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Electron-Transfer Kinetics of the Copper(II/I) Complex with 1,4,8,11-Tetrathiacyclotetradecane in Acetonitrile

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Introduction

Copper complexes with macrocyclic tetrathiaethers have been shown to undergo electron-transfer reactions that follow a dual-pathway mechanism (Figure 1).[2] This mechanism arises from a conformational (and coordination number) change and an electron-transfer step that occur in a sequential, rather than concerted, manner. The copper(II) complex with [14]aneS$_4$ ([14]aneS$_4$ represents 1,4,8,11-tetrathiacyclotetradecane) is six-coordinate (with solvent or anion molecules occupying the apical sites in the distorted octahedron),[3] and the copper(I) complex is four-coordinate with a distorted-tetrahedral geometry.[4] This change in coordination is believed to reduce the overall rate of reduction or oxidation. However, a study of five-coordinate copper complexes[5] that have the same coordination in the Cu(II) and Cu(I) forms yielded self-exchange rate constants (k_{11} = 10^2−10^4 M^{-1} s^{-1}) that are similar to the self-exchange rate constant (k_{11} = 10^4 M^{-1} s^{-1}) for the Cu$^{II/I}$([14]aneS$_4$) complex.[2] A direct comparison is somewhat difficult because the electron-transfer reactions of the five-coordinate copper complexes were conducted in acetonitrile, while the those of Cu$^{II/I}$([14]aneS$_4$) were studied in water.

The only previously published study on electron-transfer kinetics of a copper(II/I) complex in both solvents (vide infra) showed a 40-fold decrease in the self-exchange rate constant upon going from water to acetonitrile.[6] This difference is much larger than expected on the basis of the solvent dielectric and suggests that the solvent directly influences the electron-transfer process. To determine the influence of solvent and allow a more direct comparison between self-exchange rate constants of coordination-invariant and coordination-variant copper complexes, the electron-transfer kinetics of Cu$^{II/I}$([14]aneS$_4$) have now been studied in acetonitrile.

Experimental Section

Preparation of Reagents. The acetonitrile used in this research was purchased from Fisher Scientific (HPLC grade) and was used as received. Karl Fisher titrations indicated that no more than 0.017% w/w (i.e., about 7 mM) water was present in the acetonitrile even after the bottle had been open for 2−3 weeks. No attempt was made to dry the solvent since initial experiments showed that adding small amounts (up to 3% w/w) of water had no effect on the observed kinetics of Cu$^{II/I}$([14]aneS$_4$) reacting with three selected reagents: Co^{II}(bpy)$_3$, Mn^{III}(bpyO$_2$)$_3$, Fe^{III}(bpy)$_3$ (see footnote a in Table 1 for ligand abbreviations). Copper(II) and sodium perchlorate salts were prepared as previously reported.[7] The sodium perchlorate was recrystallized from acetonitrile before use. Copper(I) perchlorate was prepared by crystallization from acetonitrile using the method of Hathaway et al.[8] Complexes of copper(II) and copper(I) with [14]aneS$_4$ were prepared by dissolving an excess of the ligand in a solution of copper(II) or copper(I) perchlorate which had been standardized against EDTA.[9] The reagent Mn^{II}(bpyO$_2$)$_3$ was prepared by dissolving an excess of bpyO$_2$ (Aldrich) in a solution containing Mn(ClO$_4$)$_2$ (GFS Chemicals) which had been recrystallized three times from water before use. [*Warning: Metal perchlorates are potentially explosive and should never be heated to dryness.*] All other counter-reagents were prepared by standard literature methods.[10] Solutions of the +2 reductants were prepared by dissolving a weighed sample in deaerated acetonitrile. The solutions were placed over thallium shot (Aldrich) to ensure that the counter-reagent existed in the +2 state and deaerated until just before use. Solutions of the +3 oxidants were prepared by controlled-potential bulk electrolysis of a solution containing the corresponding reactant in the +2 state. These solutions were deaerated during the electrolysis and used immediately after preparation. The ionic strength of all solutions was maintained at 0.10 M with sodium perchlorate. The deaeration of the solutions was performed with chromous-scrubbed nitrogen. The stream of nitrogen was dried with Drierite (anhydrous CaSO$_4$) and saturated with acetonitrile before passing through any solutions.

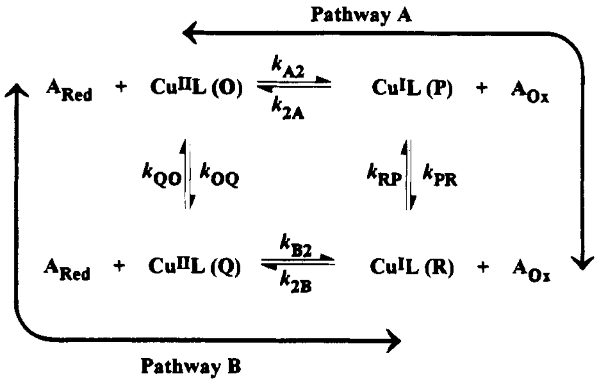

Figure 1. Dual-pathway mechanism proposed for electron-transfer reactions of copper(II/I) complexes with macrocyclic tetrathiaethers. Species O and R represent the stable conformers, and species P and Q represent the metastable intermediates. Species A represents the counter-reagent.

Stopped-Flow Kinetics. All kinetic determinations were performed on a Durrum-Gibson stopped-flow spectrophotometer, which included a newly-modified flow system designed and built by Tritech Scientific Ltd., interfaced to an Insight 486 PC. The original flow system contained rubber gaskets which leaked when studies were attempted in acetonitrile. All of the gaskets in the Tritech system are Teflon

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Table 1. Second-Order Electron-Transfer Rate Constants and Self-Exchange Electron-Transfer Rate Constants Obtained for $Cu^{II/I}([14]aneS_4)$ Using Selected Counter-Reagents in Acetonitrile Solution at 25 °C and $\mu = 0.10$ M ($NaClO_4$)

reagent[a]	E^f,V vs Fc[b]	k_{22}, $M^{-1}\,s^{-1}$	10^8r, cm	$10^{-5}k_{12}$ (or k_{21}), $M^{-1}\,s^{-1}$	log k_{11}, $M^{-1}\,s^{-1}$
CuII/I([14]aneS4)	0.205		4.4[c]		
reducing agents					
$Co^{II}(bpy)_3$	−0.076	0.645[d]	7.0[e]	0.057(2)	3.24
$Ru^{II}(NH_3)_4bpy$	0.127	5.50 × 10^5 [d]	4.4[c]	2.7(6)	3.55
$Ru^{II}(NH_3)_5isn$	−0.012	4.71 × 10^5 [d]	3.8[f]	26(1)	3.53
oxidizing agents					
$Mn^{III}(bpyO_2)_3$	0.442	80[g]	4.0[g]	0.42(3)	3.23
$Ni^{III}([14]aneN_4)$	0.591	3.3 × 10^3 [h]	3.6[i]	1.72(5), 1.31(6)	0.63, 0.34
$Fe^{III}(4,7\text{-}Me_2phen)_3$	0.538	2.7 × 10^7 [j]	6.6[c]	5.9(2), 10.4(6)	−1.02, −0.50
$Fe^{III}(bpy)_3$	0.669	3.7 × 10^6 [j]	6.0[c]	22(1)	−0.65

[a] bpy = bipyridine; isn = isonicotinamide; $bpyO_2$ = *N*,*N'*-dioxo-2,2'-bipyridine; $[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane; 4,7-Me_2phen = 4,7-dimethyl-1,10-phenanthroline. Formal potentials and k_{22} values of these reagents refer to the III/II redox couple, except for $Cu^{II/I}([14]aneS_4)$. [b] Fc = ferrocenium/ferrocene redox couple. [c] Martin, M. J.; Endicott, J. F.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1987**, *26*, 3012–3022. [d] The self-exchange rate constants for these reagents were determined as part of this work by applying the Marcus relationship to the second-order rate constants obtained for the oxidation of $Co^{II}(bpy)_3$ by (i) $Mn^{III}(bpyO_2)_3$ (to determine the k_{22} value for the $Co^{III/II}(bpy)_3$ redox couple), (ii) $Ru^{III}(NH_3)_4bpy$, and (iii) $Ru^{III}(NH_3)_5isn$ (see text for details); also see the supplementary material for specific experimental data. [e] Tsukahara, K.; Wilkins, R. G. *Inorg. Chem.* **1985**, *24*, 3399–3402. [f] Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883–892. [g] Reference 12. [h] Macartney, D. H.; Mak, S. *Can. J. Chem.* **1992**, *70*, 39–45. [i] Fairbank, M. G.; Norman, P. R.; McAuley, A. *Inorg. Chem.* **1985**, *24*, 2639–2644. [j] Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1978**, *82*, 2542–2549.

which does not suffer from this leakage problem. The temperature of the flow system was maintained at 25 °C with a circulating water bath (Haake). The slower cross-reactions were carried out under pseudo-first-order conditions (one reagent in at least 10-fold excess). The faster cross-reactions were carried out under second-order conditions, and the data were treated with a previously described method.[2]

Cyclic Voltammetry. The formal potentials of all metal complexes were measured by cyclic voltammetry using a BAS-100 electrochemical analyzer (Bioanalytical Systems). A 3 mm glassy-carbon-disk working electrode, platinum-wire auxiliary electrode, and an aqueous Ag/AgCl reference electrode were used in generating the cyclic voltammograms. Ferrocene (Sigma Chemical Co.) was employed as an internal standard in all measurements, and the formal potentials are referenced to this redox couple. All systems appeared reversible up to a scan rate of 500 mV/s with the peak separation ≅70 mV. The ionic strength of all solutions was maintained at 0.10 M with sodium perchlorate which also served as the supporting electrolyte.

Results

The electron-transfer kinetics of $Cu^{II/I}([14]aneS_4)$ were studied by reducing the Cu(II) complex or by oxidizing the Cu(I) complex with a suitable counter-reagent. The formal potentials of the counter-reagents were measured rather than taken from literature sources. A summary of the formal potentials measured in this work is in Table 1. The self-exchange rate constants for many metal complexes in acetonitrile have been summarized by Wherland,[11] but none were suitable for *reducing* the $Cu^{II}([14]aneS_4)$ complex on the time scale of the stopped-flow method. Therefore, we first determined the self-exchange rate constants for three metal complexes that could be used as reducing agents for $Cu^{II}([14]aneS_4)$. The self-exchange rate constant for $Co^{III/II}(bpy)_3$ was determined by reacting $Co^{II}(bpy)_3$ with $Mn^{III}(bpyO_2)_3$, the self-exchange rate constant of which has been previously determined in acetonitrile.[12] Subsequently, the self-exchange rate constants for $Ru^{III/II}(NH_3)_4bpy$ and $Ru^{III/II}(NH_3)_5isn$ were determined from reactions with $Co^{II}(bpy)_3$. The cross-reaction rate constants, in units of $M^{-1}\,s^{-1}$, for these reactions were as follows (25 °C, $\mu = 0.10$ M): for $Co^{II}(bpy)_3 + Mn^{III}(bpyO_2)_3$, 7.9(5) × 10^5; for $Co^{II}(bpy)_3 + Ru^{III}(NH_3)_4bpy$, 3.3(1) × 10^4; and for $Co^{II}(bpy)_3 + Ru^{III}(NH_3)_5isn$, 3.45(5) × 10^3 (values in parentheses represent the standard deviations relative to the last significant digit listed). These second-order rate constants can then be used to calculate the self-exchange rate constants by means of the Marcus cross-relation. The resultant values are summarized in Table 1.

The electron-transfer kinetics of $Cu^{II/I}([14]aneS_4)$ were studied using seven different counter-reagents. At least four different concentrations of counter-reagent, usually spanning a 10-fold range, were used in the kinetic determinations. For each concentration, 10–12 determinations were performed, and the rate constants were averaged. The original experimental rate constants are available as supplementary material. Each reaction behaved as a second-order reaction (i.e., second-order rate constants were constant or pseudo-first-order rate constants were directly proportional with the concentration of the reagent in excess). The results for these reactions are summarized in Table 1. The second-order rate constants varied from 5.7(2) × 10^3 to 1.04(6) × 10^6 $M^{-1}\,s^{-1}$ which represents a considerable range of thermodynamic driving force.

Discussion

Comparison of electron-transfer kinetics from one complex to another is generally performed by calculating a self-exchange rate constant using the Marcus expression.[13] The most familiar form is

$$k_{12} = \sqrt{k_{11}k_{22}K_{12}f_{12}}\,W_{12}$$

where k_{12} is the cross-reaction rate constant, k_{11} is the self-exchange rate constant for the copper complex, k_{22} is the self-exchange rate constant for the counter reagent, K_{12} is the equilibrium constant for the reaction, f_{12} is the Marcus nonlinear correction term, and W_{12} is a work term. Application of this equation to the measured cross-reaction rate constants provides self-exchange rate constants for the copper complex which are summarized in Table 1.

All of the reductions of $Cu^{II}L$ and the slowest $Cu^{I}L$ oxidation yield the same value for k_{11} within experimental error. This would indicate that these four reactions proceeded by the same pathway. The two fastest oxidations yield values for k_{11} that are essentially the same but are about 10^4 times smaller than the k_{11} value from reductions and the slowest oxidation. These

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results are consistent with the dual-pathway mechanism proposed for this system in water.[2] On the basis of our earlier analysis, the larger value for k_{11} represents pathway A (Figure 1), and the smaller value pathway B. The intermediate value for k_{11} obtained from the oxidation with $\mathrm{Ni^{III}([14]aneN_4)}$ has been observed with other Cu(II/I) systems,[14] where it has been interpreted to indicate conformational "gating". When the conformational change becomes rate determining, the reaction should become first-order. Such first-order behavior was not observed during this investigation as the reaction with $\mathrm{Ni^{III}([14]aneN_4)}$ always appeared as a second-order reaction. Our failure to demonstrate the onset of first-order behavior is not understood at this time. A possible explanation for this would be that the reaction actually involves a "ladder" mechanism.[15] This will be the subject of future investigation.

Comparison with our previous aqueous studies on $\mathrm{Cu^{II/I}([14]aneS_4)}$ is illuminating. The average values for log k_{11} characteristic of pathway A are 3.46 and 3.82 in acetonitrile and water,[2] respectively. These values are surprisingly similar, but dielectric effects need to be considered before a valid comparison can be made. It is assumed that before reaction can take place, an outer-sphere association between the two reactants must occur.[16,17]

$$\mathrm{Cu^{II}L^* + Cu^{I}L} \overset{K_{os}}{\rightleftharpoons} \underset{\substack{\text{outer-sphere}\\ \text{precursor complex}}}{(\mathrm{Cu^{II}L^{*}\cdot Cu^{I}L})} \overset{k_{et}}{\rightleftharpoons}$$

$$\underset{\substack{\text{outer-sphere}\\ \text{successor complex}}}{(\mathrm{Cu^{I}L^{*}\cdot Cu^{II}L})} \rightleftharpoons \mathrm{Cu^{I}L^* + Cu^{II}L}$$

An equilibrium constant, K_{os}, is used to describe the ratio between unassociated reactants and an outer-sphere associated species preceding the actual electron-transfer step represented by rate constant k_{et}. The K_{os} value is dependent on solvent dielectric, ionic strength, and charge of the reactants.

The self-exchange rate constant can be described by the following equation:[16,17]

$$k_{11} = K_{os}k_{et}$$

Assuming a center-to-center distance of closest approach of 8.8×10^{-8} cm, the value of K_{os} in water is 0.68 $\mathrm{M^{-1}}$ and 0.37 $\mathrm{M^{-1}}$ in acetonitrile. The log k_{et} values from pathway A are then calculated to be 3.89 and 4.00 in acetonitrile and water, respectively. These values are much closer than warranted by our experimental error and would indicate that differences in solvent reorganization do not significantly influence the self-exchange process for $\mathrm{Cu^{II/I}([14]aneS_4)}$.

For pathway B, the average log k_{11} in water[2] is −0.010 and the average log k_{11} in acetonitrile is −0.67. These values lead to calculated values of log k_{et} of 0.16 and −0.24 in water and acetonitrile, respectively. These values are still well within our experimental error, particularly since pathway B is only observed on the very fastest cross-reactions where the experimental data are less accurate.

It is conceivable that the $\mathrm{Cu^{II}L}$ species exists in acetonitrile solution as the di-aquo complex, $\mathrm{Cu^{II}L(H_2O)_2}$, due to contamination from water. However, a previous study[9] showed a difference in the electronic spectra of the $\mathrm{Cu^{II}([14]aneS_4)}$ complex as the visible peak maximum shifted from 570 nm in water to 560 nm in acetonitrile. This difference would seem to indicate that the predominant species in acetonitrile differs from that in aqueous solution.

On the basis of direct NMR line-broadening measurements, Swaddle and co-workers[6] reported that the self-exchange rate constant of bis(2,9-dimethyl-1,10-phenanthroline)copper(II/I) ($\mathrm{Cu^{II/I}(dmp)_2}$) was 40 times larger in water ($2 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$) than in acetonitrile ($5 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$). These authors attributed this large difference to differences in solvent reorganization, particularly because the copper(II) complex has at least one solvent molecule associated with it. However, chloride ion was present in their aqueous solutions but absent in their acetonitrile solutions. Chloride ion is a known inner-sphere bridging species and could cause the reaction to proceed by a faster inner-sphere mechanism. In considering this issue, these authors concluded that a chloride inner-sphere mechanism was unlikely in their study because the self-exchange rate constant shows no dependence on concentration in aqueous solution. However, in other studies in this laboratory, we have observed that even a stoichiometric quantity of chloride ion can accelerate the self-exchange rate of $\mathrm{Cu^{II/I}L}$ systems markedly. Since our results indicate that the difference between the self-exchange rate constants in water and acetonitrile for $\mathrm{Cu^{II/I}[14]aneS_4}$ is small, and can be accounted for on the basis of solvent dielectric, we suspect that Swaddle's aqueous data on $\mathrm{Cu^{II/I}(dmp)_2}$ may reflect a significant chloride effect.

Stanbury and Wilson have reported the self-exchange rate constants for a series of five-coordinate copper complexes in acetonitrile.[5] The self-exchange rate constants for these coordination-invariant complexes (1.8×10^3 to $3.5 \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$) are similar to the self-exchange rate constants for $\mathrm{Cu^{II/I}([14]aneS_4)}$ in both water and acetonitrile. Our current results support our previous conclusion that the coordination-invariant systems do not react more rapidly than our systems which involve both an exchange of inner-sphere solvent and a change in coordination geometry.

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Supplementary Material Available: Tables of experimental rate constants measured for all reactions (6 pages). Ordering information is given on any current masthead page.

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