Conformationally-controlled electron-transfer reactions as manifested with copper(II)/(I) macrocyclic ligand complexes

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Abstract. Studies on the electron-transfer kinetics of copper(II)/(I)-macrocyclic polythiaether complexes have included rapid-scan cyclic voltammetry, stopped-flow kinetic measurements on several cross reactions involving both Cu(II) reduction and Cu(I) oxidation, and direct NMR measurements of the Cu(II)-Cu(I) self-exchange electron-transfer rate constants. The results demonstrate that the reaction mechanism for these systems conforms to a dual-pathway "square" scheme in which, under appropriate conditions, conformational changes become rate-limiting in one direction, resulting in the condition known as "gated" behavior. The current studies represent the first thorough documentation of gated electron-transfer in Cu(II)/(I) systems.

INTRODUCTION

The role of conformational change in controlling electron-transfer reaction rates has been recognized as an issue of major importance in biological systems. More than twenty years ago, Vallee and Williams (ref. 1) proposed that the protein matrix in metalloenzymes imposes a strain upon the bonds at the active metal site such that bond rearrangement is minimized during the chemical reaction. In elucidating this so-called "entatic" (strained) state hypothesis, these authors focused on redox-active iron and copper enzymes, recognizing that the changes in bond lengths and/or angles, which normally accompany a change in the oxidation state of these metal ions, comprise a major contribution to the activation parameters for their electron-transfer reactions. Thus, Vallee and Williams concluded that increasing the rigidity of the coordination sphere would reduce the activation energy and result in more rapid reactions.

More recently, mounting evidence has been reported that conformational changes may themselves become the rate-limiting processes in redox-active metalloenzymes. Among the blue copper proteins belonging to the class known as blue electron carriers, limiting first-order kinetics have been observed in the reduction of rusticyanin (ref. 2) and in the oxidation of azurin (refs. 3, 4). Both observations have been attributed to conformational changes preceding the electron-transfer step. For each of these proteins, spectral evidence has been obtained for the existence of two conformers of the copper site (refs. 2, 5). Additional evidence for rate-limiting conformational control in redox-active metalloenzymes has been claimed in the case of intra- and inter-molecular electron-transfer reactions of heme proteins and cytochrome *c* oxidase (ref. 6).

Recent theoretical treatises have been presented by Hoffman and Ratner (ref. 7) and by Brunschwig and Sutin (ref. 8) to describe reaction mechanisms in which conformational changes and the electron-transfer step occur sequentially, rather than concertedly. Both sets of authors have incorporated into their theories the existence of intermediate conformers for both the oxidant and reductant resulting in a dual-pathway square scheme (see below). Depending upon the reaction conditions and the conformational constraints of the system, the recently developed theories predict that a variety of kinetic behaviors may be anticipated for such systems (refs. 7, 8), including, under appropriate conditions, "gated" (or "directional") electron-transfer in which the rate of conformational change ultimately limits the rate of the reaction *in one direction*. It has been speculated that conformational control of this type is employed in biological systems to impede undesired back reactions resulting in a "molecular switch" (ref. 9). Although this mechanistic behavior would appear to be of major importance, the conditions leading to the various types of theoretically predicted behavior have not heretofore been thoroughly explored or characterized experimentally.

Copper(II)/(I) redox couples appear to represent optimal systems for investigating gated electron-transfer behavior as a result of the significant structural differences characteristic of these two oxidation states (ref. 10). In our laboratories, we have found that complexation of the copper ion by macrocyclic polythiaether ligands results in two favorable properties for such studies: (i) thiaether sulfur donor atoms promote high

Cu(II)/(I) redox potentials (ref. 11) due to the low thermodynamic stability of the Cu(II) species (ref. 12), thereby making the Cu^IL species more readily accessible for study; and (ii) the structural constraints inherent in the macrocyclic ligands permit at least some level of control over the energetics associated with conformational change (ref. 13). During the past decade, we have conducted extensive electron-transfer kinetic measurements on a broad series of copper-polythiaether complexes (refs. 14 - 16). Only recently, however, have we managed to generate well-documented evidence for the onset of conformationally-controlled electron-transfer behavior (refs. 17, 18). A brief summary of these studies is reported here.
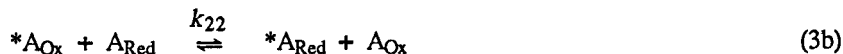
THEORETICAL CONSIDERATIONS

Most Cu(II)/(I) kinetic studies which have been published in the literature have been limited to reactions involving the *reduction* of the $Cu^{II}L$ species (L = a coordinated ligand) by various reducing agents, A_{Red}:

$$Cu^{II}L + A_{Red} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} Cu^IL + A_{Ox} \tag{1}$$
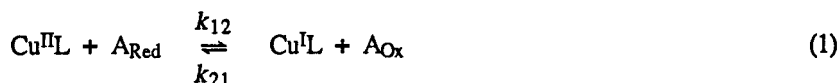
Occasionally, *oxidation* studies on corresponding Cu^IL species (i.e., the reverse of reaction 1) have also been reported. If these reactions take place by an outer-sphere mechanism (in which no bridging ligand is involved), both the forward and the reverse cross-reaction rate constants should conform to the Marcus cross relation (ref. 19) as represented in eq 2, where k_{ij} refers to the overall cross-reaction rate constant

$$k_{ij} = \{k_{11} k_{22} K_{ij} f_{ij}\}^{1/2} W_{ij} \tag{2}$$

(either k_{12} or k_{21}), K_{ij} represents the equilibrium constant for the appropriate forward or reverse process in reaction 1, f_{ij} is a non-linear correction term, W_{ij} is a work term (electrostatic) correction, and k_{11} and k_{22} represent self-exchange rate constants for the two constituent redox couples,

$$*Cu^{II}L + Cu^IL \underset{}{\overset{k_{11}}{\rightleftharpoons}} *Cu^IL + Cu^{II}L \tag{3a}$$

$$*A_{Ox} + A_{Red} \overset{k_{22}}{\rightleftharpoons} *A_{Red} + A_{Ox} \tag{3b}$$

Of those few $Cu^{II/I}L$ systems for which cross-reaction kinetic studies have been published involving *both* the reduction *and* oxidation kinetics of the copper complex (generally involving polypyridyl ligands), the Cu(II)/(I) self-exchange rate constant values, $k_{11(Red)}$ and $k_{11(Ox)}$, as calculated from k_{12} and k_{21}, respectively, are frequently in disagreement (refs. 15, 16). For example, in 1979 Augustin and Yandell studied the reduction kinetics of $Cu^{II}(bpy)_2(H_2O)$ and $Cu^{II}(phen)_2(H_2O)$ (bpy = bipyridine, phen = 1,10-phenanthroline) using horse heart cytochrome c(II) (ref. 20) and obtained $k_{11(Red)}$ values which were 10^5 *smaller* than the corresponding $k_{11(Ox)}$ values reported two years earlier by Holwerda and coworkers based on the use of $Co^{III}(EDTA)$ as oxidant (ref. 21). In commenting on this huge discrepancy, Holwerda later suggested that it was attributable to differences between the extent of Cu^{II}-H_2O bond breaking (and Cu^I-H_2O bond making) in the activated complexes of self-exchange and cross reactions (ref. 22), while Yandell later suggested the possibility that conformational changes in the copper complex might be rate-limiting in the reduction reactions (ref. 23). Several other investigators have attempted to explain the disagreement in these values without arriving at a satisfactory consensus regarding the cause (ref. 24).

The foregoing controversy was heightened in 1983 in a communication by Lee and Anson (ref. 25) in which they discussed the discrepancies between Holwerda's and Yandell's studies and concluded that *the Cu(II) and Cu(I) species did not contribute equally to the reorganizational energy.* They suggested, therefore, that **Marcus theory does not apply to Cu(II)/(I) systems.** Subsequently, Lee and Anson attempted to obtain a direct measurement of the self-exchange rate constant for $Cu^{II/I}(phen)_2$ using an unorthodox electrochemical approach in which the Cu(I) species was adsorbed onto the electrode surface and immersed in a solution containing the Cu(II) species (ref. 26). They obtained a self-exchange rate constant intermediate between the values calculated by Yandell and Holwerda and concluded that this result supported their hypothesis.

Proposed square scheme mechanism for Cu(II)/(I) systems   The homogeneous cross-reaction kinetics of the Cu(II)/(I)-polythiaether ligand systems studied in our laboratories within the past few years have generally shown that the self-exchange rate constants obtained by applying the Marcus equation to cross reactions involving $Cu^{II}L$ reduction (i.e., $k_{11(Red)}$) are much larger than the values obtained in a similar manner from reactions involving Cu^IL oxidation ($k_{11(Ox)}$), the difference ranging from 30- to 10^7-fold (refs. 15, 16). We have proposed that this behavior is the result of a dual-pathway square scheme mechanism (Scheme I) in which $Cu^{II}L(O)$ and $Cu^IL(R)$ represent the stable conformers (or configurations)

of the two oxidation states while $Cu^{II}L(Q)$ and $Cu^{I}L(P)$ represent metastable conformers (or configurations). The governing theory for a general mechanism of this type has recently been described by Hoffman

Scheme I

PATHWAY A

PATHWAY B
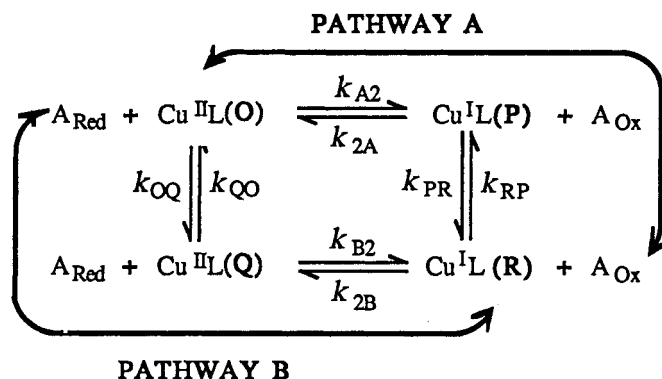
and Ratner (ref. 7) and by Brunschwig and Sutin (ref. 8). These authors have noted, in particular, that "gated" (or "directional") electron transfer may be anticipated with such a mechanism whenever one of the rate constants for conformational interconversion (k_{OQ}, k_{QO}, k_{PR} or k_{RP}) becomes rate-limiting.

An examination of the kinetic expressions applicable to Scheme I reveals the conditions necessary to bring about gated electron-transfer behavior. Assuming the steady state approximation for the proposed metastable intermediates, **Q** and **P**, the overall differential expressions can be represented as follows:

Reduction of $Cu^{II}L$

$$-\frac{d[Cu^{II}L]}{dt} = \left(\frac{k_{A2}\,k_{PR}}{k_{2A}\,[A_{Ox}] + k_{PR}} + \frac{k_{B2}\,k_{OQ}}{k_{B2}\,[A_{Red}] + k_{QO}}\right)[O]\,[A_{Red}] \tag{4}$$

Oxidation of $Cu^{I}L$

$$-\frac{d[Cu^{I}L]}{dt} = \left(\frac{k_{2A}\,k_{RP}}{k_{2A}\,[A_{Ox}] + k_{PR}} + \frac{k_{2B}\,k_{QO}}{k_{B2}\,[A_{Red}] + k_{QO}}\right)[R]\,[A_{Ox}] \tag{5}$$

where [O], [R], $[A_{Ox}]$ and $[A_{Red}]$ represent the molar concentrations of the stable conformers of $Cu^{II}L$ and $Cu^{I}L$ and the oxidized and reduced forms of the counter reagent, respectively. The first parenthetical term on the right side of each equation represents the kinetic contribution of pathway A while the second term represents pathway B. Depending upon which of these terms is dominant (i.e., whether pathway A or B is favored), a number of unique behaviors may result.

For systems where pathway A is dominant, the following limiting expressions emerge:

Reduction of $Cu^{II}L$

Pathway A dominant: $\left(\dfrac{k_{A2}\,k_{PR}}{k_{2A}\,[A_{Ox}] + k_{PR}}\right) \gg \left(\dfrac{k_{B2}\,k_{OQ}}{k_{B2}\,[A_{Red}] + k_{QO}}\right)$

If $k_{2A}\,[A_{Ox}] \ll k_{PR}$: $-\dfrac{d[Cu^{II}L]}{dt} = k_{A2}\,[O]\,[A_{Red}]$ \qquad (4a)

If $k_{2A}\,[A_{Ox}] \gg k_{PR}$: $-\dfrac{d[Cu^{II}L]}{dt} = K_{A2}\,k_{PR}\,\dfrac{[O]\,[A_{Red}]}{[A_{Ox}]}$ \qquad (4b)

Oxidation of $Cu^{I}L$

Pathway A dominant: $\left(\dfrac{k_{2A}\,k_{RP}}{k_{2A}\,[A_{Ox}] + k_{PR}}\right) \gg \left(\dfrac{k_{2B}\,k_{QO}}{k_{B2}\,[A_{Red}] + k_{QO}}\right)$

If $k_{2A}\,[A_{Ox}] \ll k_{PR}$: $-\dfrac{d[Cu^{I}L]}{dt} = K_{PR}^{-1}\,k_{2A}\,[R]\,[A_{Ox}]$ \qquad (5a)

If $k_{2A}\,[A_{Ox}] \gg k_{PR}$: $-\dfrac{d[Cu^{I}L]}{dt} = k_{RP}\,[R]$ \qquad (5b)

Of these latter expressions, eqs 4a and 5a represent the situation in which **P** and **R** are fully equilibrated leading to normal Marcus behavior. Under these circumstances, the existence of intermediate species is not apparent in the kinetic data. By contrast, eqs 4b and 5b represent the condition where the **P** ⇌ **R** conformational interconversion is the rate-limiting step, resulting in "gated" electron-transfer behavior. Similar limiting expressions can be generated for Pathway B.

RESULTS AND DISCUSSION

The results of recent studies on the kinetics of cross-reactions of five closely related Cu(II)/(I)-polythiaether complexes are presented in Table I. The self-exchange rate constants in the last two columns were calculated using eq 2 for $Cu^{II}L$ reduction ($k_{11(Red)}$) and $Cu^{I}L$ oxidation ($k_{11(Ox)}$), respectively. In each case, the range of values listed represents the results of reactions with at least four selected counter reagents. Also included in this Table are the results of recent NMR line-broadening measurements on four of these systems to provide a direct measurement of k_{11} (designated as $k_{11(ex)}$).

TABLE I. Comparison of Self-Exchange Electron-Transfer Rate Constants for Cu(II)/(I) Systems in Aqueous Solution at 25 °C As Determined Directly from NMR Line-Broadening and As Calculated from Reduction and Oxidation Cross Reactions Utilizing the Marcus Relationship

Complexed Ligand	NMR $\log k_{11(ex)}$	Marcus Calculations from Cross Reactions	
		$\log k_{11(Red)}$	$\log k_{11(Ox)}$
[13]aneS$_4$	5.60	5.8 → 6.5	-2.3 → 4.9
[14]aneS$_4$	3.88	3.4 → 4.0	0 → 2.6
[15]aneS$_4$	3.70	3.1 → 4.0	1.2 → 3.3
syn-[14]aneS$_4$-diol	3.40	3.5 → 3.9	-0.2 → 2.6
anti-[14]aneS$_4$-diol		4.1 → 4.4	-1.9 → 2.7
Z-cyhx-[14]aneS$_4$	4.78		
E-cyhx-[14]aneS$_4$	<2.5		

[14]aneS$_4$ syn-[14]aneS$_4$-diol   anti-[14]aneS$_4$-diol   Z-cyhx-[14]aneS$_4$ E-cyhx-[14]aneS$_4$
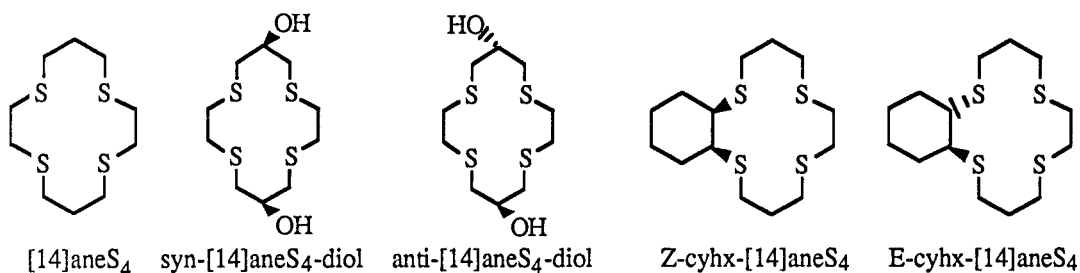
Under normal circumstances, it would be expected that all of the k_{11} values should lie within about an order of magnitude (due to large uncertainties in the many parameters used in making such calculations). It will be noted that both the $k_{11(ex)}$ and $k_{11(Red)}$ values are within this margin of error for all systems. However, the $k_{11(Ox)}$ values are, in all cases, considerably smaller and tend to span a very wide range.

A thorough multi-faceted study has now been completed on the $Cu^{II/I}$([14]aneS$_4$) system which includes rapid-scan cyclic voltammetric studies (up to 80 kV s^{-1}) to determine the values of the individual rate constants for conformational change. Previously, we reported the results of low temperature (down to -77 °C) cyclic voltammetric studies on the $Cu^{II/I}$([14]aneS$_4$) system which permitted us to observe all of the processes associated with Scheme I (refs. 16, 27). Those studies, as well as the more recent work, have indicated that intermediate species **P** is much more stable than intermediate **Q**. Under conditions of low driving force, where the different conformational species are always equilibrated, pathway A should be favored. Thus, the NMR measurements, which are carried out under equilibrium conditions, must represent pathway A.

The rapid-scan cyclic voltammetric measurements have made it possible to evaluate the individual constants associated with each of the conformational interconversions in Scheme I (ref. 18). The resultant values for 25 °C in 80% methanol are as follows (all values in s^{-1}): $k_{PR} = 3 \times 10^3$, $k_{RP} = 60$, $k_{OQ} \approx 5$, $k_{QO} \approx 1.2 \times 10^5$. The 25 °C formal potentials for the **O** ⇌ **P** and **Q** ⇌ **R** redox pairs have also been determined from

the rapid-scan voltammetric measurements in 80% methanol as $E_{OP}{}^f = 0.59$ V and $E_{QR}{}^f \approx 0.95$ V, respectively, while the overall potential value is $E_{OR}{}^f = 0.69$ V. Since the last potential is 0.10 V higher than the corresponding aqueous value (ref. 28), we have assumed that the same solvent correction applies to the microscopic redox couples. These corrected aqueous microscopic potential values and the NMR value for $k_{11(ex)}$ have then been applied to the Marcus relationship (eq 2) to generate estimates of k_{2A} for reactions with various counter reagents.

As noted in the preceding section, the applicable limiting equations for systems in which pathway A is dominant are dependent on the relative magnitude of k_{2A} [A_{Ox}] and k_{PR} (eqs 4a, 4b, 5a, 5b). Using our calculated values of k_{2A} and our experimental value of k_{RP}, we have calculated the "critical" concentration of the oxidized form of the counter reagent which would cause these two terms to become equal (i.e., [A_{Ox}] = k_{PR}/k_{2A}), thereby indicating the conditions under which a transition to gated behavior should occur (ref. 17). For most of the *reductants* with which we have reacted Cu^{II}([14]aneS$_4$), these "critical" values of [A_{Ox}] range from 0.1 to 100 M, greatly exceeding the concentrations used in our kinetic measurements. Thus, we conclude that eq 4a should apply to the kinetic measurements for all *reduction* studies which have been conducted with this system and **normal Marcus behavior should be observed**. This explains the good agreement obtained between the $k_{11(Red)}$ values and the NMR value for $k_{11(ex)}$ as shown in Table I. For the strongest oxidizing agents, however, the critical values of [A_{Ox}] are well below 10^{-6} M, indicating that, for these reagents, our kinetic measurements involving Cu^IL oxidation were carried out under conditions where the rate for the electron-transfer step exceeds the rate of conformational change $R \rightarrow P$. Thus, the smallest "apparent" values of $k_{11(Ox)}$ in Table I either reflect the rate constant for conformational change or a complete switch to pathway B.

For the oxidation of Cu^I([14]aneS$_4$) with two reagents having an intermediate "driving force," $Ru^{III}(NH_3)_4bpy$ and Ni^{III}([14]aneN$_4$), the calculated critical concentrations are about 10^{-3} and 10^{-5} M, respectively, almost exactly the concentration levels which we used in our kinetic measurements. Presumably, therefore, these latter oxidation reactions are entering into the region of conformationally-limited behavior. To test the premise that the onset of conformationally-limiting behavior had been reached, a large number of stopped-flow kinetic studies were carried out using Ni^{III}([14]aneN$_4$) as the oxidant in which the concentration of the latter reagent was varied by 1000-fold (8 µM to 8 mM). Since it was not clear that either limiting condition applied (i.e., either eq 5a or 5b), however, the entire first term in eq 5 was presumed to represent the observed (apparent) second-order rate constant, k_{21}. By inverting this term, the variables may be separated to produce a simple linear expression,

$$\frac{1}{k_{21}} = \frac{[A_{Ox}]}{k_{RP}} + \frac{K_{PR}}{k_{2A}} \tag{6}$$

where $K_{PR} = k_{PR}/k_{RP}$. A plot of $(k_{21})^{-1}$ as a function of [Ni^{III}([14]aneN$_4$)] (i.e., [A_{Ox}]) yielded a reciprocal slope of $k_{RP} = 50 \pm 10$ s^{-1}. This is in close agreement with the value obtained from the rapid-scan cyclic voltammetric measurements in 80% methanol as cited above (i.e., $k_{RP} = 60$ s^{-1}) and demonstrates that the onset of conformationally-limited electron-transfer kinetics has occurred.

Similar extensive cross reaction studies involving $Cu^{II/I}$([13]aneS$_4$) and $Cu^{II/I}$([15]aneS$_4$) have also been carried out in our laboratories. These specific complexes were selected to represent systems with differing geometric preferences in either the oxidized or reduced state relative to $Cu^{II/I}$([14]aneS$_4$). Therefore, it was postulated that the onset of gated electron-transfer behavior might involve different limiting conditions. As noted in Table I, both of these latter systems also show consistent $k_{11(Red)}$ values which are in agreement with the $k_{11(ex)}$ values determined by NMR line-broadening measurements; and, once again, the corresponding $k_{11(Ox)}$ values tend to decrease as the product of $K_{21} k_{22}$ increases (i.e., as k_{21} increases). Interestingly, the trends suggest that the pertinent rate constant for conformational change, k_{RP} is larger in both of these latter systems than in the corresponding $Cu^{II/I}$([14]aneS$_4$) system. Examination of the oxidation behavior in terms of eq 6 is now in progress.

In examining our ability to control the rate constants associated with conformational change in the Cu(II)/(I) systems, we have recently begun an investigation of the electron-transfer kinetics of cyclohexyl derivatives of [14]aneS$_4$ including the Z and E isomers. Table I lists the preliminary values for $k_{11(ex)}$ for these two Cu(II)/(I) systems as determined from NMR line-broadening measurements. In both cases, the rate constants are considerably different than that for the parent system. This implies that the electron-transfer kinetics for Cu(II)/(I) may be controlled with appropriate manipulation of the ligand structure. Other studies on complexes involving non-cyclic branched ligands indicate that pathway B is favored over pathway A for ligand systems which accommodate tetrahedral coordination more readily than planar coordination. As a result, gated behavior is observed for $Cu^{II}L$ *reduction* rather than for Cu^IL *oxidation* in such systems. These results suggest that it will be possible to control both the conditions for the onset of gated electron-transfer behavior and the direction in which such gated behavior is likely to occur.

REFERENCES

1. B. L. Vallee and R. J. P. Williams, Proc. Natl. Acad. Sci. USA 59, 498-505 (1968).
2. A. G. Lappin, C. A. Lewis and C. A. Ingledew, Inorg. Chem. 24, 1446-1450 (1985).
3. P. Rosen and I. Pecht, Biochemistry 15, 775-786 (1976).
4. M. C. Silvestrini, M. Brunori, M. T. Wilson and V. M. Darley-Usmar, J. Inorg. Biochem. 14, 327-338 (1981).
5. A. G. Szabo, T. M. Stepanik, D. M. Wayner and N. M. Young, Biophys. J. 41, 233-244 (1983).
6. (a) R. Bechtold, C. Kuehn, C. Lepre and S. S. Isied, Nature 322, 286-288 (1986). (b) J. Feitelson and G. McLendon, Biochemistry 30, 5051-5055 (1991). (c) B. G. Malmstrom and T. Nilsson, Ann. N.Y. Acad. Sci. 550, 177-184 (1988). (d) J. M. Nocek, N. Liang, S. A. Wallin, A. G. Mauk and B. M. Hoffman, J. Am. Chem. Soc. 112, 1623-1625 (1990). (e) M. T. Wilson, T. Alleyne, M. Clague, K. Conroy and B. El-Agez, Ann. N. Y. Acad. Sci. 550, 167-176 (1988). (f) L.-H. Zang, A. H. Maki, J. Am. Chem. Soc. 112, 4346-4351 (1990). (g) S. S. Isied, Electron Transfer in Biology and the Solid State, pp. 91-100, M. K. Johnson, R. B. King, D. M. Kurtz, Jr., C. Kutal, M. L. Norton and R. A. Scott, Eds., American Chemical Society, Washington, D.C. (1990). (h) M. C. Walker and G. Tollin, Biochemistry 30, 5546-5555 (1991). (i) S. A. Wallin, E. D. A. Stemp, A. M. Everest, J. M. Nocek, T. L. Netzel and B. M. Hoffman, J. Am. Chem. Soc. 113, 1842-1844 (1991).
7. (a) B. M. Hoffman and M. A. Ratner, J. Am. Chem. Soc. 109, 6237-6243 (1987); cf., ibid., 110, 8267. (b) B. M. Hoffman, M. A. Ratner and S. A. Wallin, Electron Transfer in Biology and the Solid State, pp. 125-146, M. K. Johnson, R. B. King, D. M. Kurtz, Jr., C. Kutal, M. L. Norton and R. A. Scott, Eds., American Chemical Society, Washington, D.C. (1990).
8. (a) B. S. Brunschwig and N. Sutin, J. Am. Chem. Soc. 111, 7454-7465 (1989). (b) N. Sutin and B. S. Brunschwig, Electron Transfer in Biology and the Solid State, pp. 65-88, M. K. Johnson, R. B. King, D. M. Kurtz, Jr., C. Kutal, M. L. Norton and R. A. Scott, Eds., American Chemical Society, Washington, D.C. (1990).
9. J. M. Pratt, J. Inorg. Biochem. 28, 145-153 (1986).
10. (a) B. J. Hathaway, Coord. Chem. Rev. 35, 211-252 (1981). (b) B. J. Hathaway and D. E. Billing, Coord. Chem. Rev. 5, 143-207 (1970).
11. A. W. Addison, Inorg. Chim. Acta 162, 217-220 (1989).
12. M. M. Bernardo, M. J. Heeg, R. R. Schroeder, L. A. Ochrymowycz and D. B. Rorabacher, Inorg. Chem. 31, 191-198 (1992).
13. (a) V. B. Pett, L. L. Diaddario, Jr., E. R. Dockal, P. W. Corfield, C. Ceccarelli, M. D. Glick, L. A. Ochrymowycz and D. B. Rorabacher, Inorg. Chem. 22, 3661-3670 (1983). (b) P. W. R. Corfield, C. Ceccarelli, M. D. Glick, I. W.-Y. Moy, L. A. Ochrymowycz and D. B. Rorabacher, J. Am. Chem. Soc. 107, 2399-2404 (1985).
14. D. B. Rorabacher, M. J. Martin, M. J. Koenigbauer, M. Malik, R. R. Schroeder, J. F. Endicott and L. A. Ochrymowycz, Copper Coordniation Chemistry: Biochemical and Inorganic Perspectives, pp. 167-201, K. D. Karlin and J. Zubieta, Eds. Adenine Press, Guilderland, New York (1983).
15. M. J. Martin, J. F. Endicott, L. A. Ochrymowycz and D. B. Rorabacher, Inorg. Chem. 26, 3012-3022 (1987).
16. D. B. Rorabacher, M. M. Bernardo, A. M. Q. Vande Lande, G. H. Leggett, B. C. Westerby, M. J. Martin and L. A. Ochrymowycz, Pure Appl. Chem. 60, 501-508 (1988).
17. N. E. Meagher, K. L. Juntunen, C. A. Salhi, L. A. Ochrymowycz and D. B. Rorabacher, J. Am. Chem. Soc., in press.
18. P. V. Robandt, R. R. Schroeder and D. B. Rorabacher, submitted for publication.
19. (a) R. A. Marcus, J. Chem. Phys. 24, 966-978 (1956). (b) R. A. Marcus, Discuss. Faraday Soc. 29, 21-31 (1960). (c) R. A. Marcus, J. Chem. Phys. 43, 679-701 (1965). (d) R. A. Marcus and N. Sutin, Biochim. Biophys. Acta 811, 265-322 (1985).
20. (a) M. A. Augustin and J. K. Yandell, Inorg. Chim. Acta 37, 11-18 (1979). (b) M. A. Augustin and J. K. Yandell, Inorg. Chem. 18, 577-583 (1979).
21. G. S. Yoneda, G. L. Blackmer and R. A. Holwerda, Inorg. Chem. 16, 3376-3378 (1977).
22. R. A. Holwerda, Inorg. Chem. 21, 2107-2109 (1982).
23. J. K. Yandell, Copper Coordination Chemistry: Biochemical and Inorganic Perspectives, pp. 157-166, K. D. Karlin and J. Zubieta, Eds., Adenine Press, Guilderland, New York (1983).
24. (a) A. G. Lappin, M. P. Youngblood and D. W. Margerum, Inorg. Chem. 19, 407-413 (1980). (b) N. Al-Shatti, A. G. Lappin and A. G. Sykes, Inorg. Chem. 20, 1466-1469 (1981). (c) K. M. Davies, Inorg. Chem. 22, 615-619 (1983).
25. C.-W. Lee and F. C. Anson, J. Phys. Chem. 87, 3360-3362 (1983).
26. C.-W. Lee and F. C. Anson, Inorg. Chem. 23, 837-844 (1984).
27. M. M. Bernardo, P. V. Robandt, R. R. Schroeder and D. B. Rorabacher, J. Am. Chem. Soc. 111, 1224-1231 (1989).
28. M. M. Bernardo, R. R. Schroeder and D. B. Rorabacher, Inorg. Chem. 30, 1241-1247.