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Ligand Effects on the Chemical Activity of Copper(I) Complexes: Outer- and Inner-Sphere Oxidation of $Cu^{I}L$

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The effect of the ligands acetonitrile (AN), fumaric acid (H_2fum) and 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane (L^1) on the kinetics of oxidation of Cu^{I} complexes by $[(cyclam)Ni^{III}(SO_4)_2]^-$ and $[(NH_3)_5Co^{III}Cl]^{2+}$ in aqueous solutions via an outer- and inner-sphere mechanism, respectively, has been studied. The effects of the ligands on the electron self-exchange rate constants have also been evaluated. All ligands studied stabilize Cu^{I} in aqueous solution but affect the redox potential of the $Cu^{II/I}L$ couple differently. The ligands decrease the rate of the redox reactions and the electron self-exchange rate constants. The results indicate that acetonitrile and alkenes should not be used as solvents for $[Cu^{I}L]^{+}$-catalyzed processes that involve redox steps. On the other hand, the results also suggest that $[Cu^{I}L^{1}]^{+}$ should be a good catalyst for such processes.

Introduction

Copper complexes are used as catalysts for a variety of important redox processes[1–18] such as the Ullmann reaction and are present in various enzymes. As Cu^{+}_{aq} is not stable due to its disproportionation to Cu^{2+}_{aq} and Cu^{0},[19] and as the solubility product of Cu_2O in neutral and alkaline solutions is very low,[20] ligands are required in order to stabilize it. The electron transfer in these processes involves an unusually large change in the coordination geometry: Cu^{II} complexes generally exist as Jahn–Teller distorted octahedra (though other configurations are known), while Cu^{I} complexes are usually four-coordinate tetrahedral or linear species. These large changes in the complex geometry during redox processes are expected to slow them down, therefore the choice of ligands has a major effect on the rates of catalytic processes involving copper complexes.

In general, redox processes proceed by one of two mechanisms: outer sphere or inner sphere. It therefore seemed of interest to study the effect of different types of ligands on the kinetics of oxidation of $[Cu^{I}L^{i}]^{+}$ complexes by an outer sphere and an inner sphere oxidizing agent. For this purpose, the following reactions were studied:

$$[(cyclam)Ni^{III}(SO_4)_2]^- + [Cu^{I}L]^{+} \xrightarrow{k_1} [(cyclam)Ni^{II}(SO_4)_2]^{2-} + [Cu^{II}L]^{2+} \quad (1)$$

$$[(NH_3)_5Co^{III}Cl]^{2+} + [Cu^{I}L]^{+} \xrightarrow{k_2} \text{Products} \quad (2)$$

as $[(cyclam)Ni^{III}(SO_4)_2]^-$ and $[(NH_3)_5Co^{III}Cl]^{2+}$ are known to be an outer-sphere and an inner-sphere oxidant, respectively.[21–23]

In the present study the effect of several ligands that are used, or have been recommended for use, in catalytic processes on the electron self-exchange rate of the $Cu^{II/I}L$ couple has been studied. The ligands chosen affect the redox potential of the $Cu^{II/I}_{aq}$ couple differently — two of them shift it anodically and the other cathodically. They bind to Cu^{I} and Cu^{II} ions in different modes. The first ligand, acetonitrile (AN), which is used as a solvent in many industrial synthetic processes catalyzed by copper(I),[24–26] is a σ donor and a π acceptor in its complexes with Cu^{I} and is not a ligand of Cu^{II} in aqueous solutions at acetonitrile concentrations below 1 M. The second ligand is fumaric acid (fum). Many polymerization processes and other synthetic processes catalyzed by Cu^{I} complexes involve alkenes as substrates,[27,28] and it has been suggested that in order to decrease pollution these reactions should be carried out using the neat alkenes without any solvent.[28] However, alkenes form relatively stable π complexes with Cu^{I},[9,29–31] therefore it is of interest to study the effect of an alkene on the kinetics of the reaction. Fumaric acid was chosen as a model for this study as it is known to bind to copper ions via its π system[29–33]). 2,5,8,11-Tetramethyl-2,5,8,11-tetra-

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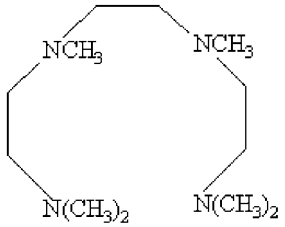

Figure 1. L^1 = 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane.

azadodecane (L^1; Figure 1) shifts the redox potential of the $Cu^{II/I}{}_{aq}$ couple cathodically.[9,29,30,34–37] However, it shifts equilibrium (3) to the left:

$$2Cu^{+}{}_{aq} \leftrightarrows Cu^{2+}{}_{aq} + Cu^{0}\ K_3{}^{[19]} = 1 \times 10^6\ \text{M}^{-1} \quad (3)$$

this stems from

$$2Cu^{I}L_n \leftrightarrows Cu^{II}L_m + Cu^{0} + (2n - m)L\ K_4 \quad (4)$$

where $K_4 = ([Cu^{II}L_m][L]^{2n-m})/[Cu^{I}L_n]^2 = (K^{II}[Cu^{2+}{}_{aq}][L]^m\text{-}[L]^{2n-m})/(K^{I}[Cu^{+}{}_{aq}][L]^n)^2 = K^{II}[Cu^{2+}{}_{aq}]/(K^{I})^2[2Cu^{+}{}_{aq}]^2 = 10^6K^{II}/(K^{I})^2$, and K^{II} and K^{I} are $[Cu^{II}L_m]/([Cu^{2+}{}_{aq}][L]^m)$ and $[Cu^{I}L_n]/([Cu^{+}{}_{aq}][L]^n)$, respectively.

Equilibrium (4) will be shifted to the left if $(K^{I})^2 > K^{II}$, whereas the redox potential of the $Cu^{II}L_m/Cu^{I}L_n$ couple is shifted cathodically if $K^{II} > K^{I}$. Thus, the addition of ligands for which both of these criteria are fulfilled to a mixture of $Cu^{2+}{}_{aq}$ and Cu^0 should improve the catalytic properties of this mixture as they stabilize Cu^{I} and increase its reducing power. With regards to this property, L^1 is special.

Each of the ligands chosen for this study affects the redox potential of the copper complex differently (Table 1) as each has a different effect on the geometric structure and the electronic configuration of the copper complex. Thus, $[Cu^{I}AN]^+$, $[Cu^{I}(AN)_2]^+$, and $[Cu^{I}(fum)]$ complexes are probably linear, whereas the $(Cu^{I}L^1)^+$ complex is tetrahedral, therefore it was expected that each of them would affect the rate constant of the redox reactions differently. Awareness of the effect of the ligands on the rate constants of outer- and inner-sphere reactions is essential for the design of good copper catalysts.

Table 1. The rate constants for reactions (1) and (2).

$[Cu^{I}L]^+$	E^0 [V][a]	k_1 [$M^{-1}s^{-1}$]	k_{-11} [$M^{-1}s^{-1}$]	k_2 [$M^{-1}s^{-1}$]
$Cu^{+}{}_{aq}$	0.15	3.0×10^4	2.7×10^{-4}	5.4×10^4
$[Cu^{I}fum]^+$	0.38[29]	$\leq3.0\times10^1$	$\leq3.0\times10^{-7}$	1.0×10^2
$[Cu^{I}AN]^+$	0.35[38–41]	$\approx8.5\times10^2$	$\approx9.7\times10^{-5}$	2.2×10^2
$[Cu^{I}(AN)_2]^+$	0.41[38–41]	$\approx5.0\times10^1$	$\approx2.2\times10^{-6}$	9.3
$[Cu^{I}L^1]^+$	0.08[35]	2.3×10^4	1.4×10^{-5}	2.4×10^4

[a] E^0 is the redox potential for the $[Cu^{II/I}L]^{2+/+}$ couple with respect to NHE.

Results

$[(cyclam)Ni^{III}(SO_4)_2]^-$ and $[(NH_3)_5Co^{III}Cl]^{2+}$ in excess were used as reagents, each one separately, with $Cu^{I}L$ (L = AN, fum, L^1). We decided to study systems with an excess of these complexes due to the possibility of some dioxygen leakage, which means that the $[Cu^{I}L]^+$ concentration is less accurate (the reactions with L^1 and fum were also studied with $[Cu^{I}L]^+$ in excess — the rate constants are the same). The observed rate constants depend linearly on the $[(cyclam)Ni^{III}(SO_4)_2]^-$ and $[(NH_3)_5Co^{III}Cl]^{2+}$ concentrations (see, for example, Figure 2). The slope of these lines equals the rate constant of the reaction under the experimental conditions. The rate constants thus obtained for all the complexes studied are summarized in Table 1.

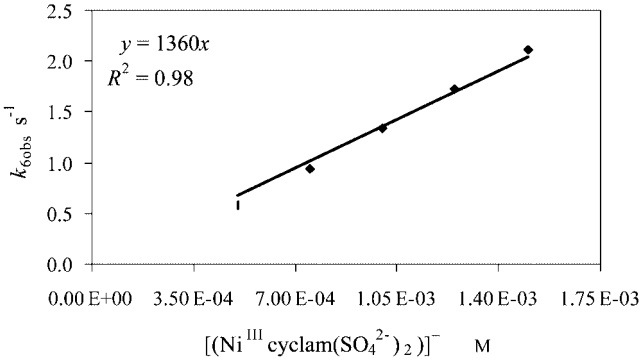

Figure 2. Dependence of $k_6$obs on $[(cyclam)Ni^{III}(SO_4)_2]^-$. The experiments were performed in solutions containing 2.0×10^{-4} M $[Cu^{I}]_T$, 2.5×10^{-3} M fum, μ = 0.30 M, He-saturated at pH 3.0. As $[(cyclam)Ni^{III}(SO_4)_2]^-$ is stable in the absence of $[Cu^{I}L]^+$, the slope was calculated assuming that the line passes through the origin.

Derivation of $k(Cu^{+}{}_{aq})$, the Rate Constant of Reactions (5) and (9)

$$[(cyclam)Ni^{III}(SO_4)_2]^- + Cu^{+}{}_{aq} \xrightarrow{k(Cu^{+}{}_{aq})} [(cyclam)Ni^{II}(SO_4)_2]^{2-} + Cu^{2+}{}_{aq} \quad (5)$$

The effect of fum concentration on the rate of reaction (6) was measured by changing its concentration $[(0.25\text{–}1.13)\times10^{-2}$ M].

$$[(cyclam)Ni^{III}(SO_4)_2]^- + [Cu^{I}L]^+ \xrightarrow{k_6} [(cyclam)Ni^{II}(SO_4)_2]^{2-} + [Cu^{II}L]^{2+} \quad (6)$$

$[Cu^{I}]_T = [Cu^{I}L] = [[Cu^{I}(H_2fum)]^+ + [Cu^{I}(Hfum)] + Cu^{+}{}_{aq}]$ (It should be noted that at pH 3.0 the equilibrium reaction $HO_2CCH{=}CHCO_2H \rightleftarrows HO_2CCH{=}CHCO_2^- + H^+$; pK_{a1} = 2.9[29] dictates that about 50% of the two species exist in the solution. The pK_a of fumarate bound to Cu^{I} is similar.[29])

$$[(cyclam)Ni^{III}(SO_4)_2]^- + [Cu^{I}(H_2fum)]^+/Cu^{I}(Hfum) \xrightarrow{k_7} [(cyclam)Ni^{II}(SO_4)_2]^{2-} + [Cu^{II}(H_2fum)]^{2+}/[Cu^{II}(Hfum)]^+ \quad (7)$$

The rate law for reaction (6) is $-d[Ni^{III}]/dt = k_6[Cu^{I}]_T[Ni^{III}]$. As $[Cu^{I}]_T << [Ni^{III}]$, this rate law can be rewritten as $-d[Ni^{III}]/dt = k_{6obs}[Cu^{I}]_T$, where $k_{6obs} = k_6[Ni^{III}]$.

The rate constants k_{6obs} at each fum concentration depend linearly on the $[(cyclam)Ni^{III}(SO_4)_2]^-$ concentration (Figure 2). The dependence of k_6 on fum concentration is plotted in Figure 3.

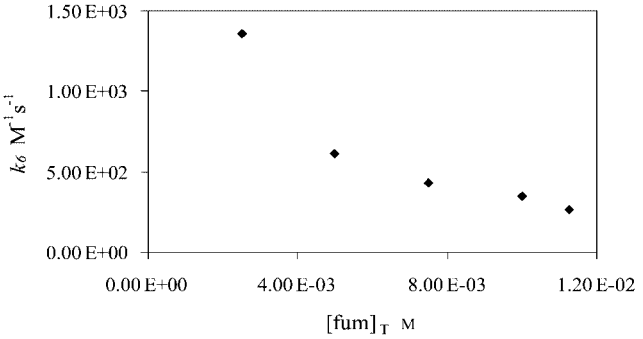

Figure 3. k_6 as a function of fumaric acid concentration. The experiments were carried out at $[Cu^I]_T = 2.0 \times 10^{-4}$ M, $\mu = 0.30$ M, pH 3.0; the solutions were He-saturated.

It was decided to assume, as a first approximation, that the contribution of $[Cu^I(fumH_2)]^+$ and $[Cu^I(fumH)]$ species to the rate is negligible, i.e. $k_7 = 0$ and reaction (5) is the only reaction which contributes to k_6. Therefore, the rate law can be written $-d[Ni^{III}]/dt = k_5[Cu^+_{aq}][Ni^{III}]$.

From the equilibrium constant of reaction (8):

$$Cu^+_{aq} + fumH_2/fumH^- \leftrightarrows [Cu^I(fumH_2)]^+/[Cu^I(fumH)]; \quad K_8 \text{ (at pH 3.0)}^{[29]} = 8.70 \times 10^3 \text{ M}^{-1} \quad (8)$$

$[Cu^+_{aq}]$ can be expressed as

$K_8 = [Cu^IL]/([Cu^+_{aq}][L])$

$[Cu^+_{aq}] = [(Cu^IL)]/(K_8[L]) = ([Cu^I]_T - [Cu^+_{aq}])/K_8[L]$

$[Cu^+_{aq}] = [Cu^I]_T/(K_8[L] + 1)$

Therefore, under these assumptions, $-d[Ni^{III}]/dt = k_5[Cu^I]_T/(K_8[L] + 1)[Ni^{III}]$.

Plotting k_6 (at different fum concentrations) as a function of $1/(K_8[L] + 1)$ (Figure 4) yields a straight line with a slope which equals k_5. Thus, the rate constant of reaction (5), k_5, is found to be $(3.0 \pm 0.3) \times 10^4$ M^{-1} s^{-1}.

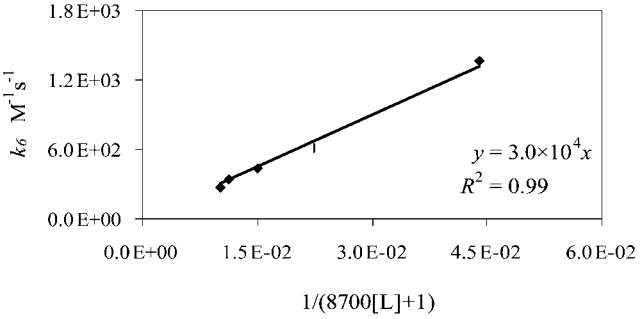

Figure 4. k_6 as a function of 1/(8700[fum] + 1). The experiments were carried out at $[Cu^I]_T = 2.0 \times 10^{-4}$ M, $\mu = 0.30$ M, pH 3.0; the solutions were He-saturated.

From the fact that no intercept is obtained in Figure 4 one can calculate that $k_7 \leq 30$ M^{-1} s^{-1} (this is the upper limit of the rate constant assuming that the error of the experiments is ±10%).

The rates of reactions (9) and (10) were studied using an analogous approach.

$$[(NH_3)_5Co^{III}Cl]^{2+} + Cu^+_{aq} \xrightarrow{k_9} \text{products} \quad (9)$$

$$[(NH_3)_5Co^{III}Cl]^{2+} + [Cu^I(fumH_2)]^+/[Cu^I(fumH)] \xrightarrow{k_{10}} \text{products} \quad (10)$$

The results yield $k_9 = (5.4 \pm 0.5) \times 10^4$ M^{-1} s^{-1}. This rate constant is in good agreement with an earlier study.[23] The intercept in Figure 5 gives a value for k_{10} of ≤ 100 M^{-1} s^{-1}.

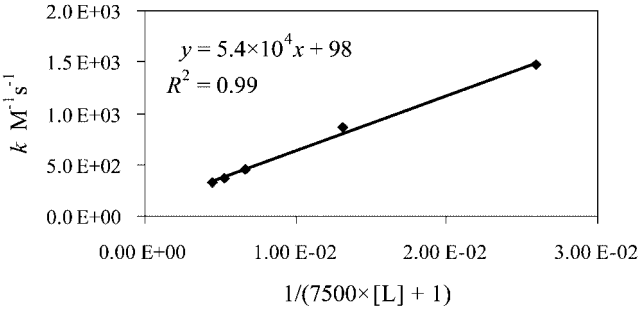

Figure 5. k as a function of 1/(7500[L] + 1), for the reduction of $[(NH_3)_5Co^{III}Cl]^{2+}$ by Cu^I in the presence of fumarate. The experiments were carried out at $[Cu^I]_T = 4.0 \times 10^{-4}$ M, $\mu = 0.20$ M, pH 2.0; the solutions were saturated with He. k = the rate constant observed at each fumaric acid concentration.

Oxidation of $[Cu^I(AN)_n]^+$

The apparent rate constants of reaction (11) were measured at different acetonitrile concentrations. The results are summed up in Table 2.

$$[(cyclam)Ni^{III}(SO_4)_2]^- + [Cu^I(AN)_n]^+ \xrightarrow{k_{11}} [(cyclam)Ni^{II}(SO_4)_2]^{2-} + [Cu^{II}(AN)_n]^{2+} \quad (11)$$

The results show that k_{11} decreases with an increase in acetonitrile concentration (Figure 6). Under the experimental conditions used here four Cu^I complexes are present in the solution,[38–41] namely Cu^+_{aq}, $[Cu^I(AN)]^+$, $[Cu^I(AN)_2]^+$, and $[Cu^I(AN)_3]^+$. Therefore, it is reasonable to assume that the dependence of k_{11} on acetonitrile concentration stems from the relative concentrations of these complexes in the solutions and the rate constants of reactions (5), (12), (13), and (14).

$$[(cyclam)Ni^{III}(SO_4)_2]^- + [Cu^I(AN)]^+ \xrightarrow{k_{12}} [(cyclam)Ni^{II}(SO_4)_2]^{2-} + [Cu^{II}(AN)]^{2+} \quad (12)$$

$$[(cyclam)Ni^{III}(SO_4)_2]^- + [Cu^I(AN)_2]^+ \xrightarrow{k_{13}} [(cyclam)Ni^{II}(SO_4)_2]^{2-} + [Cu^{II}(AN)_2]^{2+} \quad (13)$$

$$[(cyclam)Ni^{III}(SO_4)_2]^- + [Cu^I(AN)_3]^+ \xrightarrow{k_{14}} [(cyclam)Ni^{II}(SO_4)_2]^{2-} + [Cu^{II}(AN)_3]^{2+} \quad (14)$$

The stability constants of the different $[Cu^I(AN)_n]^+$ complexes are known, although their accuracy is not very high, as can be seen from the different values given by different authors.[38–42] The results in Table 2 suggest that (1) the observed rate constants approach a limiting value at high acetonitrile concentration, i.e. the observed reaction is not due

Table 2. The observed rate constants for reaction (11).

AN [M]	$[Cu^{+}_{aq}]$ [M]	$[[CuAN]^{+}]$ [M]	$[[Cu(AN)_2]]^{+}$ [M]	$[[Cu(AN)_3]^{+}]$ [M]	k_{11} [$M^{-1}s^{-1}$]	k_{11} calculated [$M^{-1}s^{-1}$]
0.096	4.9×10^{-7}	8.8×10^{-5}	1.01×10^{-4}	1.05×10^{-5}	630	470
0.14	2.5×10^{-7}	6.7×10^{-5}	1.15×10^{-4}	1.8×10^{-5}	420	370
0.17	1.9×10^{-7}	5.9×10^{-5}	1.19×10^{-4}	2.2×10^{-5}	390	330
0.19	1.5×10^{-7}	5.3×10^{-5}	1.20×10^{-4}	2.5×10^{-5}	220	290
0.24	9.6×10^{-8}	4.3×10^{-5}	1.24×10^{-4}	3.2×10^{-5}	125	240
0.29	6.7×10^{-8}	3.6×10^{-5}	1.25×10^{-4}	3.9×10^{-5}	120	200
0.38	3.7×10^{-8}	2.7×10^{-5}	1.22×10^{-4}	5.1×10^{-5}	95	160
0.67	1.1×10^{-8}	1.4×10^{-5}	1.08×10^{-4}	7.9×10^{-5}	88	90

The $[Cu^{I}(AN)_n]^{+}$ concentrations were calculated from the stability constant of the following reactions:

$Cu^{+}_{aq} + AN \leftrightarrows [Cu^{I}AN]^{+}$ K[42] = 1.9×10^{3} M^{-1}

$Cu^{+}_{aq} + 2AN \leftrightarrows [Cu^{I}(AN)_2]^{+}$ β_2[42] = 2.2×10^{4} M^{-2}

$Cu^{+}_{aq} + 3AN \leftrightarrows [Cu^{I}(AN)_3]^{+}$ β_3[42] = 2.4×10^{5} M^{-3}

by the following equations:

$[Cu^{I}]_T = 2.0\times10^{-4}\ M = [Cu^{+}_{aq}](1 + K_1[AN] + \beta_2[AN]^2 + \beta_3[AN]^3)$

$[[Cu^{I}AN]^{+}] = [Cu^{+}_{aq}]\times\beta_1\times[AN]$

$[[Cu^{I}(AN)_2]^{+}] = [Cu^{+}_{aq}]\times\beta_2\times[AN]^2$

$[[Cu^{I}(AN)_3]^{+}] = [Cu^{+}_{aq}]\times\beta_3\times[AN]^3$

This set of equilibria constants was chosen as they were measured at similar ionic strengths to those used in this study. The use of the stability constants reported by Jordan et al.[41] does not affect the derived rate constants considerably.

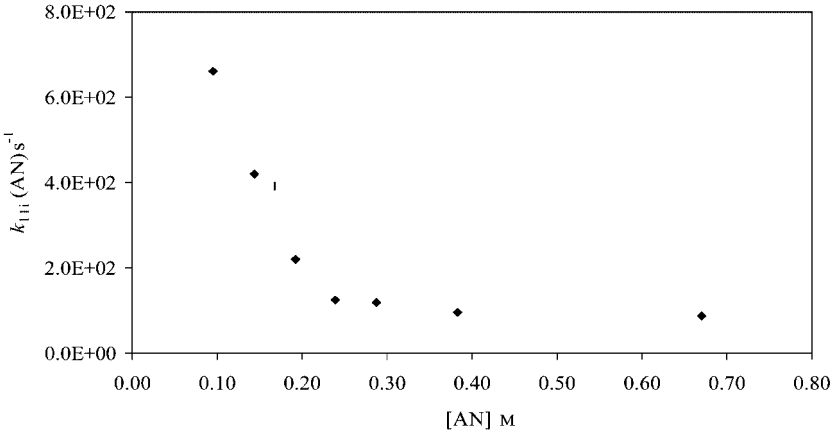

Figure 6. k_{11} as a function of acetonitrile concentration. The experiments were carried out at $[Cu^{I}]_T = 2.0\times10^{-4}$ M, μ = 0.30 M, pH 3.0; the solutions were He-saturated.

only to reaction (5) and (2) the observed rates at high acetonitrile concentration seem to be independent of $[Cu^{I}(AN)_3]^{2+}$, i.e. one can assume that k_{14} is negligible. Following these assumptions, and with k_5 determined above, k_{12} and k_{13} were calculated by repetitive approximations. The deviations of the calculated rate constants from the experimental ones are probably due mainly to the uncertainties in $K([Cu^{I}(AN)]^{+})$, $K([Cu^{I}(AN)_2]^{+})$ and $K([Cu^{I}(AN)_3]^{+})$.

The rate constants of reactions (15), (16), and (17) were evaluated analogously.

$$[(NH_3)_5Co^{III}Cl]^{2+} + [Cu^{I}(AN)]^{+} \xrightarrow{k_{15}} \text{products} \quad (15)$$

$$[(NH_3)_5Co^{III}Cl]^{2+} + [Cu^{I}(AN)_2]^{+} \xrightarrow{k_{16}} \text{products} \quad (16)$$

$$[(NH_3)_5Co^{III}Cl]^{2+} + [Cu^{I}(AN)_3]^{+} \xrightarrow{k_{17}} \text{products} \quad (17)$$

The rate constants are summed up in Table 3.

Table 3. Basicity of the ligands and stability constants of their copper complexes in aqueous solutions.

	log K	
	L^{1}[35,37]	fum[29]
$LH^{+} + H^{+} \rightleftarrows LH_2^{+}$	8.50	3.1
$LH_2^{+} + H^{+} \rightleftarrows LH_3^{+}$	5.40	
$LH_3^{+} + H^{+} \rightleftarrows LH_4^{+}$	1.70	
$L + Cu^{+} \rightleftarrows CuL^{+}$	11.0	3.94 (pH 3.0), 3.88 (pH 2.0)

Evaluation of the Self-Exchange Rate Constants, k'_{11}, of Reaction (18) for the Complexes Studied

According to the Marcus theory,[43–46] for reactions proceeding by the outer-sphere mechanism, k'_{12}, the rate constant of the cross reaction, reaction (1), depends on three parameters: the equilibrium constant of the cross reaction (K_{12}) and the electron self-exchange rate constants k'_{11} [reaction (18)] and k'_{22} (the electron self-exchange rate con-

stant for the $[(cyclam)Ni^{III/II}(SO_4)_2]^{-/2-}$ couple). The equilibria constants K_{12} are known from the redox potentials of the different complexes. Some of them were calculated from the known stability constants of the different complexes using the Nernst equation,[29,35,37,41] and k'_{22} was measured by the following procedure: the rate of the reaction of ascorbate (HA^-) with $[(cyclam)Ni^{III}(SO_4)_2]^-$ at pH 4.9 was measured [reaction (19)].

$$[Cu^{I}L]^+ + [*Cu^{II}L]^{2+} \rightarrow [Cu^{II}L]^{2+} + [*Cu^{I}L]^+ \quad (18)$$

$$HA^- + [(cyclam)Ni^{III}(SO_4)_2]^- \rightarrow HA^{\cdot} + [(cyclam)Ni^{II}(SO_4)_2]^{2-};\ k_{19} = 2.7\times10^4\ M^{-1}s^{-1} \quad (19)$$

The electron self-exchange rate constant for the ascorbate couple is known.[47] From these values, a value of $k'_{22} = 1.1\times10^3\ M^{-1}s^{-1}$ for $[(cyclam)Ni^{III}(SO_4)_2]^-$ at $\mu = 0.30$ M is obtained. Using these data and the measured rate constants for reaction (1) (neglecting the electrostatic work term, which is small for reactions of relatively large ions with small charges in solutions with a relatively high ionic strength) the self-exchange rate constants, k'_{11}, of the $Cu^{II}L/Cu^{I}L$ couples, reaction (18), were calculated by applying the Marcus cross relation. These results are summed up in Table 1.

The results obtained for the self exchange of $Cu^{2+/+}_{aq}$ [reaction (20)] are in very good agreement with those of Davies et al.,[48] who obtained $k'_{11} = 2.0\times10^{-4}\ M^{-1}s^{-1}$.

$$Cu_{aq}^{+} + *Cu_{aq}^{2+} \overset{k'_{11}}{\rightarrow} Cu_{aq}^{+} + *Cu_{aq}^{2+} \quad (20)$$

This observation suggests that the value used for k'_{22} and the experimental approach used are adequate, although the value reported by Sisley and Jordan,[49] $k'_{11} = 5\times10^{-7}\ M^{-1}s^{-1}$, is considerably lower. Recently,[40] the electron self-exchange of $[Cu^{II/I}(AN)_n]^+$ (n = 3 or 4) was reported to be around $5\times10^{-9}\ M^{-1}s^{-1}$ in solutions containing 50–97.5% AN. The authors state that "the various Cu^{II} solvates have similar self-exchange constants", although this is clearly not the case for $[Cu^{I}(AN)]^+$ and $[Cu^{I}(AN)_2]^+$ measured in the present study, which shows that k'_{11} decreases with an increase in n. The value reported for n = 3–4 is orders of magnitude smaller than that for n = 2, and this observation is in agreement with the assumption that k_{14} is very small and can be neglected.

It is of interest to note that all the ligands studied by us lower the self-exchange rate constant relative to that of $Cu^{2+/+}_{aq}$. This observation is not general,[50] and the self-exchange rate constants of copper enzymes are about ten orders of magnitude higher.[51–53]

Discussion

The three ligands chosen for this study slow down the rates of reduction of both $[(cyclam)Ni^{III}(SO_4)_2]^-$, an outer-sphere oxidant, and $[(NH_3)_5Co^{III}Cl]^{2+}$, an inner-sphere oxidant, although this is clearly not a general observation as L^1 accelerates the rate of reduction of NO_2^- by Cu^{I}.[18] The effect of L^1, which shifts the redox potential of the $Cu^{2+/+}_{aq}$ couple cathodically,[34–36] on the rate constants is considerably smaller than would be expected.

It is of interest to note that AN and H_2fum not only shift the redox potential of the $Cu^{2+/+}_{aq}$ couple anodically but also considerably decrease the rate of the electron self-exchange reaction [reaction (18)]. The combination of the effect of these ligands on the redox potential and on the electron self-exchange rate constants suggests that their complexes are poor catalysts for Cu^{I}-catalyzed processes that involve a redox process. Thus, it is concluded that acetonitrile and alkenes should not be used as solvents for such processes. On the other hand, the electron self-exchange rate of the $[Cu^{II/I}L^1]^{2+/+}$ couple is only slightly lower than that of the $Cu^{2+/+}_{aq}$ couple and L^1 shifts the redox potential of the $Cu^{II/I}$ couple cathodically. The contribution of these effects explains the observation that $[Cu^{I}L^1]^+$ is a very good catalyst[54] for Cu^{I}-catalyzed processes.

Experimental Section

Materials: $CuSO_4$, Cu^0, acetonitrile (AN), fumaric acid (H_2fum), L^1, sodium perchlorate, and perchloric acid were ordered from Aldrich. $[(cyclam)Ni^{III}(SO_4)_2]H$[55] and $[(NH_3)_5Co^{III}Cl](ClO_4)_2$[23] were synthesized according to literature procedures. All solutions were prepared from A.R. grade chemicals and from deionized water further purified by passing through a Milli Q Millipore setup (final resistivity > 10 MΩ cm^{-1}).

Solutions of the $[Cu^{I}L]^+$ complexes were prepared by a comproportionation process [reaction (4)]. The solutions' color changed after several hours from blue (indicating $[Cu^{II}L]^{2+}$ complexes) to colorless (indicating $[Cu^{I}L]^+$ complexes). Solid copper metal was added to deaerated solutions containing $CuSO_4$ and an excess of L.

Reaction (1) was studied at $\mu = 0.30$ M, maintained by the addition of Na_2SO_4 in order to stabilize $[(cyclam)Ni^{III}(SO_4)_2]^-$. The stability constant of $[(cyclam)Ni^{III}(SO_4)_2]^-$ is $K = [[(cyclam)Ni^{III}(SO_4)_2]^-]/[[(cyclam)Ni^{III}(H_2O)_2]^{3+}[SO_4^{2-}]^2] = 5\times10^6\ M^{-2}$,[56,57] therefore a high concentration of SO_4^{2-} is essential. Solutions of $[(cyclam)Ni^{III}(SO_4)_2]^-$ were prepared by literature procedures.[56,58] Reaction (2) was studied at $\mu = 0.20$ M. The reactions were carried out at the appropriate pH, i.e. that at which the ligands bind to the copper ion. The experiments with AN and $H_n$fum (n = 0–2) as ligands were carried out at pH 3.0. The experiments with L^1 were carried out at pH 6, where L^1 also acts as a buffer. Table 3 sums up the pK's of the ligands and the binding constants of $[Cu^{I}L]^+$. All $[Cu^{I}L]^+$, $[(cyclam)Ni^{III}(SO_4)_2]^-$, and $[(NH_3)_5Co^{III}Cl]^{2+}$ complexes were handled under strictly anaerobic conditions, using the syringe technique. All experiments were carried out at room temperature (22 °C). Blank experiments demonstrated, as expected, that the different $[Cu^{II}L]^{2+}$ complexes do not react with $[(cyclam)Ni^{III}(SO_4)_2]^-$ or $[(NH_3)_5Co^{III}Cl]^{2+}$.

Kinetic Measurements: Stopped-flow experiments were carried out using an SX.18 Applied PhotoPhysics stopped flow machine that enables kinetic measurements of reactions with half lifetimes above 2 ms. A 05-109 Spectra Kinetics Monochromator, which enables measurements in the range 200–700 nm, was used. The optical path was 10 mm.

The absorbance was followed as a function of time at the appropriate absorption bands of the complexes. The disappearance of [(cy-

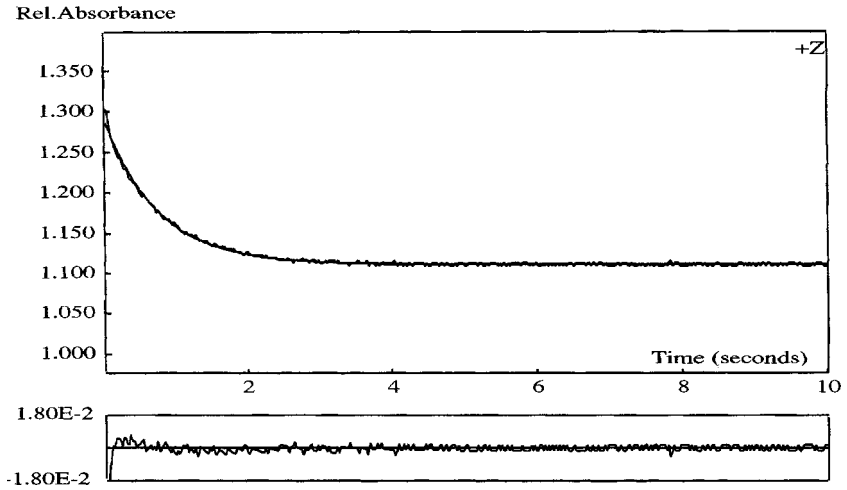

Figure 7. Dependence of $[(cyclam)Ni^{III}(SO_4)_2]^-$ concentration on time. The experiments were carried out at $[Cu^{I}]_T = 2.0 \times 10^{-4}$ M, 2.5×10^{-3} M fum, $\mu = 0.30$ M, pH 3.0; the solutions were He-saturated.

clam)$Ni^{III}(SO_4)_2]^-$ and $[(NH_3)_5Co^{III}Cl]^{2+}$ was followed at 435 and 530 nm, respectively (Figure 7). The formation of $[Cu^{II}L]^{2+}$ was followed at $\lambda > 600$ nm. Each kinetic run was repeated at least five times using at least two independently prepared stock solutions. The error limit of the measured rates is $\leq 10\%$.

The Δ(absorbance) observed was always in agreement with expectations based on $[Cu^{I}L]^+$ and $\varepsilon[Ni^{III}L(SO_4)_2]^-$ and $\varepsilon[(NH_3)_5Co^{III}Cl]^{2+}$.

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