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A Facile Reduction of Copper(II) Leading to Formation of Stable Copper(I) Complexes. Redox Properties of Four- and Five-coordinate Copper Complexes

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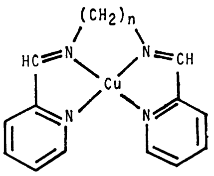
Schiff bases derived from 2-pyridinecarbaldehyde and 1,6-hexanediamine or bis(2-aminoethyl) disulfide gave stable Cu(I) complexes instead of Cu(II) complexes by reactions with copper(II) perchlorate. The facile reduction of copper(II) has been discussed on the basis of systematic comparisons of redox and ESR properties of about 20 complexes of similar structures.

In the course of our study on biological coppers[1)] and model compounds,[2–4)] we found that some Schiff base ligands derived from 2-pyridinecarbaldehyde (pca) and 1,6-hexanediamine (heda) or bis(2-aminoethyl) disulfide (baed) afford stable copper(I) complexes in spite of the use of divalent copper as starting material. We have systematically investigated redox and ESR properties of some four- and five-coordinate copper complexes in order to shed light on this novel phenomenon. Diamines employed in this study to derive Schiff bases with pca were as follows: heda, 1,5-pentanediamine (peda), 1,4-butanediamine (buda), 1,3-propanediamine (prda), 1,2-ethanediamine (etda), baed, bis(2-aminoethyl) sulfide (baes), 2-aminoethyl 3-aminopropyl sulfide (aeps), *N*-(2-aminoethyl)-1,3-propanediamine (aepd), *N*-(2-aminoethyl)-1,2-ethanediamine (aeed), and bis(2-aminoethyl) ether (baee).



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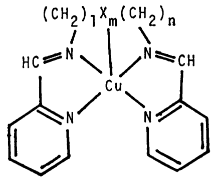
n=5: Cu(pca=peda=pca)
n=4: Cu(pca=buda=pca)
n=3: Cu(pca=prda=pca)



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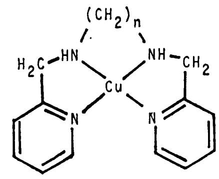
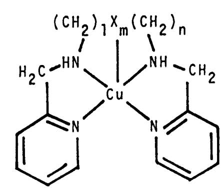
X=S, l=2, m=1, n=3: Cu(pca=aeps=pca)
X=N, l=2, m=1, n=2: Cu(pca=aeed=pca)
X=N, l=2, m=1, n=3: Cu(pca=aepd=pca)
X=O, l=2, m=1, n=2: Cu(pca=baee=pca)



n=6: Cu(pca-heda-pca)
n=5: Cu(pca-peda-pca)
n=4: Cu(pca-buda-pca)
n=3: Cu(pca-prda-pca)
n=2: Cu(pca-etda-pca)



X=S, l=2, m=2, n=2: Cu(pca-baed-pca)
X=S, l=2, m=1, n=2: Cu(pca-baes-pca)
X=S, l=2, m=1, n=3: Cu(pca-aeps-pca)
X=N, l=2, m=1, n=2: Cu(pca-aeed-pca)
X=N, l=2, m=1, n=3: Cu(pca-aepd-pca)

Experimental

Materials. Copper(II) perchlorate hexahydrate, heda, peda, buda, prda, etda, and aeed were purchased from Nakarai Chemicals Ltd., and baed, aeps, and baee from Aldrich. Diamines with single thio group, baes and aeps, were prepared according to literatures.[3,5)] All other reagents used were of the highest grade commercially available.

Preparation of Complexes. *$\mathrm{Cu^I}$(pca=heda=pca)*:** To a 80 ml of neutral or basic aqueous ethanol (1 : 1 by volume) solution of heda (1.16 g) was added twice as much amount of pca (2.14 g) to give 2 : 1 pca: heda Schiff base, and was treated with 3.71 g of $\mathrm{Cu(ClO_4)_2 \cdot 6H_2O}$. A brown complex precipitated very soon. On account of its poor solubility in most solvents, the precipitate was washed by aqueous ethanol instead of being recrystallized. Found: C, 46.57; H, 4.79; N, 12.39; Cu, 13.1%. Calcd for $\mathrm{C_{18}H_{22}N_4Cu(ClO_4) \cdot H_2O}$: C, 46.25; H, 5.18; N, 11.99; Cu, 13.6%.

$\mathrm{Cu^I}$(pca=baed=pca). This brown complex was prepared by the same method as that in $\mathrm{Cu^I}$(pca=heda=pca). Found: C, 36.39; H, 3.55; N, 10.45; Cu, 11.5%. Calcd for $\mathrm{C_{16}H_{18}N_4S_2Cu(ClO_4) \cdot 2H_2O}$: C, 36.29; H, 4.19; N, 10.58; Cu, 12.0%.

The other parent copper(II) complexes were prepared according to the methods in previous papers[3,6,7)] as diperchlorate except Cu(pca=prda=pca), Cu(pca=baee=pca), Cu(pca–prda–pca) and Cu(pca–heda–pca) which were monochloride monoperchlorate. All these compounds were identified based on elemental analyses and IR spectra.

Measurements. Cyclic voltammetry was performed at 25 °C with a three electrode system consisting of platinum working and auxiliary electrodes and a standard calomel electrode. Voltammograms were generated using a Yanagimoto P-1000 voltammetric analyzer and an NF FG-121G function generator and recorded on a National VP-6421 X-Y recorder for *N,N*-dimethylformamide (DMF) solutions of complexes (*ca.* $5 \times 10^{-3}\,\mathrm{mol \cdot dm^{-3}}$, $I=0.1$ (tetrabutylammonium perchlorate)). E° values were determined as the midpoints between the peak potentials. Absorption spectra were recorded in 1 cm- or 1 mm-path length quartz cell in the range 270—700 nm with a Hitachi 323 spectrophotometer at room temperature. Electron spin resonance spectra of copper(II) complexes were obtained using a JEOL JES-FE1X instrument at 77 K. Infrared spectra were measured using a Hitachi 260-10 grating infrared spectrophotometer by KBr disk method. Copper contents of complexes were determined by a Nippon Jarrell-Ash AA-1 atomic absorption spectrometer. DMF was used as solvent throughout measurements unless otherwise specified. The magnetic susceptibility was determined at room temperature by using a Gouy magnetic apparatus.

** The notation "pca=heda=pca" represents hereafter the 2 : 1 Schiff base derived from pca and heda, and "pca–heda–pca" the aorresponding reduced ligand.

Results and Discussion

Brown copper(I) complex, Cu^{I}(pca=heda=pca), unexpectedly precipitated immediately after addition of Cu(ClO$_4$)$_2$ to pca=heda=pca in aqueous ethanol, instead of producing green Cu^{II}(pca=heda=pca). Reduction of copper(II) to copper(I) was substantiated not only by elemental analysis but also by ESR and absorption spectroscopy. Copper(II) content was several percent, which was determined by double integration of ESR signals using Cu(imidazole)$_4$ as standard. Addition of H_2O_2 or permission to stand Cu^{I}(pca=heda=pca) in H_2O–DMF for several days presented full copper(II) ESR signal (Fig. 1), and the solution turned green.

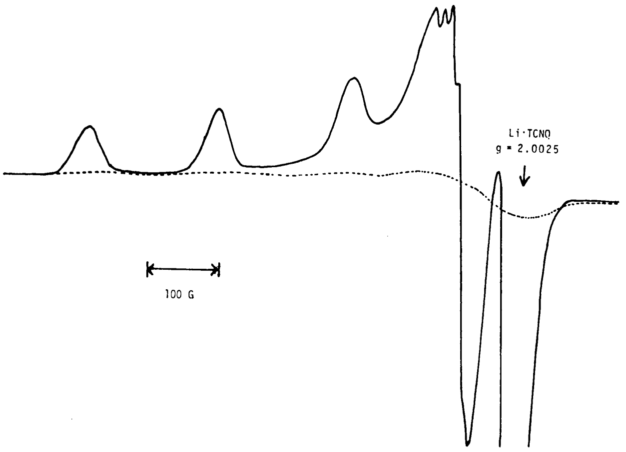


Fig. 1. ESR spectra of isolated Cu(pca=heda=pca) (------) and H_2O_2-treated Cu(pca=heda=pca) (——).

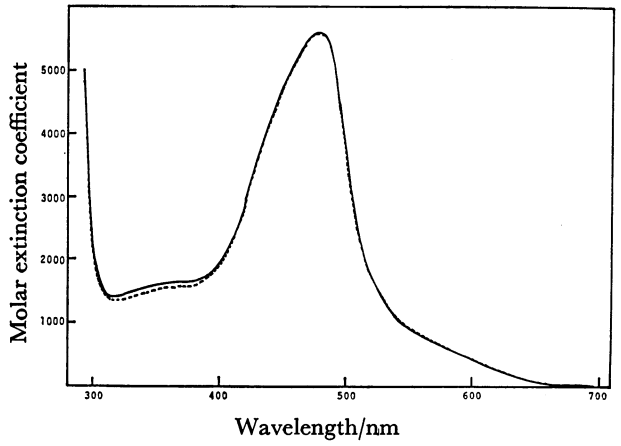


Fig. 2. Absorption spectra of authentic (——) and isolated (------) Cu(pca=heda=pca).

An authentic copper(I) complex solution prepared by using Cu^{I}(CH$_3$CN)$_4$(ClO$_4$) as copper(I) source afforded a quite similar absorption spectrum as that of the isolated Cu(pca=heda=pca) (Fig. 2), exhibiting an intense MLCT band at 478 nm. Magnetic moment per copper atom was calculated from susceptibility to be 0.62 BM (1 BM=9.274×10^{-24} A m^2) at room temperature, indicating that paramagnetic copper(II) was really a trivial contaminant. The present quite rapid reduction of copper, which occurs much readily in alkaline medium than in neutral aq ethanol, might be accompanied by generation of 2-pyridinecarboxylic acid from free 2-pyridinecarbaldehyde in the system. In fact, thin layer chromatography on silica gel plate has suggested the formation of 2-pyridinecarboxylic acid in the brown reaction mixture. A green copper(II) complex which was precipitated in acidic solution also gradually turned brown in DMF. Copper does not seem to be reduced by a concomitant oxidation of the coordinated ligand, since the IR spectrum of brown Cu^{I}(pca=heda=pca) is similar to green intact copper(II) complexes providing with various lengths of methylene chain.

In line with this, the quite similar reduction of copper(II) ligated by pca=baed=pca has been observed. However, pure Cu(I) complex has not been isolated: Cu(II) content determined by ESR spectrum was 35% and magnetic moment of this complex was evaluated as 1.55 BM at room temperature. The extremely delicate difference in stabilizing Cu(I) complex of the present kind might be interpreted on the basis of the greater size of sulfur over a methylene group. The dithio group would not bind copper, or if any, the interaction of the dithio group with copper will be rather weak. These examples suggest that the facile reduction of Cu(II) to Cu(I) may occur when providing the ligand with methylene chain of appropriate length. In the case of the present series of complexes, diamines having six methylene groups or equivalent length as half moiety of Schiff base are considered to best suit the condition.

In order to understand this phenomenon, redox potentials of copper have been compared for about 20 copper complexes. E° values and ESR parameters to exhibit properties of parent copper(II) complexes are

Table 1. Redox potentials and ESR parameters of copper complexes

Complex	ESR parameters			
	$E^\circ vs.$SCE / V	$g_{//}$	$g_{\perp}$	$-A_{//}\times10^4$ / cm^{-1}
Cu(pca=heda=pca)	+0.13	2.27	2.07	16.5
Cu(pca=peda=pca)	+0.00	2.24	2.07	14.0
Cu(pca=buda=pca)	−0.10	2.22	2.06	15.0
Cu(pca=prda=pca)	−0.08	2.24	2.06	18.4
Cu(pca=baed=pca)	+0.06	2.29	2.05	16.4
Cu(pca=baes=pca)	+0.00	2.27	2.06	16.9
Cu(pca=aeps=pca)	+0.12	2.17	2.08	17.1
Cu(pca=aepd=pca)	−0.16	2.21	2.06	17.8
Cu(pca=aeed=pca)	−0.14	2.22	2.06	18.5
Cu(pca=baee=pca)	−0.02	2.24	2.06	15.4
Cu(pca–heda–pca)	−0.19	2.22	2.06	17.3
Cu(pca–peda–pca)	−0.13	2.23	2.06	14.8
Cu(pca–buda–pca)	−0.25	2.22	2.06	15.5
Cu(pca–prda–pca)	−0.33	2.22	2.05	19.1
Cu(pca–etda–pca)	−0.33	2.23	2.04	17.7
Cu(pca–baed–pca)	−0.25	2.27	2.07	18.2
Cu(pca–baes–pca)	−0.19	2.21	2.06	16.7
Cu(pca–aeps–pca)	+0.01	2.20	2.06	17.0
Cu(pca–aepd–pca)	−0.52	2.20	2.06	18.1
Cu(pca–aeed–pca)	−0.43	2.21	2.06	18.3

tabulated in Table 1. For Cu(pca=heda=pca) and Cu(pca=baed=pca) copper(I) complexes were used for determining E° values since pure green Cu(II) complexes have not been isolated. As clearly seen from Table 1, Cu(pca=heda=pca) and Cu(pca=baed=pca) exhibited higher redox potentials over zero volt. In contrast to this, the analogues with shorter methylene chain lengths exhibited lower E° values. This implies that the former two bear the favorable chain length adaptable to tetrahedral coordination around Cu(I). In addition, the present copper(II) complexes display a trend toward tetrahedral distortion, as visualized in $g_{//}$—$A_{//}$ profile for $Cu(N)_4$-type complexes as described by Peisach and Blumberg.[8)]

The single thio group-containing five coordinate Schiff base complexes also exhibited higher redox potentials. These complexes, Cu(pca=baes=pca) and Cu(pca=aeps=pca) also tend to be reduced spontaneously in DMF, although Cu(I) complexes have not yet been isolated. Other five coordinate Schiff base complexes devoid of thio group display lower E° values and favor a copper(II) state. The reduction of Schiff bases prominently lowered E° values (0.2—0.3 V), hence the stabilization of copper(I) state cannot be realized even by pca–heda–pca and pca–baed–pca. Thus it can be considered that the aliphatic amine is not necessarily favorable for stabilizing the copper(I) state.

The present unexpected reduction of copper(II) and stabilization of Cu(I) in the presence of air is anticipated to afford a clue to appreciate the nature of biological coppers and to design model compounds.

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