and -52 cm^{-1}, respectively). From all these results, it may be concluded that the spin exchange interaction propagated by the

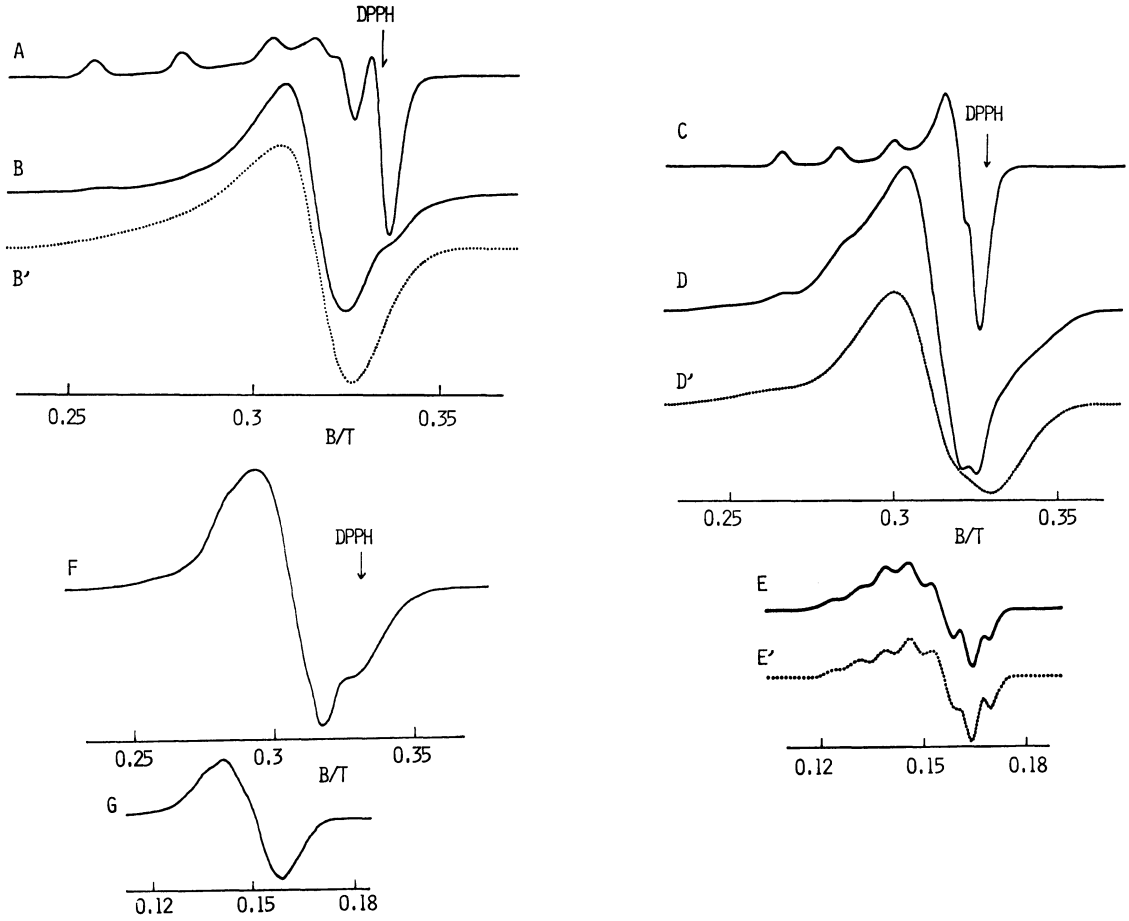

Fig. 1 ESR spectra of frozen aqueous solutions of (A) Cu-Dien, (B) Cu-Dien + 0.5 Imidazole, (C) Cu-EDDA, (D,E) Cu-EDDA + 0.5 Imidazole, and (F,G) Cu-NTA + 0.5 Imidazole at 77 K (pH 10.0, borate buffer; [Cu] = 10 mM; [$NaNO_3$] = 0.3 M). The curves of B', D', and E' show simulation spectra; (B'), calculated with the parameters of r = 6.0 Å, ξ = 90°, D = E = 0 cm^{-1}, $g_{\parallel}$ = 2.230, $g_{\perp}$ = 2.055, $A_{\parallel}$ = 0.0085 cm^{-1}, $A_{\perp}$ = 0.001 cm^{-1}, and ΔH_1 = 5.0 mT; (D',E'), calculated with the parameters of r = 6.0 Å, ξ = 90°, D = 0.02 cm^{-1}, E = 0.015 cm^{-1}, $g_{\parallel}$ = 2.285, $g_{\perp}$ = 2.07, $A_{\parallel}$ = 0.008 cm^{-1}, $A_{\perp}$ = 0.001 cm^{-1}, ΔH_1 = 7.5 mT, and ΔH_2 = 2.5 mT (ΔH_1 and ΔH_2 express the line widths of ΔM = 1 and 2 spectra, respectively; 1 T = 10^4 Gauss).

imidazolate-bridge is sensitively and subtly dependent on environmental and structural factors. Fig. 1E shows the most well-resolved half-field spectrum in this work. This spectrum, together with its $\Delta M = 1$ spectrum, is satisfactorily simulated with the parameters of $r = 6.0$ Å, $\xi = 90°$, and J-dependently reasonable D and E values.

The formation of μ-Im-Cu_2 complexes is expressed as the following equation (with charge omitted; L = arbitrary ligand and Im = imidazole or imidazolate (imidazolyl)): 2 CuL + Im $\rightleftharpoons$ $(CuL)_2Im$. The formation constant (K) at ∿0°C can be roughly estimated by comparison between the real integrated spectral intensities of monomer and dimer species around 0.3 T. The K values thus determined at the same condition as written in Fig. 1 were as unexpectedly large as 10^7–10^8 for most cases in this work. This result is suggestive in considering the chemical and biological importance of imidazole.

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