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Spectral and Redox Behavior of some Copper(II) Complexes with Tetradentate Bis(pyridyl)–dithioether Ligands

D. E. NIKLES, M. J. POWERS and F. L. URBACH

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.

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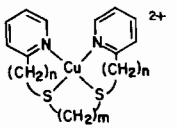
Suggestions that the active site in certain 'blue' copper proteins contains at least one sulfur ligand [1–6], followed by the recent X-ray crystal structures of plastocyanin [7a] and azurin [7b] showing copper ion coordinated to both cysteine mercaptide sulfur and methionine thioether sulfur as well as two histidine imidazole donors, have greatly increased interest in sulfur containing copper complexes. Two striking properties of 'blue' copper proteins are an intense absorption band [4, 8–10] near 600 nm (ϵ = 1200–5700 M^{-1} cm^{-1}) and relatively high Cu(II)/Cu(I) reduction potentials [8–11] ($E^{0'}$ = +184 to +767 mV). Most interpretations of the 600 nm band [4, 5] focus on the interaction between the copper ion and the cysteine mercaptide donor and assign the absorption to Cu(II) ← S(σ) ligand to metal charge transfer (LMCT). Recent reports that intense absorptions near 600 nm also occur in copper(II) complexes with macrocyclic polythioether ligands [12] and with one example of a bis(pyridyl)–dithioether tetradentate ligand [13], coupled with the finding of thioether coordination in plastocyanin [7a] and azurin [7b], demonstrate the need for systematic studies of copper–thioether complexes. Only a few studies [12–15] are reported and the origin of the enhanced visible absorption band is variously assigned. In the cyclic polythioether complexes this band is attributed [12–16] to a ligand field transition with intensity borrowing from charge-transfer bands at higher energy, or an admixture of some Cu(II) ← S (π) LMCT character causing an increased intensity [13, 15].

We report here a preliminary comparison of the spectral and electrochemical properties of the copper complexes with two series of tetradentate ligands, *Ia–d* and *IIa–d*, in which two thioether donors are substituted for two amine donors such that the effect of the thioether donors may be evaluated. The central position of the thioether donors in the chelating ligands ensures their binding to the copper ion and the variation in chelate ring size provides some insight into the effect of stereochemistry on the spectral and redox properties. The thioether-containing ligands, 1,6-bis(2′-pyridyl)-2,5-dithiahexane (*Ia*), 1,7-bis(2′-pyridyl)-2,6-dithiaheptane (*Ib*), 1,8-bis(2′-pyridyl)-3,6-dithiaoctane (*Ic*), and 1,9-bis(2′-pyridyl)-3,7-dithianonane (*Id*), were prepared by minor modifications of literature methods [17, 18] and were characterized by IR and NMR spectroscopy. The N_4 ligands 1,6-bis(2′-pyridyl)-2,5-diazahexane (*IIa*) and 1,7-bis-(2′-pyridyl)-2,6-diazaheptane (*IIb*) were also prepared by literature methods [18]. Ligands *IIc*, 1,8-bis(2′-pyridyl)-3,6-dimethyl-3,6-diazaoctane, and *IId*, 1,9-bis(2′-pyridyl)-3,7-dimethyl-3,7-diazanonane, were prepared by the reaction of N,N′-dimethylethylenediamine or N,N′-dimethyl-1,3-propane-diamine with 2-vinylpyridine. All of the ligands yielded Cu(II) complexes as crystalline perchlorate salts except *Id* which upon reaction with Cu(II) produced a dark green oil which slowly converted to a white Cu(I) complex of *Id*. Cuprous complexes with the stoichiometry $[Cu^{I}L]ClO_4$ were isolated as air-stable white solids with *Ia–d* by mixing equimolar amounts of $[Cu^{I}(CH_3CN)_4]ClO_4$ and the appropriate ligand in ethanol under nitrogen, or by reaction of the Cu(II) complexes with sodium ascorbate in aqueous solution.



$Cu(py_2S_2)(ClO_4)_2$

Ia n = 1, m = 2 5–5–5
Ib n = 1, m = 3 5–6–5
Ic n = 2, m = 2 6–5–6
Id n = 2, m = 3 6–6–6*

$Cu(py_2N_2)(ClO_4)_2$

IIa n = 1, m = 2 5–5–5
R = H

IIb n = 1, m = 3 5–6–5
R = H

IIc n = 2, m = 2 6–5–6
R = CH_3†

IId n = 2, m = 3 6–6–6
R = CH_3

*Isolated as $[Cu^{I}L]ClO_4 \cdot \frac{1}{2}CH_3CN$.
†Isolated as monohydrate.

The absorption spectra for the Cu(II)py_2S_2 complexes in acetonitrile (Table I) consist of three major regions: (a) a weak system of bands near 600 nm (with an additional low energy band for the Cu(II) complex of *Ia*); (b) a medium intensity band occurring between 340 and 380 nm; and (c) an intense absorption envelope near 260 nm showing little variation in absorptivity throughout the series. The Cu(II)-py_2N_2 complexes (Table I) exhibit similar band patterns near 600 and 260 nm but no absorption bands are present in the 340–380 nm region. Diffuse transmittance spectra for all of the complexes exhibit only slight differences compared to the solution spectra, suggesting there is little change in the copper coordination sphere upon dissolution in acetonitrile. Essentially the same spectra are observed in water and methanol solutions, but with significantly lower values of ϵ. The Cu(II) complex of *Ia* shows some

TABLE I. Spectral[a] and Electrochemical Behavior[b] of the Copper(II) Chelates.

Compound	Chelate Ring Size	$E^{0'}$ (mV *vs.* NHE)	ΔEp (mV)	λ_{max} (ϵ, cm^{-1} M^{-1})
$Cupy_2S_2$				
Ia	5–5–5	+709	99	925(165), 610(185), 344(2300), 263(12200)
Ib	5–6–5	+749	110	670(342), 360(3430), 263(11100)
Ic	6–5–6	+844	130	595(902), 360(5560), 270(sh),260(11300)
Id	6–6–6	+894	120	610(453), 380(5020), 263(13900)
$Cupy_2N_2$				
IIa	5–5–5	+104	100	599(182), 256(12500)
IIb	5–6–5	+30	150	596(145), 255(13500)
IIc	6–5–6	+311	207	628(277), 282(sh), 262(12000)
IId	6–6–6	+574	140	653(285), 291(sh), 264(11700)

[a]Measured in acetonitrile solution. [b]Measured in 0.1 *M* TEAP acetonitrile solution by cyclic voltammetry at a Pt or a wax impregnated graphite (WIG) electrode. All of these complexes gave $n = 1$ for controlled potential reductions at a Pt-gauze electrode.

solvent dependent changes in λ_{max} and is proposed to have a five-coordinate structure [15, 19, 20]. Extinction coefficients were found to be slightly concentration dependent, as observed by others [13], and are reported for solutions in the 0.5–1.0 m*M* range.

From a comparison of the spectra of the $Cu(II)py_2S_2$ complexes with that of the exact analog in the $Cu(II)py_2N_2$ series, some conclusions about the transition assignments can be made. The visible bands for both series occur at comparable energies and we conclude that their origin is in d → d transitions. A modest intensity enhancement is observed in the visible bands for the Cu(II) complexes with the three larger py_2S_2 ligands (*Ib–d*) but this increased absorption is not sufficient to claim that a single thioether donor would make a significant contribution to the 'blue' copper chromophore. A portion of the intensity increase can be attributed to a reduction in symmetry for the larger chelate ring sizes since the py_2N_2 series also exhibits increased ϵ values for complexes of *IIc* and *IId*. The remaining enhancement of the visible band in the py_2S_2 series probably arises from 'intensity-borrowing' from the ~ 350 nm band [21–23]. In support of this conclusion the intensity of the ~ 600 nm band in complexes *Ia–d* parallels the intensity of the ~ 350 nm band. The ~ 350 nm band observed in the $Cu(II)py_2S_2$ series is clearly absent in the $Cu(II)py_2N_2$ complexes and we concur with previous assignments [13] as a Cu(II) ← S(σ) LMCT. The energy of this transition roughly parallels the redox potential for the Cu(II)/Cu(I) couple as expected for a LMCT transition. The intense absorptions centered close to 265 nm arise from $\pi \rightarrow \pi^*$ transitions within the pyridine rings and from Cu(II) ← N LMCT transitions.

The electrochemical data (Table I) illustrate the dramatic increase in the redox potential for the Cu(II)/Cu(I) couple which is achieved by the substitution of thioether donors for amine donors. The values of $E^{0'}$ for the $Cupy_2S_2$ series are among the highest reported for the Cu(II)/Cu(I) couple [24, 25]. Other examples of high redox potential copper complexes are known with thioether-containing ligands, and with substituted 1,10-phenanthroline and 2,2′-bipyridine ligands [24, 25]. Although the peak separation, $\Delta Ep = E_a - E_c$, measured for the complexes by cyclic voltammetry is larger than the 58 mV value expected for a reversible one-electron process [26], controlled potential electrolyses on both the Cu(I)and Cu(II) species gave n values close to unity and generated the oxidized or reduced forms quantitatively as shown by spectroscopy. The redox potentials for both the $Cupy_2S_2$ and $Cupy_2N_2$ complexes are strongly solvent dependent and lower values of $E^{0'}$ are observed in DMSO or water. Peak separation and $E^{0'}$ values were also affected by the history of the electrode and a thorough cleaning routine was employed after each potential scan.

With the exception of the copper complex of *IIb*, the observed redox potentials increase monotonically as a function of increasing chelate ring size within each series. This trend probably reflects the ease with which the larger ligands can stabilize the Cu(I) form by adopting a pseudotetrahedral geometry. Recent crystal structures [27] reveal a change from square pyramidal (with coordinated perchlorate) to pseudotetrahedral geometry upon the reduction of the Cu(II) complex of *Ic* to the corresponding Cu(I) species. It is likely that this stereochemical change accounts for the non-reversible character of the electron transfer process observed in the present series of tetradentate copper complexes.

From these studies we conclude that the Cu(II) thioether chromophore does not contribute a major portion of the intensity of the 600 nm band in 'blue' copper proteins. Thioether coordination does produce

high Cu(II)/Cu(I) redox potentials and this is probably the main function of this donor atom in the 'blue' copper site. In support of this idea stellacyanin, which contains no methionine residues [28], exhibits the lowest redox potential of the 'blue' copper proteins [8].

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