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Influence of Coordination Number on Copper(I)-Copper(II) Redox Interconversions. 2.[1] $Fe(CN)_6^{4-}$ Reduction of a Sterically Constrained Bis(substituted phenanthroline) Complex of Copper(II) in Aqueous Solution

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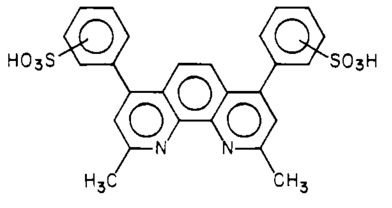
Methyl substituents in the 2,9 positions of 1,10-phenanthroline create a steric hindrance, which limits the extent of coordination to Cu(II) (bis and not tris complexes form) and restricts the number of possible geometries. The two solid forms, green (moist) and maroon (dry), which are obtained with the ligand 2,9-dimethyl-1,10-phenanthroline, have been studied briefly. It is suggested that five- and four-coordinate geometries, respectively, differing by a coordinated H_2O, are relevant. The solubility of the complex is increased by using the further modified ligand L^{2-} = 2,9-dimethyl-4,7-bis((sulfonyloxy)phenyl)-1,10-phenanthroline. The $Fe(CN)_6^{4-}$ reduction of the $Cu^{II}L_2^{2-}$ complex displays limiting kinetics, consistent with a mechanism Cu(II) $\rightleftharpoons$ *Cu(II) (k_1, k_{-1}), followed by $Fe(CN)_6^{4-}$ + *Cu(II) $\rightarrow$ $Fe(CN)_6^{3-}$ + Cu(I) (k_2). At 25 °C, pH 8.0 (collidine and borate buffers), $I = 0.10$ M ($LiClO_4$), $k_1 = 229\ s^{-1}$, and $k_1k_2/k_{-1} = 3.3 \times 10^6\ M^{-1}\ s^{-1}$. Observations are consistent with Cu(II) and *Cu(II) being five- and four-coordinate, respectively, the latter having a tetrahedral (or distorted tetrahedral) geometry closely matching that of the Cu(I) product.

Electron-transfer reactions involving the Cu(I)-Cu(II) couple are unusual in that, for simple complexes at least, the two oxidation states differ either in coordination number and/or stereochemistry. Because of the extensive reorganization requirements attendant on electron-transfer, inner-sphere mechanisms are generally preferred.[2,3] Tetrahedral coordination while common for Cu(I) is not often observed for Cu(II), which prefers alternative arrangements e.g., square planar, five-coordinate, or octahedral.[4] Square-planar and octahedral geometries become less likely, however, when a steric factor is introduced. We have conducted a search for water-soluble Cu(II) complexes in which the tetrahedral geometry is favored over the square-planar arrangement because of steric factors. Complexes of 2,9-dimethyl-1,10-phenanthroline (hereafter 2,9-DMphen), and 2,9-dimethyl-4,7-bis((sulfonyloxy)phenyl)-1,10-phenanthroline (hereafter 2,9-DM-4,7-DPSphen), with the 2,9-dimethyl groups providing a steric hindrance,[5,6] meet this requirement, although as will be seen below five-coordinate forms are also relevant. The kinetics of the reduction of the Cu(II)-(2,9DM-4,7DPSphen) complex with $Fe(CN)_6^{4-}$ display interesting features which reflect on the alternative geometry of the Cu(II) oxidant.



2,9-DM-4,7-DPSphen

Experimental Section

Preparation of Cu Complexes. The Cu(II)-(2,9-DMP-4,7-DPSphen) complex was prepared in solution (triply distilled H_2O) by mixing weighed amounts of $Cu(ClO_4)_2 \cdot 6H_2O$ (G. F. Smith) and using the acid form of the ligand L^{2-} = 2,9-dimethyl-4,7-bis((sulfonyloxy)phenyl)-1,10-phenanthroline (Sigma), which was generally in 8-fold excess of the amount required for formation of the bis complex CuL_2^{2-}. Standardization of $Cu(ClO_4)_2 \cdot 6H_2O$ was by iodometric method using sodium thiosulfate. Quantitative reduction to the Cu(I) complex was achieved (pH 8) by addition of an excess of sodium sulfite. The Cu(I) complex gives a strong absorbance peak at 483 nm (ϵ 12.3 $\times$ $10^3\ M^{-1}\ cm^{-1}$). Solutions of the Cu(II) complex (ca. 10^{-3} M) have no significant visible absorption. No solid samples were obtained. Solutions are light sensitive and were kept covered. A solid sample of the Cu(II)-(2,9-DMphen) complex was obtained by shaking 2.3 mmol of 2,9-dimethyl-1,10-phenanthroline (Sigma) with 0.45 mmol of $Cu(ClO_4)_2 \cdot 6H_2O$ in 50 mL of H_2O.[7] Undissolved ligand was filtered off, and a green solid precipitated by addition of 4 M $NaClO_4$. When the precipitate was dried over P_2O_5 in a desiccator, a purple-maroon solid is obtained which analyses[7] for $[Cu(2,9\text{-}DMphen)_2](ClO_4)_2$. The Cu(I) complex was prepared by reduction with NCS^- and yields a red solid which analyses for $[Cu(2,9\text{-}DMphen)_2]ClO_4$.[7] Solution spectra of the latter gave a peak at 454 nm (ϵ 6.2 $\times$ $10^3\ M^{-1}\ cm^{-1}$). The complex $[Cu(2,9\text{-}DMphen)(Cl)_2(H_2O)]$ was prepared by the literature method.[8]

$Fe(CN)_6^{4-,3-}$ Complexes. Sodium (and potassium) hexacyanoferrate(II), $Na_4[Fe(CN)_6] \cdot 10H_2O$ (Hopkin and Williams, AnalaR) (λ_{max} 337 nm (ϵ 350 $M^{-1}\ cm^{-1}$)), and potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$ (BDH, AnalaR) (λ_{max} 420 nm (ϵ 1000 $M^{-1}\ cm^{-1}$)), were used without further purification. Solutions of $Fe(CN)_6^{4-}$ give significant reaction with O_2 over period >40 min, and appropriate precautions were observed.

Reduction Potentials. At an ionic strength of 0.10 M the reduction potential for the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple is reported[9] to be 0.41 V. A potential of 0.594 V has been found for the Cu(II)-Cu(I) couple with 2,9-DMphen as ligand (bis complex).[6] Although a similar value (0.62 V) has been reported[10] for the corresponding couple with the 2,9-DM-4,7-DPSphen as ligand, the system is quasi-reversible, and a more extensive investigation was therefore carried out. The cyclic voltammetric behavior of the copper(II) complex (1.05 $\times$ 10^{-4} M) was determined in 0.01 M borate buffer (pH 8.0) in 0.10 M $LiClO_4$ and at 25 °C with a Bioanalytical Systems Inc. CV-1A instrument and a Tektronix 5111 storage oscilloscope. The midpoint potential shows an anodic shift from a value of 0.619 ± 0.003V (vs. NHE) at low scan rates (<0.05 V s^{-1}) to a value of 0.635 ± 0.006 V at a scan rate of 10 V s^{-1} with a concomitant increase in the peak separation from 0.075 to 0.270 V. This behavior suggests that electron transfer in the copper complex is coupled to a chemical reaction.[11]

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Table I. First-Order Rate Constants, k_{obsd}, for the $Fe(CN)_6^{4-}$ Reduction of the Cu^{II}(2,9-DM-4,7-DPSphen)$_2$ Complex, $Cu^{II}L_2^{2-}$ (1×10^{-5} M), Made Up with the Ligand L^{2-} in Excess (1.0×10^{-4} M) at pH 8.0 (Collidine or Borate as Indicated),[a] I = 0.10 M ($LiClO_4$), and λ 483 nm (Reductant in Excess)

25 °C		5 °C	
$10^5[Fe(CN)_6^{4-}]$, M	k_{obsd}, s^{-1}	$10^5[Fe(CN)_6^{4-}]$, M	k_{obsd}, s^{-1}
5.0	97[b]	5.0	77[b]
8.0	122	11.0	108
11.0	140	11.0	111[e]
15.0	150	13.0	120[c]
15.0	156[c]	15.0	131
20.0	173	20.0	141
20.0	172	30.0	157
30.0	197[c]		

[a] pH 8.03 ± 0.03. [b] $[Cu^{II}L_2^{2-}] = 0.5 \times 10^{-5}$ M, $[L^{2-}] = 5.0 \times 10^{-5}$ M. [c] Borate buffer (collidine elsewhere). [d] Na^+ salt (K^+ elsewhere). [e] $[Fe(CN)_6^{3-}] = 11.0 \times 10^{-5}$ M.

Reflectance Spectra of Cu(II)–(2,9-DMphen) Complexes. Spectra of two green solid samples consisting of the moist Cu(II)–(2,9-DMphen) complex (peaks at 380 and 730 nm) and powdered [Cu(2,9-DMphen)$(Cl)_2(H_2O)$] (peaks at 385 and 725 nm) with talc as a diluent were determined on a Unicam SP500 using filter paper as reference. The X-ray crystal structure[8] of the latter has indicated a mononuclear five-coordinate geometry.[12] The similarity of the diffuse reflectance spectra strongly suggests a similar structure, with formula $[Cu(2,9\text{-DMphen})_2(H_2O)]^{2+}$, for the moist, green solid. The low solubility of the Cu(II)–(2,9-DMphen) complex in aqueous solution containing excess 2,9-DMphen ligand precluded meaningful solution UV–visible spectrophotometric measurements.

Kinetic Studies. The following observations are relevant to choice of pH and ligand concentration required to maintain the Cu(II) as a bis complex. Singly protonated 2,9-DM-4,7-DPSphen has an acid dissociation (ring nitrogen) pK_a of 5.8[13] (cf. pK_a for 2,9-DMphen of 5.87[7]). At pH 8 protonation (<1%) does not interfere with the complexation process. Formation constants for the Cu(II)–(2,9-DM-4,7-DPSphen) complex have not been determined, but are expected to be similar to those for the formation of the mono and bis 2,9-DMphen complexes, 1.6×10^5 and 6.1×10^5 M^{-1}, respectively,[7] yielding an overall $K \approx 10^{11}$ M^{-1} for (1). Hence for Cu(II) concentrations ca. 10^{-5} M an eightfold excess of free ligand gives ratios of bis:mono:Cu^{2+} of 640:13:1. Effects of varying the pH (7.5–9.0) and excess of ligand were checked and had no effect on measured rate constants.

$$Cu^{2+} + 2(2,9\text{-DMphen}) \rightleftharpoons Cu(2,9\text{-DMphen})_2^{2+} \qquad (1)$$

Collidine, 2,4,6-trimethylpyridine, buffer (0.020 M) was used extensively, as obtained commercially (BDH, laboratory reagent). Satisfactory agreement was obtained on replacement with 10^{-2} M sodium tetraborate (Fisons, AR) buffer. All run solutions were made up to ionic strength I = 0.10 M ($LiClO_4$). Formation of Cu(I)–(2,9-DM-4,7-DPSphen) complex was monitored at the 483-nm peak position (ϵ 12.3×10^3 M^{-1} cm^{-1}), with Durrum and Applied Photophysics stopped-flow spectrophotometers. First-order plots of absorbance (A) changes log ($A_\infty - A_t$) against time were generally linear for >85% completion. Rate constants, k_{obsd}, were obtained from slopes (×2.303). A least-squares program with weighting $1/x$ (x is the reactant concentration) was used to compute kinetic parameters as in eq 5.

Results

First-order rate constants k_{obsd} for the $Fe(CN)_6^{4-}$ reduction of the Cu(II)–(2,9-DM-4,7-DPSphen) complex at 25 and 5 °C are listed in Table I. With $[Fe(CN)_6^{4-}]$ in large excess a nonlinear dependence of k_{obsd} on $[Fe(CN)_6^{4-}]$ is observed (Figure 1). Reactions at the higher $[Fe(CN)_6^{4-}]$ were at the limit of the stopped-flow range, and concentrations were restricted to the values indicated. A plot of $(k_{\mathrm{obsd}})^{-1}$ against $[Fe(CN)_6^{4-}]^{-1}$ is linear (Figure 2). The reaction sequence (2)–(3) provides a satisfactory explanation (see Discussion).

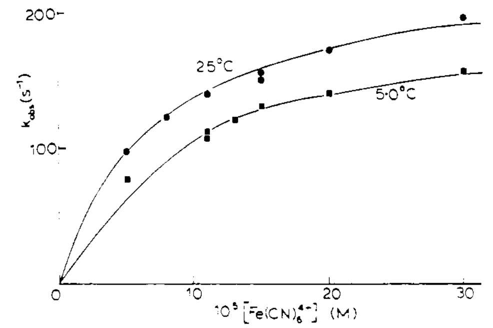

Figure 1. Variation of first-order rate constants, k_{obsd}, with $[Fe(CN)_6^{4-}]$ (reactant present in large excess) for the reduction of the Cu(II)–(2,9-DM-4,7-DPSphen) complex at pH 8.0 (collidine) and I = 0.10 M ($LiClO_4$).

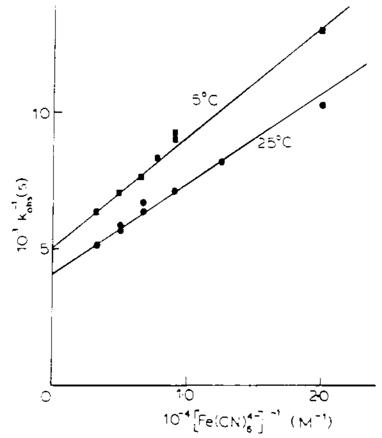

Figure 2. Reciprocal plot demonstrating the dependence of first-order rate constants, k_{obsd}, on $[Fe(CN)_6^{4-}]$ (reactant in large excess) for the $Fe(CN)_6^{4-}$ reduction of the Cu(II)–(2,9-DM-4,7-DPSphen) complex at pH 8.0 (collidine) and I = 0.10 M ($LiClO_4$).

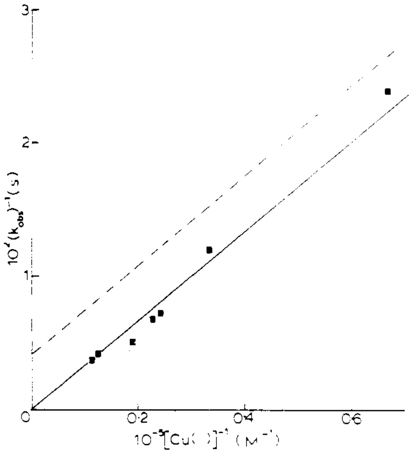

Figure 3. Reciprocal plot (25 °C) demonstrating the dependence of first-order rate constants, k_{obsd}, on [Cu(II)] (reactant in large excess) for the $Fe(CN)_6^{4-}$ reduction of the Cu(II)–(2,9-DM-4,7-DPSphen) complex at pH 8.0 (collidine) and I = 0.10 M ($LiClO_4$). The broken line is the corresponding slope (25 °C) from Figure 2.

$$\text{Cu(II)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^*\text{Cu(II)} \qquad (2)$$

$$^*\text{Cu(II)} + Fe(CN)_6^{4-} \xrightarrow{k_2} \text{Cu(I)} + Fe(CN)_6^{3-} \qquad (3)$$

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Table II. First-Order Rate Constants, k_{obsd}, for the $Fe(CN)_6^{4-}$ Reduction of Cu^{II} $(2,9\text{-DM-4,7-DPSphen})_2$ Complex, $Cu^{II}L_2^{2-}$, at 25 °C, pH 8.0, $I = 0.10$ M ($LiClO_4$), and λ 483 nm (Oxidant in Excess)

10^5[Fe(CN)$_6^{4-}$], M	10^5[Cu(II)], M	10^5[L^{2-}],^{a} M	k_{obsd}, s^{-1}
0.39	1.5	47	42^b
0.39	3.0	66	84^b
0.50	4.1	50	138^c
0.50	4.4	70	147^c
0.97	5.3	59	201^b
1.0	8.0	120	239^c
1.0	8.9	120	272^c

^{a} Total ligand concentration used. ^{b} Borate buffer. ^{c} Collidine buffer.

With application of the stationary-state approximation to [*Cu(II)], (4) is obtained, which rearranges to give (5). With

$$k_{\text{obsd}} = \frac{k_1k_2[\text{Fe(CN)}_6^{4-}]}{k_{-1} + k_2[\text{Fe(CN)}_6^{4-}]} \qquad (4)$$

$$\frac{1}{k_{\text{obsd}}} = \frac{k_{-1}}{k_1k_2}\,\frac{1}{[\text{Fe(CN)}_6^{4-}]} + \frac{1}{k_1} \qquad (5)$$

the concentration of Cu(II) in large excess (Table II) the rate dependence deriving from (2)–(3) is as in (6). A plot of

$$k_{\text{obsd}} = \frac{k_1k_2}{k_{-1}}[\text{Cu(II)}] \qquad (6)$$

$(k_{\text{obsd}})^{-1}$ against $[\text{Cu(II)}]^{-1}$ (Figure 3) gives a similar slope (k_{-1}/k_1k_2) with the 25 °C data of Figure 2, in accordance with (2)–(3). Addition of $Fe(CN)_6^{3-}$ did not affect the magnitude of rate constants (Table I). The following values were obtained from a fit of k_{obsd} to (4): at 25 °C, $k_1 = 231 \pm 6.5$ s^{-1}, $k_1k_2/k_{-1} = (3.34 \pm 0.11) \times 10^6$ M^{-1} s^{-1}; at 5 °C $k_1 = 192 \pm 8$ s^{-1}, $k_1k_2/k_{-1} = (2.51 \pm 0.13) \times 10^6$ M^{-1}. With Cu(II) in large excess a small intercept -4 ± 9 is observed, and the slope gives $k_1k_2/k_{-1} = (3.23 \pm 0.2) \times 10^6$ M^{-1} s^{-1}. From the temperature dependence the magnitude of activation parameters for k_1 is indicated; thus $\Delta H^{\ddagger}_1$ = ca. 0.3 kcal mol^{-1} and $\Delta S^{\ddagger}$ = ca. -44 cal K^{-1} mol^{-1}.

Discussion

Relevant background information and support for the kinetic interpretation in this paper is provided by the existence of two forms of the bis(2,9-DMphen) complex of Cu(II). Solid samples of the green (moist) and maroon (dry) complex were prepared. The close similarity of the diffuse reflectance spectrum of the green form to that of the complex [Cu^{II}(2,9-DMphen)(Cl)$_2$(H$_2$O)] (which is also green) is noted (see Experimental Section). A crystal structure determination of the latter has shown it to be five-coordinate.[8] A similar five-coordinate geometry and formula [Cu(2,9-DMphen)$_2$(H$_2$O)]$^{2+}$ for the moist, green solid seems likely therefore. When the precipitate is dried over P_2O_5 in a desiccator, the maroon solid is obtained, which analyses for [Cu(2,9-DMphen)$_2$](ClO$_4$)$_2$,[7] and there seems every likelihood that the geometry of this complex is tetrahedral or distorted tetrahedral.[14]

The photoredox behavior of the Cu(II)–(2,9-DMphen) complex in aqueous solution also suggests at least one water molecule in the inner-coordination sphere. Thus Sundararajan and Wehry[15] have assigned the photoredox process to (7).

$$[\text{Cu(2,9-DMphen)}_2(\text{H}_2\text{O})]^{2+} \xrightarrow{h\nu} [\text{Cu(2,9-DMphen)}_2]^+ + \text{OH} + \text{H}^+ \qquad (7)$$

Benzoate scavenging clearly implicates formation of the OH radicals as a major process accompanying the photoreduction. Solutions of the Cu(II)–(2,9-DM-4,7-DPSphen) complex are also photosensitive.

Kinetic studies on the 2,9-DM-4,7-DPSphen complex were favored because of the increased solubility as compared to the 2,9-DMphen complex. Preliminary kinetic studies on the latter have indicated that similar behavior is observed. The kinetics conform to the reaction sequence (2)–(3), which is consistent with a rapid equilibrium between five- and four-coordinate species in solution. The most realistic assignment is that the five-coordinate species is dominant and that *Cu(II) corresponds to a tetrahedral form. Apart from solvent H$_2$O favoring formation of a five-coordination complex, a further point to make here is that a tetrahedral form is expected to have greater reactivity because, by matching the geometry of the Cu(I) product, ligand reorganization prior to electron transfer is minimized.

The stationary-state approximation is used for *Cu(II) in eq 2 and 3, in deriving the rate law dependence (4). A reasonable expectation is that k_{-1} is $>k_1$ and possibly $\gg k_1$, where at 25 °C $k_1 = 231$ s^{-1}. A value $k_2/k_{-1} = 1.34 \times 10^4$ M^{-1} has been determined so that k_2 is $>3 \times 10^6$ M^{-1} s^{-1} and may well be approaching the diffusion-controlled limit bearing in mind that both reactants carry negative charges. The magnitude of activation parameters for k_1 indicate a substantial entropy effect attendant on the geometry change. It is possible that there is substantial ordering of solvent as the large planar 2,9-DM-4,7-DPSphen ligands spread out to occupy tetrahedral positions. The change in form of the rate law from (4) to (6) is determined by the relative values of the denominator term in (4), as well as the introduction of [Cu(II)] (reactant in excess) for [Fe(CN)$_6^{4-}$] in the numerator.

At this time it is not possible to categorically rule out contribution from the more direct reaction path (8), involving

$$\text{Fe(CN)}_6^{4-} + \text{Cu(II)} \xrightarrow{k_3} \text{Fe(CN)}_6^{3-} + \text{Cu(I)} \qquad (8)$$

Fe(CN)$_6^{4-}$ reduction of five-coordinate Cu(II). Other reductants are being investigated,[16] where with pyridinopentammineruthenium(II) it is found that rate constants exceed the limiting rate constant observed in the present study. Inclusion of k_3 (2.1×10^5 M^{-1} s^{-1}) could decrease k_1 to a value ca. 160 s^{-1} and modify k_2/k_{-1} to a value 2.4×10^4 M^{-1} without impairing the linearity required by the dominant pathway involving (2) and (3). At present this additional pathway remains tentative.

An alternative mechanism to (2) and (3) has been considered. This may be summarized by (9)–(10), where

$$\text{Fe(CN)}_6^{4-} + \text{Cu(II)} \overset{K}{\rightleftharpoons} \text{Fe(CN)}_6^{4-},\text{Cu}^{\text{II}} \qquad (9)$$

$$\text{Fe(CN)}_6^{4-},\text{Cu}^{\text{II}} \xrightarrow{k_4} \text{Fe(CN)}_6^{3-} + \text{Cu(I)} \qquad (10)$$

Fe(CN)$_6^{4-}$,Cu^{II} represents (a) an outer-sphere or (b) an inner-sphere (bridged) adduct. Equation 11, which can be derived,

$$k_{\text{obsd}} = \frac{k_4K[\text{Fe(CN)}_6^{4-}]}{1 + K[\text{Fe(CN)}_6^{4-}]} \qquad (11)$$

applies in both cases and is of the same form as (4). However the value of K (1.43×10^4 M^{-1}) which is evaluated is too high and quite unrealistic for the outer-sphere association of 2– and 4– reactants controlled by electrostatis alone. Inner-sphere adducts might seem more likely if Cu(II) had an affinity for the reductant ligand. For confirmation of this possibility

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$Fe(CN)_6^{3-}$ was added in a run with $Fe(CN)_6^{4-}$ as reductant (both 1.1×10^{-4} M). If this mechanism were relevant we would have expected competition of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ for the Cu(II) to have resulted in retardation. No effect was observed. The runs carried out with the Cu(II) oxidant in large excess also exclude (9)–(10). Limiting kinetics, and not a linear plot as in Figure 3, would have been expected to hold for such a mechanism to apply. This observation also rules out the so-called "dead-end" mechanism (12)–(13), which

$$Fe(CN)_6^{4-} + Cu(II) \rightleftharpoons Fe(CN)_6^{4-},Cu^{II} \qquad (12)$$

$$Fe(CN)_6^{4-} + Cu(II) \rightarrow Fe(CN)_6^{3-} + Cu(I) \qquad (13)$$

would require the adduct formed in (12) to be of the inner-sphere kind and redox inactive. This mechanism holds in the $Co^{II}(edta)^{2-}$ reduction of $Fe(CN)_6^{3-}$,[17,18] which appears to be the only example of an inorganic redox reaction known to behave in this manner.

The full reaction scheme implied in this study is as in (14).

$$Cu(II) \rightleftharpoons {}^*Cu(II) \overset{e^-}{\rightleftharpoons} Cu(I) \qquad (14)$$

Cyclic voltammetry results using different scan rates are consistent with this belief. The redox activity of *Cu(II) with $Fe(CN)_6^{4-}$ (k_2, $M^{-1}\ s^{-1}$) is of considerable interest in view of the similarity of the geometry with the Cu(I) product[19] and minimization of ligand reorganization attendant on electron transfer.[20] The matching of geometry is similar to that proposed[21] to explain the efficient electron-transfer properties of the blue Cu proteins.[22,23] Tetrahedral geometries are extremely rare for Cu(II), and although other systems have been reported,[24] the present study appears to be the first example of an inorganic Cu(I)–Cu(II) redox interconversion in aqueous solution where the matching of geometries has been shown to be a relevant factor. The rate process involving *Cu(II) (k_2 $> 3 \times 10^6\ M^{-1}\ s^{-1}$) is clearly very efficient and mimics the protein reaction.

Finally we wish to comment on the self-exchange rate constants for Cu(I)–Cu(II) reactions with 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline as ligands. Yoneda et al.[25] have calculated a rate constant of $5 \times 10^7\ M^{-1}\ s^{-1}$ for the $Cu(phen)_2^{+,2+}$ exchange based on a redox study of the $Cu(phen)_2^+$ complex. Yandell and Augustin[23] have calculated a value of 50 $M^{-1}\ s^{-1}$ for the same exchange but this time based on a study involving the reduction of $Cu(phen)_2^{2+}$. A wide discrepancy is also observed for the 2,9-DMphen complexes, where Yandell and Augustin[23] find values of $1.9 \times 10^4\ M^{-1}\ s^{-1}$ and $4.9 \times 10^4\ M^{-1}\ s^{-1}$ for studies on the reduction of $Cu(2,9\text{-}DMphen)_2^{2+}$, and Margerum and co-workers[10] report values from a lower limit of $3 \times 10^4\ M^{-1}\ s^{-1}$ to $9.0 \times 10^8\ M^{-1}\ s^{-1}$ from studies on the oxidation of $Cu(2,9\text{-}DMphen)_2^+$, depending on the choice of cross reaction. This latter paper also reports a value of $3.7 \times 10^7\ M^{-1}\ s^{-1}$ for the complex $Cu(2,9\text{-}DM\text{-}4,7\text{-}DPSphen)_2^+$ which compares with a "self-exchange" rate of $2.8 \times 10^5\ M^{-1}\ s^{-1}$ evaluated from k_1k_2/k_{-1} in the present study. The only outstanding feature of these results is that self-exchange rates evaluated from reactions involving copper(I) reactants appear consistently larger than those from reactions involving copper(II). It is possible with the 2,9-DMphen and 2,9-DM-4,7-DPSphen complexes that the reaction scheme as in (14) involving tetrahedral and five-coordinate species applies and that this is the basic source of the discrepancy. Thus the self-exchange rate of the tetrahedral complex is larger than the value for the five-coordinate complex. A similar scheme can also apply for the phen complexes, although this system is more complicated in view of the tendency of Cu(II) to form tetragonally distorted octahedral/square planar complexes, with less tendency (no steric constraint) to form tetrahedral Cu(II).

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Registry No. $Fe(CN)_6^{4-}$, 13408-63-4; $Cu(2,9\text{-}DM\text{-}4,7\text{-}DPSphen)_2^{2-}$, 75716-21-1; $[Cu(2,9\text{-}DMphen)_2(H_2O)]^{2+}$, 75764-71-5; $Cu(2,9\text{-}DMphen)Cl_2(H_2O)$, 26479-82-3.

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