complexes are stable at room temperature toward such dissociation.

Acknowledgment. We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AFOSR-75-2689.

Registry No. [CpMo(CO)$_2$(PzH)$_2$]Cl, 64129-84-6; [CpMo(CO)$_2$(PzH)$_2$][PF$_6$], 64057-34-7; CpMo(CO)$_2$(PzH)Cl, 64057-32-5; [CpMo(CO)$_2$(ImH)$_2$]Cl, 64090-75-1; [CpMo(CO)$_2$(ImH)$_2$][PF$_6$], 64057-31-4; CpMo(CO)$_2$(ImH)Cl, 64057-29-0; CpMo(CO)$_2$(C$_6$H$_4$N$_3$H)Cl, 64091-66-3; CpMo(CO)$_2$(py)Cl, 64057-28-9; [CpW(CO)$_2$(PzH)$_2$]Cl, 64057-27-8; CpW(CO)$_2$(PzH)Cl, 64057-26-7; [CpW(CO)$_2$(ImH)$_2$]Cl, 64057-25-6; CpW(CO)$_2$(ImH)Cl, 64057-37-0; CpMo(CO)$_3$Cl, 12128-23-3; CpW(CO)$_3$Cl, 12128-24-4; ^{13}C, 14762-74-4.

References and Notes

(1) For part 11 of this series see R. B. King and K.-N. Chen, *Inorg. Chem.*, **16**, 2648 (1977).
(2) Postdoctoral research associate, 1975–1977.
(3) R. B. King and K.-N. Chen, *Inorg. Chem.*, **16**, 1164 (1977).
(4) S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3165 (1967).
(5) W. Beck, A. Melnikoff, and R. Stahl, *Chem. Ber.*, **99**, 3721 (1966).
(6) A. R. Manning, *J. Chem. Soc. A*, 1984 (1967).
(7) R. B. King, R. H. Reimann, and D. J. Darensbourg, *J. Organomet. Chem.*, **93**, C23 (1975).
(8) O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Am. Chem. Soc.*, **94**, 2550 (1972).
(9) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).
(10) K. Schofield, M. R. Grimmett, and B. R. T. Keene, "Heteroaromatic Nitrogen Compounds: The Azoles", Cambridge University Press, Cambridge, England, 1976, Table A.4, pp 281–286.
(11) (a) For a general discussion of the trans effect see F. Basolo and R. G. Pearson, *Prog. Inorg. Chem.*, **4**, 381–453 (1962). (b) For a discussion of the extension of the trans effect to C$_5$H$_5$MA$_4$ systems see R. B. King and L. W. Houk, *Can. J. Chem.*, **47**, 2959 (1969).
(12) K. W. Barnett, Ph.D. Thesis, University of Wisconsin, 1967.
(13) K. W. Barnett and D. W. Slocum, *J. Organomet. Chem.*, **44**, 1 (1972).

Contribution from the Department of Chemistry,
Texas Tech University, Lubbock, Texas 79409

Kinetics of the Oxidation of Cu(phen)$_2^+$ and Cu(bpy)$_2^+$ by Aminopolycarboxylatocobalt(III) Complexes

Gerald S. Yoneda, Gary L. Blackmer, and Robert A. Holwerda*

Received May 26, 1977 AIC70385J

Considerable progress has been made recently toward understanding the mechanisms by which blue (or type 1) copper proteins donate and accept electrons.[1] We have reported that the electron-transfer reactivity of reduced (Cu(I)) stellacyanin with the ethylenediaminetetraacetatocobaltate(III) ion (Co(EDTA)$^-$) differs markedly from that observed when the tris(1,10-phenanthroline)cobalt(III) ion (Co(phen)$_3^{3+}$) is the oxidant.[2] Observed rate constants for the oxidation of cuprous stellacyanin (St(I)) by Co(EDTA)$^-$ approach a saturation limit with increasing [Co(EDTA)$^-$] at pH 7, consistent with a mechanism involving rapid preequilibrium oxidant–protein complex formation followed by rate-limiting intramolecular Cu(I) to Co(III) electron transfer

$$\mathrm{Co(EDTA)^- + St(I)} \underset{}{\overset{Q_\mathrm{p}}{\rightleftarrows}} \mathrm{Co(EDTA)^-\text{–}St(I)} \xrightarrow{k_2} \mathrm{Co(EDTA)^{2-}\text{–}St(II)}$$

(Q_p = 149 M^{-1}, k_2 = 0.169 s^{-1}; 25.1 °C, pH 7.0, μ 0.5 M (phosphate)).[2] Activation parameters based on k_2 ($\Delta H^\ddagger$ = 1.8 kcal/mol, $\Delta S^\ddagger$ = −56 cal/(mol deg)) suggest that electron transfer within the oxidant–protein complex is substantially nonadiabatic. By contrast, second-order kinetics were found for the oxidation of reduced stellacyanin by Co(phen)$_3^{3+}$ (k = 1.8 × 10^5 M^{-1} s^{-1}; 25 °C, pH 7.0, μ 0.5 M (phosphate)).[3] Activation parameters for the Co(phen)$_3^{3+}$–St(I) reaction ($\Delta H^\ddagger$ = 6.1 kcal/mol, $\Delta S^\ddagger$ = −14 cal/(mol deg)) and comparisons of apparent St(I)–St(II) self-exchange electron-transfer rate constants obtained by applying relative Marcus theory to rate data for the cross reactions with Fe(EDTA)$^{2-}$ and Co(phen)$_3^{3+}$ indicate that oxidation of the protein Cu(I) center by Co(phen)$_3^{3+}$ occurs by an adiabatic outer-sphere mechanism.[3]

The unusual redox reactivity of Co(EDTA)$^-$ with reduced stellacyanin has been attributed to the formation of an oxidant–protein precursor complex in which overlap between the donor redox orbital of the distorted tetrahedral type 1 Cu(I) center and the e$_g$ acceptor orbital of the oxidant is poor; it is thus concluded that nonadiabicity is not a requisite feature of the outer-sphere oxidation of Cu(I) by Co(EDTA)$^-$.[2] In order to provide further support for this conclusion we report here rate data for the oxidation of the bis(1,10-phenanthroline)copper(I) (Cu(phen)$_2^+$) and bis(2,2′-bipyridine)copper(I) (Cu(bpy)$_2^+$) ions by three aminopolycarboxylatocobalt(III) complexes: Co(EDTA)$^-$, Co(CyDTA)$^-$, Co(PDTA)$^-$ (CyDTA = *trans*-1,2,-diaminocyclohexanetetraacetate, PDTA = propylenediaminetetraacetate).

Experimental Section

Reagent grade chemicals and triply distilled water were used for all experiments. Nitrogen gas passed through two chromous scrubbing towers was used to deoxygenate kinetics solutions. Sodium acetate buffers were used to maintain the ionic strength at 0.5 M and the pH at 6.0 in all experiments.

Na[Co(EDTA)]·4H$_2$O,[4] K[Co(PDTA)]·H$_2$O,[5] and K[Co(CyDTA)]·3H$_2$O[6] were prepared by literature methods. The purity of these salts was established through microanalyses for C, H, and N and through comparisons of UV–visible spectra with those in the literature.[7] Solutions of the sodium salts of all oxidants were used in kinetic studies; to exchange K$^+$ for Na$^+$, solutions of K[Co(PDTA)] and K[Co(CyDTA)] were passed through a column containing Chelex 100 cation-exchange resin in the sodium form. The concentrations of oxidant solutions were evaluated spectrophotometrically using literature extinction coefficients.[7]

Solutions of Cu(phen)$_2^+$ and Cu(bpy)$_2^+$ were prepared by mixing a tenfold excess of ligand with cupric acetate and reducing anaerobically with the equivalent amount of ascorbic acid. Formation constants for Cu(phen)$_2^+$ and Cu(bpy)$_2^+$[8] ensure that these are the only Cu(I) species present in appreciable concentration under the experimental conditions. This conclusion was reinforced by demonstrating that observed rate constants do not vary as the ratio [ligand]$_\mathrm{tot}$/[Cu(I)]$_\mathrm{tot}$ is varied from 2.1 to 50. To avoid contaminating Cu(phen)$_2^+$ and Cu(bpy)$_2^+$ solutions with iron, all transfers were made using Teflon needles.

The kinetics of oxidation of Cu(phen)$_2^+$ and Cu(bpy)$_2^+$ by aminopolycarboxylatocobalt(III) complexes was monitored by following the absorbance decrease at 435 nm (Cu(I) to ligand charge-transfer absorption) using a Durrum D-110 stopped flow spectrophotometer. Pseudo-first-order conditions were employed, maintaining the concentration of the cuprous complex at ca.10–25 μM and varying the oxidant concentration from 2.5 × 10^{-4} to 2.5 × 10^{-2} M (10–1000-fold excess). Absorbance–time data were collected as photographs of traces on a Tektronix 564 B oscilloscope or as output from a Hewlett-Packard Model 7004 B X-Y recorder. Three separate runs were usually performed for each pair of solutions mixed in the stopped-flow apparatus.

Absorption spectra were recorded using a Cary 17 spectrophotometer, and pH measurements were made with an Ionalyzer Model 801 instrument.

Results and Discussion

First-order plots of ln ($A_t - A_\infty$) vs. time derived from absorbance–time data for the oxidation of Cu(phen)$_2^+$ and Cu(bpy)$_2^+$ by Co(EDTA)$^-$, Co(PDTA)$^-$, and Co(CyDTA)$^-$ were found to be linear for greater than 90% completion of the reactions. Observed rate constants (k_obsd) were derived from the linear least-squares slopes of these plots. Data obtained for Co(EDTA)$^-$ as the oxidant are given in Table I.[9] For all of the redox reactions considered, plots of k_obsd (25 °C) vs. [oxidant] were found to be linear with small positive intercepts (0.04–0.23 s^{-1}) over the 50–100-fold concentration ranges covered. We conclude that electron transfer from Cu(I) to Co(III) obeys the rate law

$$-\mathrm{d[Cu(I)]}/\mathrm{d}t = k\mathrm{[Cu(I)]\,[Co(III)]}$$

Table I. Rate Constants for the Oxidation of $Cu(phen)_2^+$ and $Cu(bpy)_2^+$ by $Co(EDTA)^-$ [a]

Temp, °C	$10^3[Co(EDTA)^-]$, M	k_{obsd}, s^{-1}	
		$Cu(phen)_2^+$	$Cu(bpy)_2^+$
8.8	2.50	0.403	
		0.424	
		0.399	
	25.00	3.94	
		4.20	
8.9	2.50		0.397
			0.399
			0.393
	25.00		3.58
			3.61
			3.51
14.7	2.50	0.540	0.497
		0.547	0.500
		0.554	
	10.00	2.07	1.97
		2.00	1.84
			1.90
	25.00	4.68	5.10
		4.78	5.00
			5.09
25.1	0.25	0.247	0.164
		0.250	0.144
		0.245	0.157
	0.50	0.357	0.250
		0.363	0.254
		0.353	0.258
	1.00	0.485	0.390
		0.468	0.400
		0.482	0.386
	2.50	0.942	0.992
		0.958	0.963
		0.933	0.942
	5.00	1.87	1.51
		1.90	1.52
		1.88	1.51
		1.94	
	12.50	4.36	3.52
		4.32	3.50
		4.35	3.47
			3.43
	25.00	7.79	6.81
		7.97	6.39
		7.96	6.61
30.3	1.00		2.69
			2.60
			2.64
	2.50		7.68
			7.52
			7.73
30.8	2.50	0.996	
		0.940	
	5.00	2.04	
		2.13	
	25.00	8.22	
		8.02	
34.6	2.50	1.17	
		1.13	
	5.00	2.09	
		2.17	
		2.31	
	25.00	11.1	
		11.1	
		10.9	
35.8	1.00		2.37
			2.47
			2.33
	2.50		10.8
			11.0
			10.9

[a] pH 6.0, μ 0.5 M (acetate).

in each case, as the small intercepts reasonably may be attributed to reactions of $Cu(bpy)_2^+$ or $Cu(phen)_2^+$ with traces of oxygen which cannot be excluded from oxidant solutions contained in the drive syringe of the stopped-flow apparatus. Second-order rate constants reported for the oxidation of $Cu(phen)_2^+$ and $Cu(bpy)_2^+$ by O_2 are 8.2×10^3 M^{-1} s^{-1} (25 °C, μ 0.05 M phosphate buffer (pH 6.1–8.1) containing 2.5 M acetonitrile)[10] and 6.5×10^3 M^{-1} s^{-1} (25 °C, 0.02 M acetate buffer (pH 5.0)),[11] respectively. Assuming that similar rate constants pertain under our conditions, we estimate that the small positive intercepts in k_{obsd} vs. [oxidant] plots could result from oxygen concentrations of ca. 10–25 μM. Room temperature second-order rate constants derived from the slopes of these plots and activation parameters obtained from linear Eyring plots of temperature dependence data[9,12] are given in Table II.

Rate constants for the six reactions under consideration are remarkably similar, spanning less than a twofold range at 25 °C; for both $Cu(phen)_2^+$ and $Cu(bpy)_2^+$, room temperature oxidation rates decrease according to $Co(EDTA)^- > Co(PDTA)^- > Co(CyDTA)^-$. This similarity extends to the activation parameters as well, particularly in the case of the $Co(EDTA)^-$ and $Co(PDTA)^-$ oxidations. Rate constants for the adiabatic, outer-sphere reduction of $Co(EDTA)^-$, $Co(PDTA)^-$, and $Co(CyDTA)^-$ by a given electron donor are expected to be similar on the basis of relative Marcus theory,[13] as standard reduction potentials[14] and self-exchange electron-transfer rate constants[15] do not vary appreciably within this family of oxidants.

Activation parameters of the oxidations of $Cu(phen)_2^+$ and $Cu(bpy)_2^+$ by $Co(EDTA)^-$, $Co(PDTA)^-$, and $Co(CyDTA)^-$ are typical of those found for adiabatic outer-sphere redox reactions and indeed are not much different from those reported for other electron-transfer reactions involving this family of oxidants.[14,16] This observation reinforces our previous conclusion[2] that the reactivity of $Co(EDTA)^-$ with Cu(I) in the blue protein stellacyanin is not typical of the interaction of Cu(I) with this oxidant. Kinetic studies of the reactions of Cr^{2+} and Fe^{2+} with $Co(EDTA)^-$ have suggested that the coordinated carboxyl groups play an important role in mediating electron transfer to the cobalt(III) center.[17,18] Considering the structure of $Co(EDTA)^-$ (Figure 1), it seems clear that substitutions on the methylene groups of the NCH_2CH_2N backbone of the ligand will have little effect on the accessibility of the π systems of these carboxyl groups to inner- or outer-sphere contact with reductants. On this basis it is not surprising that activation parameters for the oxidation of $Cu(phen)_2^+$ and $Cu(bpy)_2^+$ are insensitive even to the substitution of a cyclohexyl group for CH_2CH_2 in the backbone of the polycarboxylate ligand.

Apparent self-exchange electron-transfer rate constants calculated on the basis of relative Marcus theory have provided a convenient framework for comparing the inherent redox reactivities of blue copper proteins.[1,19] Similarly, using the equation[13]

$$\log k_{11} = 2 \log k_{12} - \log k_{22} - 16.9 \Delta E^\circ$$

it is possible to estimate self-exchange electron-transfer rate constants (k_{11}) for the $Cu(phen)_2^{+/2+}$ and $Cu(bpy)_2^{+/2+}$ couples using experimental rate constants for the cross-reactions of the cuprous complexes with $Co(EDTA)^-$ (k_{12}). The other parameters required include the self-exchange rate constant for the $Co(EDTA)^{2-/-}$ couple ($k_{22} = 3.2 \times 10^{-7}$ M^{-1} s^{-1})[20] and standard reduction potentials for $Co(EDTA)^-$ (0.40 V),[10] $Cu(phen)_2^{2+}$ (0.174 V),[8] and $Cu(bpy)_2^{2+}$ (0.120 V);[8] ΔE° represents the cell potential for the cross-reaction. On this basis we estimate self-exchange rate constants of 5×10^7 and 4×10^6 M^{-1} s^{-1} for the $Cu(phen)_2^{+/2+}$ and $Cu(bpy)_2^{+/2+}$ couples, respectively. The validity of these estimates is suggested by the observation that the Marcus equation successfully correlates cross-reaction and self-exchange rates for

Table II. Rate Parameters for the Oxidation of $Cu(phen)_2^+$ and $Cu(bpy)_2^+$ [a,b]

	$Cu(phen)_2^+$			$Cu(bpy)_2^+$		
Oxidant	$10^{-2}k$, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	$10^{-2}k$, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}
$Co(EDTA)^-$	3.12 (0.29)	6.1 (0.6)	−27 (2)	2.59 (0.42)	4.5 (0.7)	−32 (2)
$Co(PDTA)^-$	2.85 (0.72)	6.1 (1.5)	−27 (3)	2.01 (0.29)	4.1 (0.6)	−34 (2)
$Co(CyDTA)^-$	1.75 (0.28)	4.8 (0.8)	−32 (2)	1.76 (0.21)	6.5 (0.8)	−26 (2)

[a] 25.0 °C, pH 6.0, μ 0.5 M (acetate). [b] Estimated uncertainties are given in parentheses.

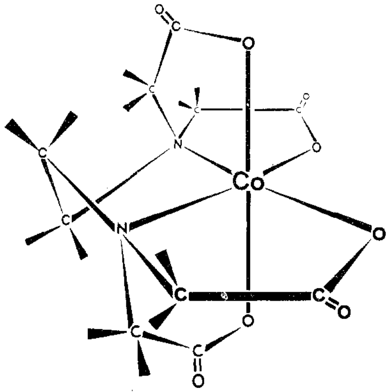

Figure 1. Structure of the $Co(EDTA)^-$ ion.

a number of reactions involving aminopolycarboxylatocobalt(III) complexes.[21] Interestingly, these self-exchange rate constant estimates are comparable to those calculated for the blue copper protein stellacyanin (ca. 10^5–10^7 M^{-1} s^{-1})[19] on the basis of rate data for cross-reactions with $Fe(EDTA)^{2-}$, $Co(phen)_3^{3+}$, and several tris complexes of 1,10-phenanthroline derivatives with cobalt(III). The inherent redox reactivities of the blue copper proteins are not uniformly high, however, as estimated k_{11} values for azurin and plastocyanin fall several orders of magnitude lower than that for stellacyanin.[1,19]

The rate constant k for an outer-sphere oxidation–reduction reaction may be expressed as

$$k = Q_p k_2$$

under conditions where formation of the precursor complex is not rate determining and second-order kinetics is observed; Q_p is the formation constant for the precursor complex and k_2 is the first-order rate constant for electron transfer within the precursor complex, forming the successor complex and ultimately products.[22] On the assumption that electrostatic factors alone govern the value of Q_p, approximate precursor complex formation constants may be obtained from the expressions[22,23]

$$Q_p = (4\pi N r^3/3000) \exp[-U(r)/RT]$$

$$U(r) = q_1 q_2/[D_s r(1 + \kappa r)]$$

where $U(r)$ is the Debye–Hückel interaction potential, r is the distance between the centers of the reactants, q_1 and q_2 are the charges on the reactants, κ is the Debye–Hückel ionic strength parameter, and D_s is the dielectric constant of the medium. Estimating ionic radii for $Co(EDTA)^-$, $Cu(phen)_2^+$, and $Cu(bpy)_2^+$ at 4.7, 6.9, and 6.5 Å, respectively, Q_p values of the order of 4 M^{-1} are calculated for the reactions of both cuprous complexes with $Co(EDTA)^-$. This value falls far below that of 149 M^{-1} observed for the oxidation of reduced stellacyanin by $Co(EDTA)^-$, as expected considering the absence of saturation in k_{obsd} vs. $[Co(EDTA)^-]$ plots for the oxidation of $Cu(phen)_2^+$ and $Cu(bpy)_2^+$. Assuming a minimum r value of 11 Å for the interaction of reduced stellacyanin with $Co(EDTA)^-$, an unreasonably high apparent protein binding site charge of ≥ 28 is calculated upon substituting the observed Q_p value into the above equations. Stellacyanin contains a maximum of 19 positively charged amino acid side chains (11 lysine, 4 histidine, 4 arginine)[24] at pH 7, and not all of these residues are expected to be tightly grouped on the protein surface near the binding site for $Co(EDTA)^-$. These calculations indicate then that the high precursor complex formation constant for the $Co(EDTA)^-$–blue copper protein reaction cannot be satisfactorily accounted for in terms of electrostatic considerations alone. Hydrogen bonding involving the coordinated carboxyl groups and van der Waals attractions established through the penetration of the hydrophobic backbone of the ligand into the interior of the protein may also be partially responsible for the unusually high Q_p value.[2]

Acknowledgment. We thank the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. G.L.B. also wishes to thank the Robert A. Welch Foundation, Grant D-531, for support.

Registry No. $Cu(phen)_2^+$, 17378-82-4; $Cu(bpy)_2^+$, 23852-07-5; $Co(EDTA)^-$, 15136-66-0; $Co(PDTA)^-$, 50545-85-2; $Co(CyDTA)^-$, 20080-68-6.

Supplementary Material Available: A complete listing of observed rate constants (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. A. Holwerda, S. Wherland, and H. B. Gray, *Annu. Rev. Biophys. Bioeng.*, **5**, 363 (1976).
(2) G. S. Yoneda and R. A. Holwerda, *Bioinorg. Chem.*, in press.
(3) J. V. McArdle, C. L. Coyle, H. B. Gray, G. S. Yoneda, and R. A. Holwerda, *J. Am. Chem. Soc.*, **99**, 2483 (1977).
(4) F. P. Dwyer, E. C. Gyarfas, and D. P. Mellor, *J. Phys. Chem.*, **59**, 296 (1955).
(5) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **81**, 2955 (1959).
(6) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 2610 (1961).
(7) (a) L. Rosenheim, D. Speiser, and A. Haim, *Inorg. Chem.*, **13**, 1571 (1974); (b) N. Tanaka and H. Ogino, *Bull. Chem. Soc. Jpn.*, **37**, 877 (1964).
(8) B. R. James and R. J. P. Williams, *J. Chem. Soc.*, 2007 (1961).
(9) See supplementary material for a complete tabulation of k_{obsd} values.
(10) A. L. Crumbliss and L. J. Gestaut, *J. Coord. Chem.*, **5**, 109 (1976).
(11) I. Pecht and M. Anbar, *J. Chem. Soc. A*, 1902 (1968).
(12) Rate constants for temperatures other than 25 °C were evaluated in some cases from $k = k_{obsd}/[\text{oxidant}]$, assuming that the reaction of Cu(I) with oxygen contributes negligibly to k_{obsd}. This assumption was made only when the oxidant concentration was high enough to ensure that the reaction of Cu(I) with Co(III) was responsible for at least 90% of the 435-nm absorbance change. Linear Eyring plots could be constructed using some rate constants obtained from the slopes of k_{obsd} vs. [oxidant] plots and others calculated as $k_{obsd}/[\text{oxidant}]$, suggesting the validity of the assumption made in obtaining the latter values.
(13) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).
(14) R. G. Wilkins and R. E. Yelin, *Inorg. Chem.*, **7**, 2667 (1968).
(15) Y. A. Im and D. H. Busch, *J. Am. Chem. Soc.*, **83**, 3362 (1961).
(16) B. Grossman and R. G. Wilkins, *J. Am. Chem. Soc.*, **89**, 4230 (1967).
(17) P. B. Wood and W. C. E. Higginson, *J. Chem. Soc. A*, 1645 (1966).
(18) P. B. Wood and W. C. E. Higginson, *J. Chem. Soc.*, 2116 (1965).
(19) S. Wherland and H. B. Gray in "Biological Aspects of Inorganic Chemistry", A. W. Addison, W. R. Cullen, D. Dolphin, and B. R. James, Ed., Wiley, New York, N.Y., 1977, p 289.
(20) Y. A. Im and D. H. Busch, *J. Am. Chem. Soc.*, **83**, 3357 (1961).
(21) L. E. Bennett, *Prog. Inorg. Chem.*, **18**, 1 (1973).
(22) N. Sutin in "Inorganic Biochemistry", G. L. Eichhorn, Ed., Vol. 2, Elsevier, Amsterdam, 1973, p 611.
(23) A. Haim and N. Sutin, *Inorg. Chem.*, **15**, 476 (1976).
(24) J. Peisach, W. G. Levine, and W. E. Blumberg, *J. Biol. Chem.*, **242**, 2847 (1967).