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Redox Behavior of Copper(II) and Copper(I) Complexes with Tetradentate Bis(pyridyl)-dithiaether and Bis(pyridyl)-diaza ligands towards Ruthenium Ammine and Bipyridyl Complexes

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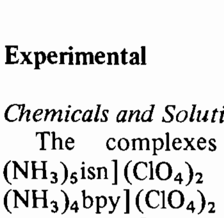
Abstract

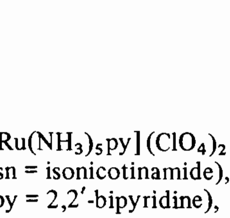
Electron transfer reactions involving the 1,8-bis-(2-pyridyl)-3,6-dithiaoctane copper(II) complex, Cu-(pdto)$^{2+}$, and a series of Ru(II) ammine and bipyridyl complexes have been studied kinetically in MES buffered 0.10 M $LiCF_3CO_2$. Values of the second-order rate constant, k_2 (M^{-1} s^{-1}) are $Ru(NH_3)_5py^{2+}$, 3.8×10^4; $Ru(NH_3)_5isn^{2+}$, 1.4×10^4; $Ru(NH_3)_4bpy^{2+}$, 2.0×10^3; *cis*-$Ru(NH_3)_4(isn)_2{}^{2+}$, 2.3×10^2; *cis*-$Ru(bpy)_2Cl_2$, 4.4×10^4; $Ru(bpy)_2C_2O_4$, 4.5×10^5; at 25.0 °C in 50% aqueous methanol. Data for the ammine complexes, which follow a linear free energy relationship between log k_2 and $E°$, the Ru(III)/Ru(II) reduction potential, suggest an outer-sphere mechanism. Inner-sphere electron transfer is indicated with $Ru(bpy)_2Cl_2$ and $Ru(bpy)_2C_2O_4$ as reductants. Oxidation of coordinated oxalate occurs with $Ru(bpy)_2C_2O_4$. The rate constant has also been determined for the oxidation of the 1,8-bis(2-pyridyl)-3,6-dimethyl-3,6-diazaoctane copper(I) complex, Cu(pdao)$^+$ by $Ru(NH_3)_5py^{3+}$ in 100% aqueous 0.10 M $LiCF_3CO_2$. A value of 1.8×10^4 M^{-1} s^{-1} was obtained at 25.0 °C and pH 6.1. Application of the Marcus relations has yielded estimated self-exchange electron-transfer rate constants of 0.63 and 8.1 M^{-1} s^{-1} for the Cu(pdto)$^{2+/+}$ and Cu(pdao)$^{2+/+}$ couples.

Introduction

Renewed interest has been shown in recent years in the structure and redox behavior of copper complexes having sulfur donor ligands, because of the insight such complexes might give into the role of the methionine and cysteine sulfur atoms which are present, along with two histidine nitrogens, in the active site of certain blue copper proteins. Although much attention has been focused on the spectroscopic and thermodynamic properties of blue copper protein model complexes [1–8], and on the factors determining the specificity of electron transfer between these metalloproteins and a variety of inorganic reactants [9, 10], relatively little work has been reported on the extent to which sulfur coordination *per se,* facilitates the electron transfer at the copper center.

With the aim of exploring the kinetic redox behavior of a copper complex in a tetradentate CuN_2S_2 ligand environment over a range of thermodynamic driving force and with a variety of reductants, we have studied electron-transfer reactions of the bis-(pyridyl)-dithiaether copper(II) complex, Cu(pdto)$^{2+}$ [pdto = 1,8-bis(2-pyridyl)-3,6-dithiaoctane] with a series of Ru(II) ammine and bipyridyl complexes. The self-exchange electron-transfer rate constant for the Cu(pdto)$^{2+/+}$ couple has been estimated and compared with that which we have determined for the Cu(pdao)$^{2+/+}$ couple which has a related CuN_4 coordination environment [pdao = 1,8-bis(2-pyridyl)-3,6-dimethyl-3,6-diazaoctane].





Experimental

Chemicals and Solutions

The complexes $[Ru(NH_3)_5py](ClO_4)_2$, $[Ru(NH_3)_5isn](ClO_4)_2$ (isn = isonicotinamide), $[Ru(NH_3)_4bpy](ClO_4)_2$ (bpy = 2,2′-bipyridine), *cis*-$[Ru(NH_3)_4(isn)_2](ClO_4)_2$, *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ and $Ru(bpy)_2C_2O_4 \cdot 3H_2O$ were prepared by published procedures [11–14]. Spectra of the ammine complexes were in good agreement with literature values. The bis(bipyridine) complexes, $Ru(bpy)_2Cl_2$ and $Ru(bpy)_2C_2O_4$ showed maxima in 50% aqueous

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methanol [λ, nm (ε): 497 (8.1×10^3), 348 (7.4×10^3) and 518 (8.9×10^3), 363 (9.1×10^3)], shifted towards the UV as compared to the spectrum reported in CH_2Cl_2 [15]. The ligand pdto and the complex [Cu(pdto)]$(ClO_4)_2 \cdot H_2O$ were prepared by the literature method [16] and recrystallized from hot water. The spectrum of the complex $[Cu(pdto)]^{2+}$ at pH 6.1 [λ, nm (ε): 600 (594); 355 (3.9×10^3); 260 (1.0×10^4)] was in good agreement with that reported in the literature. Its absorbance increased in the presence of excess pdto and became constant at [pdto]/[Cu^{2+}] = 5.2 [λ, nm (ε): 600 (650); 354 (5.0×10^3)]. An identical spectrum was observed in 50% aqueous methanol as in water. Reaction solutions of $Cu(pdto)^{2+}$ were prepared by dissolving solid [Cu(pdto)]$(ClO_4)_2 \cdot H_2O$ in water or in CH_3OH/H_2O mixtures containing excess pdto ligand at an ionic strength of 0.10 M ($LiCF_3CO_2$) and an operational pH value (normally 6.1) measured with respect to aqueous reference standards. The ligand pdao was prepared from *N,N*-dimethylethylenediamine and 2-vinyl-pyridine by the method of Nikles *et al.* [5]. The Cu(II) complex was obtained by addition of $Cu(ClO_4)_2 \cdot 6H_2O$ to the ligand in ethanol, and recrystallization of the blue precipitate from aqueous ethanol. Solutions of $Cu(pdao)^+$ were generated by controlled potential reduction of $Cu(pdao)^{2+}$ at pH 6.1 in 100% aqueous 0.10 M $LiCF_3CO_2$. UV–Vis spectra of $Cu(pdao)^+$ and $Cu(pdao)^{2+}$ were in good agreement with the literature [5]. The ligands 2,2′-bipyridine and isonicotinamide were recrystallized from hot water prior to use. MES (2-[*N*-morpholino]-ethanesulfonic acid) buffer was obtained from the Sigma Chemical Company.

Kinetic Measurements

Rate measurements were made using a thermostated Aminco-Morrow stopped-flow spectrophotometer and logarithmic amplifier, the output of which was stored digitally with a Gould 805 Biomation transient recorder. A microcomputer was interfaced to the recorder and programmed to display absorbance changes $\ln(A_t - A)$, which were linear to at least three half-lives. First-order rate constants, k_{obs}, were obtained from the slopes. Reactions were generally followed at wavelengths close to the absorption maxima of the Ru(II) reductants. The reactions were studied at 0.10 M ionic strength maintained with $LiCF_3CO_2$ and at 25.0 ± 0.05 °C. Reaction solutions were adjusted to the required operational pH with MES buffer which was normally 0.01 M during the kinetic runs. Pseudo-first-order conditions were employed with [Cu(II)] present in at least a ten-fold excess. Three separate runs were usually performed for each pair of solutions in the stopped-flow. Rate constants generally agree to ±5%.

Electrochemical Measurements

A PAR model 176 potentiostat-galvanostat coupled with a Houston Instrument model 2000 X–Y recorder was used for determination of redox potentials by cyclic voltammetry. Potentials were measured at a glassy carbon electrode *versus* SCE at 25 ± 2 °C in 0.10 M $LiCF_3CO_2$ using a Pt wire auxiliary electrode. The value of the $Cu(pdao)^{2+/+}$ potential was determined as 0.144 V *versus* NHE at pH = 6.1 in aqueous 0.10 M $LiCF_3CO_2$ from the mean of the anodic and cathodic peaks occurring at 0.184 and 0.104 V. The potential of the $Cu(pdto)^{2+/+}$ couple was measured in both aqueous 0.10 M $LiCF_3CO_2$ and in 50% aqueous methanol solutions containing 0.10 M $LiCF_3CO_2$. Values of 0.596 V and 0.652 V respectively were obtained from the anodic and cathodic peaks which had peak separations of 0.11 and 0.13 volts. Reduction potentials of 0.677 V and 0.794 V were similarly determined for the *cis*-$Ru(bpy)_2Cl_2{}^{+/0}$ and *cis*-$Ru(bpy)_2C_2O_4{}^{+/0}$ couples in 50% aqueous methanol.

Results and Discussion

Rapid electron transfer between $Cu(pdto)^{2+}$ and the ruthenium(II) reductant was observed in all the reactions studied. Table I shows kinetic data for the oxidation of $Ru(NH_3)_5py^{2+}$, $Ru(NH_3)_5isn^{2+}$, $Ru(NH_3)_4bpy^{2+}$, *cis*-$Ru(NH_3)_4(isn)_2{}^{2+}$, *cis*-$Ru(bpy)_2Cl_2$ and $Ru(bpy)_2C_2O_4$. All reactions follow the second-order rate law, rate = k[Ru(II)] [Cu(II)] with the second-order rate constant, k_2, independent of pH in the range 5.5 to 7.0 studied. The measured rate constants were also found to be insensitive to variations in the excess ligand concentration ([pdto]/[Cu(II) = 3.5–8.0]). Although most experiments were carried out in 50% *v/v* aqueous methanol solutions the rate of some reactions was also measured in aqueous media. The second-order rate constants for the $Cu(pdto)^{2+}$–$Ru(NH_3)_5isn^{2+}$ reaction was found to be virtually the same in aqueous solution as in the mixed methanol–water solvent. For reduction by $Ru(NH_3)_4bpy^{2+}$, the second-order rate constant, $4.8 \times 10^3\ M^{-1}\ s^{-1}$ was more rapid in water by a factor of 2.4. A summary of the rate data for Ru(II) reduction of $Cu(pdto)^{2+}$ is shown in Table II, and correlation of the rate constants with the thermodynamic driving force for the reactions, through the Marcus cross relations, is illustrated in Fig. 1. The finding that the Marcus relations, eqn. (1), successfully correlate rate constants with thermodynamic

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad (1)$$

$$\log f_{12} = (\log K_{12})^2/4\log(k_{11}k_{22}/Z^2)$$

TABLE I. Rate Constants for the Reduction of $Cu(pdto)^{2+}$ by Ruthenium(II) Ammine Complexes at 25.0 °C and 0.10 M Ionic Strength[a]

Initial concentration × 10^5 (M)			k_2[c]
$[Cu(pdto)^{2+}]$	[Ru(II)]	$[pdto]_T$[b]	(M^{-1} s^{-1})
$Ru(NH_3)_5py^{2+}$			
105	2.1	396	3.5×10^4
52.3	2.1	247	3.4×10^4
28.0	2.1	225	3.3×10^4
25.6	1.0	76	4.5×10^4
26.3	1.0	113	3.6×10^4
14.0	1.0	68	4.7×10^4
48.9	2.1	172	3.4×10^4
$Ru(NH_3)_5isn^{2+}$			
104	2.1	404	1.2×10^4
52.3	2.1	252	1.6×10^4
26.0	2.1	128	1.4×10^4
26.0	1.0	83	1.2×10^4
16.1	1.0	72	1.1×10^4 [d]
26.3	1.0	83	1.3×10^4 [d]
$Ru(NH_3)_4bpy^{2+}$			
106	2.1	402	1.7×10^3
58.0	2.1	253	2.1×10^3
59.1	2.5	292	1.7×10^3
30.1	2.1	229	2.4×10^3
233	1.8	175	2.1×10^3
41.0	2.8	243	1.8×10^3 [e]
23.6	1.3	73	4.8×10^3 [d]
14.7	1.3	69	4.8×10^3 [d]
$Ru(NH_3)_4(isn)_2{}^{2+}$			
104	1.8	409	2.0×10^2
51.5	1.8	248	2.3×10^2
23.6	1.8	321	2.5×10^2
$Ru(bpy)_2Cl_2$			
48.0	1.3	306	5.0×10^4
11.3	1.0	247	4.3×10^4
28.3	1.0	264	3.8×10^4
$Ru(bpy)_2C_2O_4$			
47.5	1.0	300	4.1×10^5
24.3	1.0	260	4.6×10^5
14.0	1.0	253	4.9×10^5

[a] All data in 50% aqueous methanol at pH = 6.1 (MES buffer) and $LiCF_3CO_2$ medium unless otherwise indicated. [b] $[pdto]_T = [Cu(pdto)^{2+}] + [pdto]$. [c] $k_2 = k_{obs}/[Cu(pdto)^{2+}]$, where k_{obs} is observed pseudo-first-order rate constant. [d] H_2O as solvent. [e] pH = 5.5.

TABLE II. Summary of Rate Constants for Reduction of $Cu(pdto)^{2+}$ by Ru(II) Ammine and Bipyridyl Complexes at 25.0 °C

Ru(II)	$E^{\circ}_{Ru(II)/(II)}$[a] (mV *vs.* nhe)[b]	k_2 (M^{-1} s^{-1})
$Ru(NH_3)_5py^{2+}$	329	3.8×10^4
$Ru(NH_3)_5isn^{2+}$	409	1.4×10^4
$Ru(NH_3)_4bpy^{2+}$	562	2.0×10^3
$Ru(NH_3)_4(isn)_2{}^{2+}$	688	2.3×10^2
$Bu(bpy)_2Cl_2$	644	4.4×10^4
$Ru(bpy)_2C_2O_4$	794	4.5×10^5

[a] Measured in 50% CH_3OH-H_2O and 0.10 M $LiCF_3CO_2$. $E^{\circ} = 0.652$ V for $Cu(pdto)^{2+/+}$. [b] nhe, normal hydrogen electrode.

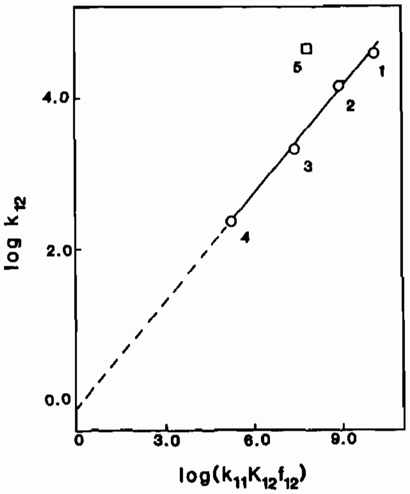

Fig. 1. Plot of the logarithms of the second-order rate constant for the reduction of $Cu(pdto)^{2+}$ by Ru(II) ammine and bipyridyl complexes *vs.* $\log(K_{12}k_{11}f_{12})$, where k_{11} is the self-exchange rate constant for the reductant [17]. 1, $Ru(NH_3)_5py^{2+}$; 2, $Ru(NH_3)_5isn^{2+}$; 3, $Ru(NH_3)_4bpy^{2+}$; 4, $Ru(NH_3)_4(isn)_2{}^{2+}$; 5, $Ru(bpy)_2Cl_2$. $k_{12} = k_2$ in Table II.

driving force for electron-transfer between $Cu(pdto)^{2+}$ and the four ruthenium(II) ammine reductants points strongly to the same, outer-sphere, mechanism being followed in all cases. Using the known self-exchange rate constants, k_{11}*, and redox potentials of the Ru(II)/Ru(III) couples, the intercept of the log k_{12} *versus* log $(K_{12}k_{11}f_{12})$ plot shown in Fig. 1, where K_{12} is the equilibrium constant for the reaction and Z is a collision number (taken to be 10^{11} M^{-1} s^{-1}), yields a value of 0.63 for the $Cu(pdto)^{2+}/Cu(pdto)^{+}$ self-exchange rate constant, k_{22}. The value of 0.47 obtained for the slope is in good agreement with the theoretical value of 0.50 predicted by eqn. (1). The

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*Values of k_{11} (M^{-1} s^{-1}) used were 1.1×10^5, $Ru(NH_3)_5py^{3+/2+}$ and $Ru(NH_3)_5isn^{3+/2+}$; 7.72×10^5, $Ru(NH_3)_4bpy^{3+/2+}$ and $Ru(NH_3)_4(isn)_2{}^{3+/2+}$; 4.9×10^7, $Ru(bpy)_2Cl_2{}^{+/0}$ [17–19].

observation that the rate constants for the reactions of the complexes *cis*-$Ru(bpy)_2Cl_2$ and *cis*-$Ru(bpy)_2C_2O_4$ with $Cu(pdto)^{2+}$ do not fall on the same line with the ammine complexes and are clearly much faster than would be predicted by their potentials, suggests that a mechanism other than simple outer-sphere electron transfer is involved in those cases. The existence of potential bridging ligands in the complexes points strongly to an inner-sphere mechanism. The bridged electron-transfer appears to have a 10^2–10^4 fold rate advantage over the outer-sphere path in these reactions. Although the bipyridyl complexes are of a different charge type to the ammine complexes, electrostatic factors would be expected to account for only a small part of the rate enhancement which is found [20]. In the $Ru(bpy)_2C_2O_4$–$Cu(pdto)^{2+}$ reaction, the reduction potential of the $Ru(bpy)_2C_2O_4^{+/0}$ couple would indicate that $Ru(bpy)_2C_2O_4^+$ is not the Ru(III) product. The coordinated oxalate is presumably oxidized during the reaction yielding a bis(bipyridyl) diaquo-ruthenium(III) or ruthenium(II) product. $Ru(bpy)_2C_2O_4$ is oxidized to $Ru(bpy)_2Cl_2^+$ by Cl_2 in HCl solution [21].

In the solid state [2], the pdto ligand provides essentially square planar coordination for the Cu(II) center, with the plane of the N and S donor atoms displaced some 0.25 Å from the metal. The coordinated perchlorate present in the crystal ($[Cu(pdto)ClO_4]ClO_4$) is presumably replaced by a labile solvent water molecule in solution. Since the $Cu(dpto)^+$ product has a 4-coordinate distorted tetrahedral structure, the appreciable inner-sphere reorganization which must accompany the redox change is consistent with the relatively slow self-exchange electron-transfer rate constant which is calculated for the $Cu(pdto)^{2+/+}$ couple from Fig. 1. Karlin and Yandell [7] have concluded from studies of a series of copper complexes having tetradentate N_2S_2 ligands that the change of coordination number on reduction rather than the rearrangement of the ligand from square planar to tetrahedral geometry makes the major contribution to the structural barrier of the reactions. The electron-transfer rate constant which we have previously determined for self-exchange in the $Cu^{2+}_{(aq)}/Cu^+_{(aq)}$ aquo ion couple ($k_{22} = 2 \times 10^{-4}$ M^{-1} s^{-1}) [22] would appear to support this conclusion. For the more rapid inner-sphere $Ru(bpy)_2Cl_2$ and $Ru(bpy)_2C_2O_4$ reactions, loss of a water molecule coordinated to $Cu(pdto)^{2+}$ in forming the bridged activated complex, prior to the electron-tranfer step, would appear to offer a more facile path for the reaction by lowering the structural barrier associated with the water loss from $Cu(pdto)^{2+}$ during the outer-sphere mechanism.

A mean second-order rate constant of 1.9×10^4 M^{-1} s^{-1} has been obtained for the oxidation of $Cu(pdao)^+$ by $Ru(NH_3)_5py^{3+}$ in aqueous 0.10 M $LiCF_3CO_2$ solution at pH 6.1 (Table III). The value of the self-exchange electron-transfer rate constant for the $Cu(pdao)^{2+/+}$ couple, 8.1 M^{-1} s^{-1}, estimated from this data compares to the value of 0.63 obtained for the $Cu(pdto)^{2+}$–$Cu(pdto)^+$ self-exchange. If the structurally related coordination environments provided by the tetradentate pdto and pdao ligands are affording comparable inner-sphere geometric constraints to the redox change, the similarity in the self-exchange rate constants would suggest that thiaether coordination, *per se,* does not offer any kinetic advantage to electron-transfer by the copper center. The principal control which sulfur donor atoms have on the reaction rate would therefore appear to be thermodynamic, arising from their influence on the operating redox potential.

TABLE III. Rate Constants for the Oxidation of $Cu(pdao)^+$ by $Ru(NH_3)_5py^{3+}$ at 25.0 °C and 0.10 M Ionic Strength[a]

$10^4 \times [Cu(pdao)]^+$	$10^5 \times [Ru(II)]$	k_2 (M^{-1} s^{-1})
3.4	1.7	2.0×10^4
3.6	1.7	1.7×10^4
7.3	1.7	1.9×10^4

[a] Aqueous $LiCF_3CO_2$, at pH = 6.1 (MES buffer).

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