

Close Cu(II)-Methyl Contact in Planar Complexes with a Pendent Alkyl Group. Implication for the Leucine Residue at the Cu Site

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Noncoordinating amino acid side chains surrounding protein metal sites and cofactors have functions such as substrate binding, stabilization of intermediates, and electron transfer. Type I copper sites in proteins exhibit differences in the coordination structure, and the axial ligand is known to be an important factor for the redox properties. The type I copper site of fungal laccase with a high redox potential has an adjacent leucine side chain in place of an axial ligand, which suggest that its alkyl group may have some influence on the properties of the Cu center. We have been studying weak interactions of side chain aromatic rings of Cu(II)-coordinated aromatic amino acids and adduct formation between Pt(II)-aromatic ligand complexes and AMP, GMP, etc. and observed that aromatic ring stacking interactions affect the electron density of the Pt(II) center as seen from the ^{195}Pt NMR. With these points in mind, we now studied the syntheses and structures of the Cu(II) complexes of 3N-donor ligands, L (= *N*-alkyl derivatives of bis(2-pyridylmethyl)amine), and their spectral and redox properties.

The complexes, $[\text{CuCIL}]^+$, with an alkyl side chain such as ethyl, propyl, and isobutyl groups were disclosed to have a planar structure with a 3N1Cl donor set. While the pendent ethyl and propyl groups in the complexes were found to be extended from the coordination plane, branched alkyl groups were located close above the Cu atom with a distance of 3.0-3.2 Å, and no disorder was found in the X-ray analysis. The complexes exhibited an absorption maximum at around 660 nm, indicating the same coordination structure for all the complexes in solution. The corresponding Pd(II) complexes have the structures very similar to those of the Cu(II) complexes, and the ^1H NMR spectra showed a larger downfield shift of the methyl proton signals for the complexes with a close $\text{CH}_3\text{-Pd(II)}$ contact than those without it. The redox potentials of the Cu(II) complexes with a short $\text{CH}_3\text{-Cu(II)}$ distance were found to be higher than those for the complexes without such a contact by 30-100 mV in CH_3CN .

These observations may suggest the possibility that the proximal branched alkyl group is in contact with the metal center and affects its redox properties.