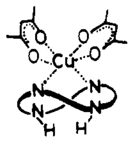
the acid dissociation constants K_3 and K_4 for H_2TPP are 10^9 times larger than those for H_2DPP; the formation of the SAT complex involving a deformation process seems to be thermodynamically unfavorable. The rapid metalation of H_2DPP is the result of high affinity for a metal ion due to nonplanarity of the porphyrin core.

Structures **1** and **2** are kinetically equivalent representations of the intermediate complex in the reaction of H_2DPP with $Cu(acac)_2$. In structure **1**, acetylacetonato anions bisligate to Cu^{2+}. In structue **2**, a single acetylacetonato anion serves as the ligand, while the other hydrogen-bonds to protons at the opposite side of Cu^{2+}. The metalation reaction proceeds only through the k_1 pathway, not through the k_2 pathway. One interpretation is that the SAT complex in the transition state of the reaction has structure **2**. The k_2 pathway is blocked by an acac ligand attached to the "back side" of the porphyrin, the acac ligand being likely to serve as an efficient proton acceptor in the k_1 pathway.



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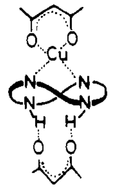

2

Similar rate enhancement caused by porphyrin ring distortion has been observed for the metalation reactions of *N*-alkylporphyrins.[6a,7a,19] However, several differences should be pointed out: (1) no saturation kinetics has been observed for *N*-alkylporphyrin systems; (2) therefore, there is no direct evidence of a SAT complex as an intermediate; (3) products of H_2DPP reactions with divalent metal ions are neutral metalloporphyrins instead of the monocationic species formed in reactions of *N*-alkylporphyrins, which are gradually dealkylated in DMF; (4) in the case of an *N*-alkylporphyrin, the metal ion may attack only one side of the porphyrin ring owing to steric hindrance of the alkyl group at the nitrogen atom.

The porphyrin core of *N*-alkyl derivatives is forced to distort from planarity by the bulky central *N*-alkyl groups. On the other hand, steric crowding of the peripheral substituents causes H_2DPP to adopt a nonplanar conformation. Hence, H_2DPP is far more appropriate as a model for the ferrochelatase transition-state intermediate in which the porphyrin ring is distorted because of steric and electronic interactions with amino acid residues in the active site.

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Kinetics of the Reaction of Copper(II) with Cobalt(II) Sepulchrate: Catalysis by Chloride Ion and Imidazole

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The kinetics of the oxidation of cobalt(II) sepulchrate by aqueous copper(II) have been studied in the presence of chloride ion, imidazole, and acetonitrile at 25 °C. The reaction rate increases with increasing concentrations of chloride ion (0.05–0.2 M in 0.50 M $HClO_4/LiClO_4$) and imidazole (0.025–0.09 M at pH 6.5, in 0.15 M $LiClO_4$), but is unaffected by 0.4 M acetonitrile (0.50 M $HClO_4/LiClO_4$). The reaction of $Cu^{2+}(aq)$ and $Co(sep)^{2+}$ is complicated by the rapid formation of copper metal, and it was necessary to use O_2 as a scavenger for $Cu^+(aq)$ in order to determine the rate constant of $5.0 \pm 0.25\ M^{-1}\ s^{-1}$ (0.02 M $HClO_4$, 0.48 M $LiClO_4$, 25 °C). This value and earlier results for reductions of Ru(III) complexes by $Cu^+(aq)$ give a self-exchange rate constant of $5 \times 10^{-7}\ M^{-1}\ s^{-1}$ for $Cu^{2+/+}(aq)$ from the Marcus cross relationship. The $Cu^{II}(Cl)_n$ complexes have rate constants of 1.6×10^3, 1.5×10^4, and $4.5 \times 10^5\ M^{-1}\ s^{-1}$ for $n = 1$–3. The change in reactivity can be accounted for in terms of Marcus theory by the increased driving force and reduced charge, with a self-exchange rate constant for the $Cu^{II/I}(Cl)_n$ species of $2 \times 10^{-4}\ M^{-1}\ s^{-1}$. The $Cu^{II}(Im)_n$ complexes show a much smaller change in reactivity (35, 70, and 120 $M^{-1}\ s^{-1}$ for $n = 2$–4) and a smaller self-exchange rate constant of $\sim 1 \times 10^{-7}\ M^{-1}\ s^{-1}$.

Introduction

It has been known for many years[1] that chloride ion catalyzes the oxidation of ascorbic acid by aqueous copper(II), and it has been determined recently[2] that the rate coefficient for the $[Cl^-][Cu^{2+}]$[ascorbate] pathway is 1.5×10^3 times larger than that for the uncatalyzed pathway. Chloride catalysis also was observed by Yandell[3] for the reaction of aqueous copper(II) and ferrocytochrome *c* in the presence of dioxygen. Yandell interpreted the results in terms of Cu(II)–Cl^- complexes, with specific rate constants for $Cu^{2+}(aq)$, $CuCl^+$, and $CuCl_2$ of 5.7, 2.3×10^2, and $5.6 \times 10^3\ M^{-1}\ s^{-1}$, respectively. The reactivity was ascribed, using Marcus theory,[4] to the increased driving force for the reaction because of the stronger complexation of Cu(I) by chloride ion. However, this interpretation predicts a Cu(II)/Cu(I) self-exchange rate constant of $5.2\ M^{-1}\ s^{-1}$, which is much higher than the current estimate[5] of $\sim 2 \times 10^{-4}\ M^{-1}\ s^{-1}$. If self-exchange rate changes are ignored, then the driving force effect predicts that $CuCl^+$ should be 15 times more reactive than $Cu^{2+}(aq)$. This is consistent with the factor of 39 found with ferrocytochrome *c*, but not with the factor of 6.4×10^2 for an outer-sphere mechanism with $CuCl^+$ in the ascorbate system. However, the latter is complicated by the possible formation of an inner-sphere Cu^{II}–ascorbate complex, so that Marcus theory may not be applicable.

In order to clarify the role of added potential ligands on oxidations by copper(II), we have studied the oxidation of a well characterized outer-sphere reagent, $Co(sep)^{2+}$,[6,7] in aqueous solution at 25 °C. The three ligands studied have been chosen because of their known complexation properties.[8] Chloride ion and imidazole complex with both Cu(I) and Cu(II), but more strongly with the former. Acetonitrile does not appear to complex

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Table I. Kinetic Results for the Oxidation of Co(sep)$^{2+}$ by Aqueous Copper(II) in the Presence of Chloride Ion[a] in 0.50 $HClO_4/LiClO_4$ at 25.0 °C

$10^2[Cu(II)]_0$, M	$10^2[Cl^-]_0$, M	$10^2[Cu(II)]_{free}$,[b] M	$10^2[Cl^-]_{free}$,[b] M	k, s^{-1} obsd	k, s^{-1} calcd[e]
0.510	5.00	0.456	4.94	1.36	1.25
0.510	7.50	0.432	7.42	2.15	2.26
0.510	9.00	0.418	8.90	3.01	3.04
0.510	12.0	0.393	11.9	4.78	5.00
0.510	15.0	0.369	14.8_5	7.30	7.61
0.510	20.0	0.335	19.8	12.7	13.5
0.600	5.00	0.536	4.93	1.46	1.47
0.600	9.00	0.492	8.89	3.80	3.56
1.20	5.00	1.07	4.87	2.80	2.89
2.00	5.00	1.79	4.79	4.36	4.71
3.00	5.00	2.70	4.69	7.05	6.87
3.00	9.00	2.48	8.46	16.4	16.4
5.00	5.00	4.51	4.50	11.2	10.8
0.510[c]	10.0	0.409_5	9.89	3.92	3.63
0.510[c]	20.0	0.335	19.8	14.3	13.5
0.510[d]	10.0	0.409_5	9.89	3.64	3.63
0.510[d]	20.0	0.335	19.8	14.0	13.5

[a] All runs are in 0.020 M $HClO_4$, unless otherwise indicated, with 3.0 × 10^{-4} M Co(sep)$^{2+}$, observed at 472 nm. [b] These concentrations refer to uncomplexed aqueous copper(II) and chloride ion calculated from the complex formation constants. [c] In 0.010 M $HClO_4$. [d] In 0.040 M $HClO_4$. [e] Calculated from least-squares best fit parameters to eq 1 as given in the text.

Table II. Kinetic Results for the Oxidation of Co(sep)$^{2+}$ by Aqueous Copper(II) in the Presence of Imidazole[a] in 0.15 M $LiClO_4$, pH 6.5, at 25.0 °C

$10^2[Cu(II)]_0$,[b] M	$10^2[Im]_0$,[b] M	$[Cu(II)]_{free}$,[c] M	$[Im]_{free}$,[c] M	k, s^{-1} obsd	k, s^{-1} calcd[e]
1.01	2.50	1.28×10^{-4}	9.02×10^{-4}	0.491	0.465
1.01	3.50	1.42×10^{-5}	2.22×10^{-3}	0.701	0.688
1.01	4.50	2.32×10^{-6}	4.15×10^{-3}	0.770	0.838
1.01	5.50	5.69×10^{-7}	6.47×10^{-3}	0.791	0.938
1.01	9.00	2.61×10^{-8}	1.58×10^{-2}	1.11	1.10
2.01[d]	5.00	1.63×10^{-4}	1.11×10^{-3}	1.00	1.02
2.01[d]	7.00	9.59×10^{-6}	3.25×10^{-3}	1.60	1.55
2.01[d]	9.00	8.95×10^{-7}	6.95×10^{-3}	1.96	1.90

[a] All runs are at pH 6.5 in an imidazole/imidazolium ion buffer, with 4.0 × 10^{-4} M Co(sep)$^{2+}$, observed at 472 nm. [b] These are the initial total concentrations of copper(II) and imidazole + imidazolium ion. [c] These concentrations refer to uncomplexed aqueous copper(II) and imidazole, calculated from the complex formation constants and pK_a = 7.03 for imidazolium ion. [d] The ionic strength is 0.18 M for these runs. [e] Calculated from least-squares best fit parameters to eq 1 as given in the text.

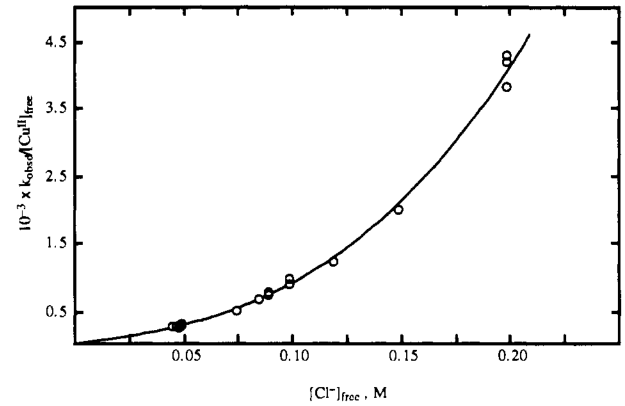

Figure 1. Chloride ion dependence of the rate constant for the oxidation of Co(sep)$^{2+}$ by aqueous copper(II) as predicted by eq 1 and parameters given in the text (25 °C in 0.50 M $LiClO_4$).

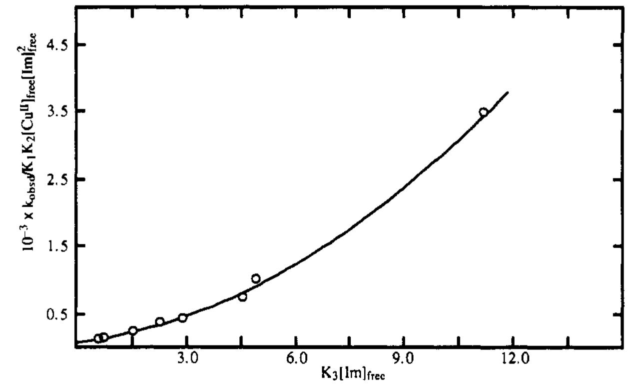

Figure 2. Dependence of the rate constant for the oxidation of Co(sep)$^{2+}$ by aqueous copper(II) and imidazole as predicted by eq 1 and parameters given in the text. K_1, K_2, and K_3 are the successive formation constants for Cu(imidazole)$_n^{2+}$ complexes. Results are at 25 °C in 0.15 M $LiClO_4$, pH 6.5.

significantly with Cu(II) in aqueous solution, but complexes strongly with Cu(I). The imidazole system is of further interest because Cu(II) in biological systems is often complexed by several imidazole functions from histidines.

The simplest view of these systems is shown in Scheme I, where only monocomplex formation is shown. If the difference between k_0 and k_1 is due solely to the thermodynamic driving force, then $k_1 \approx k_0(\beta_1^{I}/\beta_1^{II})^{1/2}$ according to the simplest Marcus cross relationship.[4] On this basis, k_1 for $CuCl^+$ should be 15 k_0, and k_1 for Cu(imidazole)$^{2+}$ should be 21 k_0. Imidazole should be at least as effective a catalyst as chloride ion. Similarly for the bis complexes, $k_2 \approx k_0(\beta_2^{I}/\beta_2^{II})^{1/2}$, and k_2/k_0 is predicted to be 2.8 × 10^2 and 34 for chloride ion and imidazole systems, respectively. Therefore a study of these two systems should provide an effective test for the influence of the driving force on the reaction rate.

Scheme I

$$Cu^{2+}(aq) + L \overset{\beta_1^{II}}{\rightleftharpoons} Cu^{II}L$$

$$Cu^{2+}(aq) + Co(sep)^{2+} \xrightarrow{k_0} Cu^+(aq) + Co(sep)^{3+}$$

$$Cu^{II}L + Co(sep)^{2+} \xrightarrow{k_1} Cu^{I}L + Co(sep)^{3+}$$

$$Cu^+(aq) + L \overset{\beta_1^{I}}{\rightleftharpoons} Cu^{I}L$$

Results

When a solution of Co(sep)$^{2+}$ is mixed with a solution containing excess copper(II) and either chloride ion or imidazole, the formation of Co(sep)$^{3+}$ can be monitored at 472 nm. The product formation appears to be a first-order process, and the rate increases with increasing copper(II) and chloride ion or imidazole concentrations. The kinetic results are summarized in Tables I and II. The simplest interpretation of such observations is that complexes of copper(II) with chloride ion or imidazole are also reactive oxidants, so that the pseudo-first-order rate constant is given by eq 1, where L is either chloride ion or imidazole and charges have been omitted for generality.

$$k_{obsd} = k_0[Cu^{II}(aq)] + \sum_{1}^{n} k_n[Cu^{II}L_n] \qquad (1)$$

For the chloride ion system, the formation constants given by Ramette[9] have been used to calculate the concentrations of the $Cu^{II}L_n$ species (n = 1–4). Then the data were fitted by least-squares methods to eq 1 to obtain k_1, k_2, and k_3 values of (1.6 ± 0.2) × 10^3, (1.5 ± 0.8) × 10^4 and (4.5 ± 0.8) × 10^5 M^{-1} s^{-1}, respectively. The observed and calculated rate constants are compared in Table I. The data do not yield a meaningful value of k_0, as can be seen from Figure 1, in which the intercept is k_0.

The imidazole system has been analyzed similarly, using the formation constants given by Smith and Martell[10] (at 0.16 M ionic

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strength). For our conditions, the dominant species are the bis-, tris-, and tetrakis(imidazole) complexes. Least-squares analysis gives values for k_2, k_3, and k_4 of 35 ± 15, 70 ± 16 and 118 ± 16 $M^{-1}\ s^{-1}$ respectively. The value of k_2 is poorly defined as can be seen from Figure 2, where k_2 is the intercept.

The reaction of aqueous copper(II) and $Co(sep)^{2+}$ has also been examined in the presence of acetonitrile. In 0.2–0.4 M aqueous acetonitrile, Cu(I) is >99% complexed as $Cu(NCCH_3)_2^+$ ($\beta_2{}^1 = 2.2 \times 10^4\ M^{-2}$),[11] but the kinetics of the redox reaction appear to be unaffected by acetonitrile at these levels. However, the system is complicated by the formation of copper metal either with or without acetonitrile, as described in the following paragraph. The formation of colloidal copper metal during spectrophotometric observations causes an increase in absorbance throughout the visible spectral region, with an apparent rate constant of 0.25 to 0.4 s^{-1} which is relatively independent of the reagent concentrations. We suspect that these rate constants really refer to the rate of agglomeration of colloidal copper(0).

If aqueous copper(II) and $Co(sep)^{2+}$ (in $HClO_4/LiClO_4$) are mixed, the spectrophotometric observations are obscured by the formation of copper metal. This was surprising because Espenson and co-workers[12] found that Cr(II), which is a stronger reducing agent than $Co(sep)^{2+}$, does not cause fast reduction of Cu(I) to copper metal. We have confirmed these observations[12] and find that copper metal appears only after 1–2 h even with 6×10^{-3} M excess Cr(II) in 4×10^{-3} M Cu(I). Shaw and Espenson[12b] attribute the slowness of the Cu(I)/Cr(II) reaction to the "nucleation barrier for forming metallic copper". Clearly this is not a significant hurdle for $Co(sep)^{2+}$ because we always observe rapid copper metal formation on mixing Cu^{2+}(aq) and $Co(sep)^{2+}$, even with Cu(II) in excess, and on mixing Cu^+(aq) with excess $Co(sep)^{2+}$. Rapid formation of copper metal is not so surprising because Cu(I) is a stronger oxidizing agent than Cu(II) ($E°(Cu^{II}/Cu^{I}) = 0.16$ V; $E°(Cu^{I}/Cu^{0}) = 0.52$ V),[13] but it is not clear if Cr(II) or $Co(sep)^{2+}$ shows unusual reactivity with Cu^+(aq). It appears that the system can be represented in general by Scheme II.

Scheme II

$$Cu^{II}(L)_n + Co(sep)^{2+} \xrightarrow{k^{II}} Cu^{I}(L)_n + Co(sep)^{3+}$$

$$Cu^{I}(L)_n + Co(sep)^{2+} \xrightarrow{k^{I}} Cu^0 + nL + Co(sep)^{3+}$$

$$Cu^{II}(L)_n + Cu^0 + nL \xrightarrow{k_C} 2Cu^{I}(L)_n$$

The fact that copper metal forms in the presence of acetonitrile, but not in chloride and imidazole media, shows that formation of Cu(0) is not prevented just by stabilization of Cu^I. The reduction potentials for the $Cu^I(L)_2$ complexes are 0.22, –0.11, and 0.26 V for chloride, imidazole, and acetonitrile, respectively, so that all three are thermodynamically capable of being reduced by $Co(sep)^{2+}$. The qualitative differences in the three systems may reside in the relative values of k^{II} and k^{I}. Chloride ion and imidazole cause k^{II} to increase and may make it sufficiently larger than k^{I} so that all the $Co(sep)^{2+}$ is oxidized before the k^{I} path becomes competitive. Another possibility is that Cu(0) is rapidly removed because chloride ion and imidazole catalyze the comproportionation reaction (k_C), while acetonitrile is not a catalyst because it does not complex with Cu^{II}.

In order to quantify the $Cu^{2+/+}$(aq) system, the amount of Cu(0) formed was determined as a function of the Cu^{2+}(aq) concentration. For reaction solutions initially containing 2.0×10^{-3} M $Co(sep)^{2+}$ and 0.01, 0.02, 0.05, and 0.10 M Cu^{2+}(aq), it was found that 94%, 86%, 69%, and 59%, respectively, of the maximum Cu(0) was collected.[14] In order to explain the variations in the amount of Cu(0) produced, we have set k_C small enough (1×10^{-3}) so that it does not contribute, because of the unfavorable equilibrium constant for comproportionation (1.8×10^{-6} M). With this assumption, the observations depend on the ratio k^I/k^{II}. If $k^I/k^{II} = 80$,[14] the predicted amounts of Cu(0) are 93%, 88%, 73%, and 58%, for the solutions initially containing 0.01, 0.02, 0.05, and 0.10 M Cu^{2+}(aq), respectively, in good agreement with the amounts found.

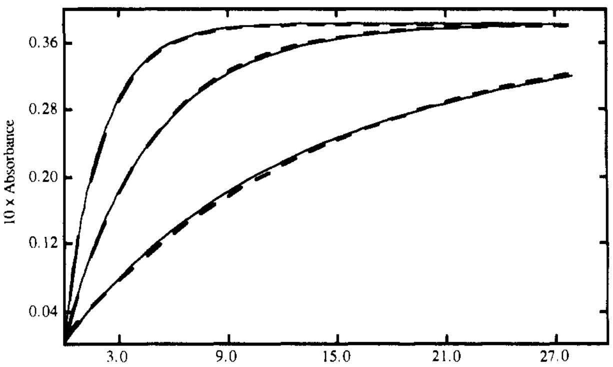

Figure 3. Absorbance–time profiles for the oxidation of 3.5×10^{-4} M $Co(sep)^{2+}$ in the presence of 5.8×10^{-4} M O_2 with $[Cu^{II}(aq)] = 0$, 0.025, and 0.075 M in the order of increasing rate. The dashed curves are calculated from the experimentally observed first-order rate constants. The full curves are calculated from numerical integration of the reactions in Scheme II with $k^{II} = 5$, $k^{I} = 400$, and $k_C = 1 \times 10^{-3}\ M^{-1}\ s^{-1}$ plus the reactions of $Co(sep)^{2+} + O_2$ ($k = 66\ M^{-1}\ s^{-1}$) and $Cu^I(aq) + O_2$ ($k = 5 \times 10^4\ M^{-1}\ s^{-1}$, a value large enough to prevent this reaction from being rate controlling).

The value of k^I/k^{II} shows that Cu^+(aq) is just 80 times more reactive than Cu^{2+}(aq). Therefore, an appropriate scavenger might be able to trap the Cu^+(aq) and prevent formation of Cu(0) so that the rate of the $Cu^{2+}(aq) + Co(sep)^{2+}$ reaction could be measured. Preliminary analysis indicated that O_2 could be suitable for this purpose. The rate constant for the oxidation of $Co(sep)^{2+}$ by O_2 has been reported[15] as 43 $M^{-1}\ s^{-1}$ (0.20 M NaCl). We have measured a rate constant of 0.066 s^{-1} in 5.8×10^{-4} M O_2[16] and 3.47×10^{-4} M $Co(sep)^{2+}$ after stopped-flow mixing (0.02 M $HClO_4$, 0.48 M $LiClO_4$, 25 °C). Second-order analysis gives a specific rate constant of 66 $M^{-1}\ s^{-1}$ (see Figure 3). The rate constant for oxidation of Cu^+(aq) by O_2 has been variously reported[17–19] with the most recent value[17] of $5 \times 10^6\ M^{-1}\ s^{-1}$. As long as the value is $>10^4$, O_2 should be a suitably reactive scavenger. The only limitation will be that the oxidation by Cu^{2+}(aq) must have a halftime less than ~10 s to compete with oxidation of $Co(sep)^{2+}$ by O_2.

When a solution of Cu^{2+}(aq) under 1 atm of O_2 is mixed with a solution of $Co(sep)^{2+}$ under argon in a stopped-flow system, the absorbance increases at 472 nm as expected for formation of $Co(sep)^{3+}$. The rate has been studied for Cu^{2+}(aq) concentrations between 0.025 and 0.15 M with 3.54×10^{-4} M $Co(sep)^{2+}$ and 5.8×10^{-4} M O_2 (0.02 M $HClO_4$, 0.48 M $LiClO_4$, 25 °C). The absorbance time curves have been analyzed by fitting to synthetic curves generated from the set of differential equations required to describe the system. This was done because the O_2 is not in pseudo-first-order excess and the $O_2 + Co(sep)^{2+}$ reaction is a significant competitor at the lower Cu^{2+}(aq) concentrations.

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(14) These percentages are the maximum values obtained from replicate experiments since the experimental errors, such as incomplete reduction of $Co(sep)^{3+}$, air oxidation of $Co(sep)^{2+}$ and Cu^+(aq), and presence of colloidal Cu(0), all lead to lower percentages.

(15) If this ratio is 70 or 90, the predicted percentages at 0.10 M Cu^{2+}(aq) are 54 and 60, respectively; therefore, the ratio is estimated to have an uncertainty of ±10.

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Table III. Rate Constants and Related Data for Redox Reactions of Cu$^{2+/+}$(aq) at 25 °C in 1 M HClO$_4$/LiClO$_4$ Unless Otherwise Indicated

reactant[a]	$E°$, V	k_{11}, M^{-1} s^{-1}	k_n, M^{-1} s^{-1} obsd	k_n, M^{-1} s^{-1} calcd[l]
Co(sep)$^{2+}$	−0.26[b]	9.0[g]	5.0[j]	5.2
(NH$_3$)$_5$Ru(py)$^{3+}$	0.42[c] (0.30)[d]	4.7×10^5 [h]	47[h]	69
(NH$_3$)$_5$Ru(isn)$^{3+}$	0.44[c] (0.384)[d]	4.7×10^5 [h]	5.4×10^2 [h]	10^2
(NH$_3$)$_4$Ru(bpy)$^{3+}$	0.58[e] (0.51)[d]	1.2×10^7 [h]	3.8×10^3 [h]	4.5×10^3
cis-(NH$_3$)$_4$Ru(isn)$_2$$^{3+}$	0.70[c]	1.2×10^7 [m]	4.4×10^4 [h]	3.5×10^4
Ru(bpy)$_3$$^{3+}$	1.26[f]	2.0×10^9 [i]	4.3×10^8 [k]	4.1×10^8

[a] The ligands py, isn, and bpy are pyridine, isonicotinamide, and 2,2′-bipyridine, respectively. [b] Reference 7; in 0.1–0.2 M NaClO$_4$. [c] Gaunder, R. G.; Taube, H. *Inorg. Chem.* **1970**, *9*, 2627; in 1 M KCl. [d] Bernhard, P.; Sargeson, A. M. *Inorg. Chem.* **1987**, *26*, 4122; in 0.1 M LiCF$_3$SO$_3$/CF$_3$SO$_3$H. [e] Estimated from the ionic strength effect on the py and isn complexes. [f] Lin, C. T.; Böttcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536; in 1 M H$_2$SO$_4$. [g] Reference 21. [h] Reference 5 and references therein. [i] Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615. [j] This work; $\mu = 0.5$ M. [k] Hoselton, M. A.; Lin, C.-T.; Schwarz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1978**, *100*, 2383, in 0.5 M HClO$_4$; similar rate constants for several tris(phenanthroline) derivatives also were obtained. [l] Calculated using ionic radii of 3.7 and 3.8 Å for Cu^{2+}(aq) and Cu$^+$(aq) and $k_{22} = 5 \times 10^{-7}$ M^{-1} s^{-1}. The radii for the Ru complexes are given by Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883. [m] The size correlation of Brown and Sutin implies that the self-exchange rate of *cis*-(NH$_3$)$_4$Ru(isn)$_2$$^{3+}$ will be similar to that of (NH$_3$)$_4$Ru(bpy)$^{3+}$, as suggested by a reviewer.

Table IV. Summary of Thermodynamic and Kinetic Information for the Oxidation of Co(sep)$^{2+}$ by Copper(II) Species

oxidant	$E°$, V (Cu^{II}L$_n$/Cu^{I}L$_n$)	k_{22},[a] M^{-1} s^{-1}	k_n, M^{-1} s^{-1} obsd	k_n, M^{-1} s^{-1} calcd[b]
Cu^{2+}(aq)	0.17	5.0×10^{-7}	5.0	6.4
Cu(Cl)$^+$	0.308	2.0×10^{-4}	1.6×10^3	1.6×10^3
Cu(Cl)$_2$	0.459	2.0×10^{-4}	1.5×10^4	3.1×10^4
Cu(Cl)$_3$$^-$	0.474	2.0×10^{-4}	4.5×10^5	1.0×10^5
Cu(Im)$^{2+}$	0.327	1.0×10^{-7}		25
Cu(Im)$_2$$^{2+}$	0.362	1.0×10^{-7}	35	43
Cu(Im)$_3$$^{2+}$	(0.32)[c]	1.0×10^{-7}	70	22
Cu(Im)$_4$$^{2+}$	(0.29)[c]	1.0×10^{-7}	120	14

[a] Self-exchange rate constant for Cu$^{2+/+}$ species used for calculated values. [b] Calculated from eq 2 with self-exchange rate constants of 9.0 ($\mu = 0.5$ M for Cl$^-$ complexes) and 5.0 ($\mu = 0.15$ M for imidazole complexes) for Co$^{II/III}$(sep), and including work terms using the following radii (Å): Co(sep)$^{3+}$, 4.2; Co(sep)$^{2+}$, 4.4; Cu^{2+}(aq), 3.7; Cu$^+$(aq), 3.8; Cu^{II}(Cl)$_n$, 3.9; Cu^{I}(Cl)$_n$, 4.0; Cu^{II}(Im)$_n$, 5; Cu^{I}(Im)$_n$, 5.1. [c] Estimated by assuming that $\log(\beta_n^{II}/\beta_n^{I})$ is the same for imidazole as the known values for pyridine.

Representative results are shown in Figure 3, and the analysis gives $k_{aq}^{II} = 5.0 \pm 0.25$ M^{-1} s^{-1} ($=k_0$ in eq 1).

Discussion

The rate constants and related thermodynamic parameters for the reductions of copper(II) species by Co(sep)$^{2+}$ are summarized in Table IV. Since Co(sep)$^{2+}$ is substitution inert, these reactions must be outer-sphere and will be analyzed in terms of the following equations derived from Marcus theory.

$$k_n = (k_{11}k_{22}K_nf_{12})^{1/2}W_{12} \tag{2}$$

Here k_{11} and k_{22} are the self-exchange rates for the oxidant and reductant, K_n is the equilibrium constant, and the f_{12} and work term corrections (W_{12} and w_{ij}) have been calculated from the following expressions.[20]

$$\ln(f_{12}) = \frac{\left(\ln K_n + \dfrac{(W_{12} - W_{21})}{RT}\right)^2}{4\ln\left(\dfrac{k_{11}k_{22}}{Z^2}\right) + \left(\dfrac{W_{11} + W_{22}}{RT}\right)}$$

$$W_{12} = \exp\left(\frac{-(W_{12} + W_{21} - W_{11} - W_{22})}{2RT}\right)$$

$$w_{ij} = \frac{4.225 \times 10^3 z_1z_2}{r(1 + 0.329r\sqrt{\mu})}$$

Here Z is the collision frequency, taken to be 1×10^{11} M^{-1} s^{-1}, r is the sum of the radii of the reactants in Å, μ is the ionic strength, z_i is the charge on the ion, the numerical constants are for water at 25 °C and w_{ij} values are in cal mol^{-1}. The self-exchange rate constants for Co(sep)$^{3/2+}$ are taken from the results of Doine and Swaddle.[21]

The rate constants for the reactions of Cu^{2+}(aq) or Cu$^+$(aq) with several outer-sphere reagents are collected in Table III. The results for the six systems have been analyzed with eq 2 to determine if they yield a constant self-exchange rate constant (k_{22}) for Cu$^{2+/+}$(aq). It is found that a value of $k_{22} = 5 \times 10^{-7}$ M^{-1} s^{-1} gives excellent agreement between calculated and observed rate constants for five of the six systems, with rate constants varying over 8 orders of magnitude. For (NH$_3$)$_5$Ru(isn)$^{3+}$, the predicted rate constant is about seven times smaller than observed. This level of disagreement is not unreasonable for the theory,[22] but looks poor compared to the other systems. The reduction of the isonicotinamide complex by Cu$^+$(aq) could proceed by an inner-sphere mechanism, as has been found for their reduction by Cr^{2+}(aq).[23]

The present estimate of the Cu$^{2+/+}$(aq) self-exchange rate constant of 5×10^{-7} M^{-1} s^{-1} is 400 times smaller than that obtained by Davies,[5] although only one rate constant has been added to the data base. This difference is due mainly to our use of reduction potentials at $\mu = 1$ M wherever possible, while recalculation indicates that Davies used values at $\mu = 0.1$ M, although the rate constants are at the higher ionic strength. The inclusion of the work term corrections has an effect at about the 20% level for these systems.

The results for the chloride and imidazole complexes are summarized in Table IV. If the work terms are neglected ($w_{ij} = 0$) for the chloride system, then eq 2 predicts that k_n only increases by a factor of 12 for $n = 1$–3, while the observed factor is 2.8×10^2. However, the chloride ion complexes have charge differences which should be taken into account with the work terms (w_{ij}) in Marcus theory. These calculated values, which are shown in the last column in Table IV, are in satisfactory agreement with the observed values even if a single self-exchange rate constant of 2×10^{-4} M^{-1} s^{-1} is assumed for all of the chloride complexes. Some variation of the latter value, of course, would improve the agreement, but this seems to be unwarranted given the normal level of agreement expected with the theory. The conclusion is that the outer-sphere reactivity of the copper(II)–chloride complexes can be explained by Marcus theory if the changes in driving force and charge are taken into account. It appears that inner-sphere chloride ions increase the self-exchange rate relative to the Cu$^{2+/+}$(aq) system. However, this does not appear to be a monotonic increase to the value of 5×10^7 M^{-1} s^{-1} found by McConnell and Weaver[24] in 12 M HCl. The latter value may

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(20) Marcus, R. A.; Sutin, N. *Biochem. Biophys. Acta* **1985**, *811*, 265. Zahir, K.; Espenson, J. H.; Bakac, A. *J. Am. Chem. Soc.* **1988**, *110*, 5059.

(21) Doine, H.; Swaddle, T. W. *Inorg. Chem.* **1991**, *30*, 1858.

(22) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.

(23) Gaunder, R. G.; Taube, H. *Inorg. Chem.* **1970**, *9*, 2627.

(24) McConnell, H. M.; Weaver, H. C. *J. Chem. Phys.* **1956**, *25*, 307.

refer to an inner-sphere process, or result from structural changes of the species due to dehydration.

The imidazole complexes change much less in reactivity with increasing *n* than the chloro complexes. This is consistent with the smaller changes in driving force and their constant 2+ charge. However, eq 2 predicts that k_2 for imidazole and k_1 for chloride should be similar if the self-exchange rates are the same. Since the values actually differ by a factor of ~45, the implication is that the self-exchange rate with imidazole is $(45)^2$ times smaller, or $\sim 1 \times 10^{-7}$ M^{-1} s^{-1}. This also is consistent with the fact that the imidazole complexes are only slightly more reactive than Cu^{2+}(aq), despite their substantially larger driving forces. The calculated values for $n = 3$ and 4 are uncertain because β_n^{I} values can only be estimated from the pyridine analogues.

One purpose of this study was to provide some insight into the strong chloride catalysis of the oxidation of ascorbic acid by Cu(II)[2] by studying the chloride ion effect with a known outer-sphere reducing agent. The chloride ion independent path for the ascorbate reaction gives an experimental rate constant of 4.4 M^{-1} s^{-1} for the oxidation of the ascorbate anion, if an outer-sphere mechanism is assumed. The self-exchange rate constant used in the present work, along with the values suggested by Hoddenbagh and Macartney[25] for the ascorbate species, predicts a much smaller value of 1.3×10^{-5} M^{-1} s^{-1}. The predicted rate constant of 4.0×10^{-3} for outer-sphere oxidation by $CuCl^+$ also does not agree with the experimental value of 2.8×10^3 M^{-1} s^{-1}. This level of disagreement, in combination with the good agreement found here for $Co(sep)^{2+}$, implies that the ascorbate reactions are not outer-sphere, and probably proceed through an inner-sphere Cu^{II}–ascorbate complex as in Scheme I.

As already noted, the rapid reduction of Cu(I) by $Co(sep)^{2+}$ came as an unexpected complication for these studies. By comparison to Cr(II), it appears that $Co(sep)^{2+}$ is unusually reactive toward Cu^+(aq). However, if one accepts the conclusion of Creaser et al.[7a] that the self-exchange rate for $Cr^{3+/2+}$(aq) is really $\sim 5 \times 10^{-10}$ M^{-1} s^{-1}, then eq 2 predicts that $Co(sep)^{2+}$ should be about 10^4 times more reactive than Cr^{2+}(aq), and the different behavior of the two systems is more understandable. It should be noted that the self-exchange rate for $Cr^{3+/2+}$(aq) just mentioned and the value used here for $Cu^{2+/+}$(aq) predict a rate constant of 6.4×10^{-4} M^{-1} s^{-1} for Cr^{2+}(aq) + Cu^{2+}(aq), in poor agreement with the approximate value of 0.17 M^{-1} s^{-1} obtained by Shaw and Espenson.[12b] It may be that this minor contribution to the rate has more of a medium effect component than suggested by the final conclusions of Shaw and Espenson.

Experimental Section

Materials. (1,3,6,8,10,13,16,19-Octaazabicyclo[6.6.6]eicosane)cobalt(III) trichloride ($Co(sep)Cl_3$) was obtained from Aldrich Chemical Co. Chloride ion free solutions of $Co(sep)^{3+}$ were prepared by washing a 10-mL solution of ~0.06 g of $Co(sep)Cl_3$ onto a column of 5 g of a weak acid cation exchange resin (Rexyn 102(Na^+), Fisher) and then washing the resin with water until the eluate was free of chloride ion. Then the resin containing the $Co(sep)^{3+}$ was physically separated and treated with 2 M $HClO_4$ to pH ~0.8. The golden yellow supernatant solution was separated from the resin by filtration and adjusted to pH 6.2–6.5 by addition of NaOH. The product solution contains about 2.5×10^{-3} M $Co(sep)^{3+}$, as determined from the absorbance at 472 nm (ϵ = 109 M^{-1} cm^{-1}),[6] and has an ionic strength of ~0.42 M. For the stopped flow studies, these solutions were diluted to $\sim 7 \times 10^{-4}$ M in $Co(sep)^{3+}$ and the ionic strength was adjusted to 0.50 M with $LiClO_4$. For the Cu(0) product analysis, the more concentrated solutions required were prepared by the reaction of $Co(sep)Cl_3$ with silver perchlorate.

The $Co(sep)^{2+}$ was prepared by reduction of $Co(sep)^{3+}$ over amalgamated zinc under an atmosphere of argon which had been passed through a scrubber of aqueous chromium(II) sulfate.

The analysis for copper metal was done by collecting the product on a wet 0.22-μm Millipore filter, washing it twice with water and then dissolving the copper metal in 4 mL of warm 0.5 M nitric acid and diluting the solution to 25.0 mL with water. A 3.50-mL aliquot of a stock solution of bathocuproine disulfonate (300 mg in 10.0 mL of water) was diluted to 100 mL with a sodium acetate solution (45 g of $NaO_2CCH_3 \cdot 3H_2O$ per 100 mL of water). The analyte solution was prepared by treating a 2.00 mL of the Cu(II)/HNO_3 solution with 75 mg of ascorbic acid and 2.50 mL of the bathocuproine disulfonate/acetate solution and diluting to 25.0 mL with water. The procedure is based on the method of Zak.[26] The absorbance was recorded in 2.00-cm path length cells at 485 nm. The relationship between absorbance and copper content was determined by dissolving a known weight of copper metal in nitric acid, from which it was found that absorbance = 2.51×10^4 [Cu] + 0.0183.

Kinetic Measurements. Near neutral solutions of $Co(sep)^{2+}$ under argon were mixed with equal volumes of copper(II) solutions containing either chloride ion and $HClO_4$ or imidazole at pH 6.5. The spectrophotometric change was monitored at 472 nm, which is a maximum for $Co(sep)^{3+}$. For the oxidation of $Co(sep)^{2+}$ by Cu^{2+}(aq), the latter solution was under an atmosphere of dioxygen which was used to scavenge the Cu(I).

The least-squares and numerical integration methods have been described previously.[27]

Instrumentation. Routine electronic spectra were recorded on a Cary 219 or a Hewlett-Packard 8451 spectrophotometer. The stopped-flow measurements were on a Tritech Dynamic Instruments Model 1024 system described previously.[27]

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