

Figure 2. Metal-ligand stretch region of the infrared spectra of $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$.

large amount of $\text{Fe}(\text{CO})_5$ produced in the reaction. The compound has been reported to decompose on standing at room temperature and on vacuum transfer from one vessel to another.^{21,19} Van Dam and Oskam¹⁶ suggested that the $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ sample used in the UPS study of Baerends et al.¹⁷ was contaminated with $\text{Fe}(\text{CO})_5$ because of decomposition in the spectrometer. However, we have observed that the thermal and photochemical decomposition of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ results only in the production of $\text{Fe}_3(\text{CO})_{12}$ and C_2H_4 . It is possible that the sample of Baerends et al. had not been originally free of $\text{Fe}(\text{CO})_5$, as was also the case in our earlier XPS study.¹ Because of these prior difficulties in the preparation and handling of this important compound, the synthesis and characterization of $\text{Fe}(\text{C}-\text{O})_4\text{C}_2\text{H}_4$ are described in some detail below.

Diiron enneacarbonyl in pentane was treated with C_2H_4 at 50 atm for 48 h. The excess C_2H_4 was vented, and the mixture of $\text{Fe}(\text{CO})_5$

and $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ was separated from the solvent by fractional condensation on a vacuum line at -63°C . The $\text{Fe}(\text{CO})_5\text{-Fe}(\text{C}-\text{O})_4\text{C}_2\text{H}_4$ mixture was separated by reduced-pressure fractional distillation with a 15-cm Vigreux column, a 0°C condenser, and a four-arm fraction collector cooled to 0°C . Nitrogen was bled into the still pot to prevent bumping and to maintain the pressure at 12 mm. The majority of the material distilled at $19\text{--}26^\circ\text{C}$ and was primarily $\text{Fe}(\text{CO})_5$ contaminated with a small amount of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$. Iron tetracarbonyl ethylene was collected at $31\text{--}34^\circ\text{C}$. The middle portion of this fraction (bp $33\text{--}34^\circ\text{C}$) was distilled into a vial and stored in vacuo at -78°C in the dark prior to obtaining the XPS spectrum. The absence of $\text{Fe}(\text{CO})_5$ in the sample of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ was confirmed by gas-phase infrared spectroscopy.²² Spectra were obtained on a Perkin-Elmer 597 infrared spectrometer with use of a 10-cm path length cell and a sample pressure of ~ 8 mm. The metal-ligand stretch regions of $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ are shown in Figure 2. The absence of bands at 610, 467, and 421 cm^{-1} in the infrared spectrum and the narrowness of the boiling range are our principal evidence that the $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ sample was free of $\text{Fe}(\text{CO})_5$.

Gas-phase X-ray photoelectron spectra were obtained with a GCA/McPherson ESCA 36 spectrometer by a method described previously.² The vapor from $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ held at -25°C was passed into the gas cell of the spectrometer, which was at ambient temperature. The spectra obtained did not vary during the run. Spectra were calibrated by using the $\text{N}_2\ 1s$, $\text{Ne}\ 1s$, and $\text{Ne}\ 2s$ reference peaks.

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Electron-Transfer Reactions of Copper(III)-Peptide Complexes with Ruthenium(II) Ammine and Copper(II)-Peptide Complexes

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The self-exchange rate constants for five copper(III, II) peptides have been determined by using the reactions of copper(III) α -aminoisobutyryl- α -aminoisobutyryl- α -aminoisobutyric acid with the copper(II) complexes. Copper(III)-peptide complexes are rapidly reduced by $\text{Ru}(\text{NH}_3)_6^{2+}$, $\text{Ru}(\text{NH}_3)_5(\text{py})^{2+}$, and $\text{Ru}(\text{NH}_3)_5(\text{pic})^{2+}$ at rates that are accurately predicted from the Marcus theory and the determined self-exchange rate constants for copper(III, II) peptides and the ruthenium complexes. The activation parameters for the reactions of copper(III) α -aminoisobutyryl- α -aminoisobutyryl- α -aminoisobutyramide with $\text{Ru}(\text{NH}_3)_6^{2+}$ are $\Delta H^\ddagger = 1.5 \pm 0.3\text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -21 \pm 2\text{ cal K}^{-1}\text{ mol}^{-1}$. For the corresponding reaction with $\text{Ru}(\text{NH}_3)_5(\text{py})^{2+}$, the values are $\Delta H^\ddagger = 1.8 \pm 0.6\text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -25 \pm 2\text{ cal K}^{-1}\text{ mol}^{-1}$. The data support an outer-sphere mechanism of electron transfer for all the reactions.

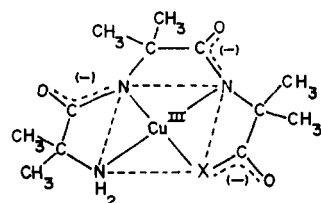
Introduction

Copper(III) peptides, which are d^8 low-spin square-planar complexes,¹⁻³ undergo electron-transfer reactions by at least two different pathways. In the reductions with IrCl_6^{3-} and $\text{Fe}(\text{CN})_6^{4-}$ the extraordinary speed of the reactions (corresponding to an apparent self-exchange rate constant of approximately $10^8\text{ M}^{-1}\text{ s}^{-1}$ for $\text{Cu}(\text{III})\text{-Cu}(\text{II})$) strongly suggests inner-sphere mechanisms.^{4,5} In these cases chloride or cyanide

bridges between the metal centers can form readily along the open axial positions of the copper(III) complexes. Although only weak axial coordination occurs with copper, this appears to provide a favorable inner-sphere pathway for rapid electron transfer. On the other hand, the electron-exchange reaction of $\text{Cu}^{\text{III}}(\text{H}_2\text{Aib}_3)$ (I) with $\text{Cu}^{\text{II}}(\text{H}_2\text{Aib}_3)^-$ (see ref 6 for abbreviations) was measured directly by ^1H NMR line broadening⁷ and gave a self-exchange rate constant of $5.5 \times 10^4\text{ M}^{-1}$

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- Abbreviations used: G, glycol; A, alanyl; V, valyl; Aib, α -aminoisobutyryl; OCH₃, terminal ester; a, terminal amide; C, cyclo(β -alanyl-glycyl- β -alanyl-glycyl); H_nL refers to a peptide ligand with n deprotonated peptide nitrogens coordinated to the metal; py, pyridine; pic, 4-methylpyridine.
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I: X = O
II: X = NH

s^{-1} . The magnitude of this rate constant was in agreement with values from a number of cross-reactions between Cu(III) peptides and Cu(II) peptides. It was proposed that these reactions either proceeded by an outer-sphere electron-transfer process or involved weak bridging by axial water between copper(III) and copper(II).⁷

In the present work we examine the cross-exchange reactions of $Cu^{III}(H_{-3}Aib_3)$ with a series of $Cu^{II}(H_{-3}L)$ peptide complexes where ΔE° values for the reactions vary from -0.03 to $+0.29$ V. An excellent Marcus correlation is found with an average self-exchange rate constant of $2.1 \times 10^4 M^{-1} s^{-1}$ for the $Cu^{III,II}(H_{-3}L)$ series. Because the E° value (0.37 V vs. NHE) for the $Cu^{III,II}(H_{-3}Aib_3)$ couple is much lower than the E° value for the $Cu^{III,II}(H_{-2}Aib_3)$ couple (0.66 V), it is also possible to study the electron-transfer reactions of $Cu^{III}(H_{-3}Aib_3)$ (II) with $Ru(NH_3)_5X^{2+}$ (where X = py, pic, or NH_3 and E° is 0.310, 0.265, or 0.065 V, respectively). Other copper(III)-peptide complexes, with more positive E° values, react too rapidly with these ruthenium(II) complexes. Since the ruthenium(II) complexes have no bridging ligands, the electron-transfer reactions should proceed by an outer-sphere mechanism if pyridine-ring overlap with axial positions on copper(III) is not important. Rate constants and activation parameters have been reported for the Ru(III)-Ru(II) self-exchange reactions.^{8,9} We find that the rates of electron transfer between Cu(III) and Ru(II) agree well with values calculated by the Marcus theory, which leads to the conclusion that these reactions are indeed outer-sphere processes, uncomplicated by any special pyridyl-ring conduction effects. The results also indicate that the Cu(III)-Cu(II) exchange reactions are outer-sphere processes.

Experimental Section

Copper Peptides. Peptide ligands containing the Aib residue were synthesized in this laboratory.^{10,11} Other oligopeptides were purchased from Biosynthetika, Oberdorf, Switzerland. The copper(II) complexes were formed by addition of a 10% molar excess of the ligand to a $Cu(ClO_4)_2$ solution and adjustment of the pH to 9–9.5 with NaOH to give the fully deprotonated complexes. The complexes were oxidized at a potential 0.2 V greater than E° with use of a flow-through graphite-powder working electrode packed in a porous-glass column wrapped externally with a platinum auxiliary electrode.¹² Copper(III) complexes containing the Aib residue are thermally stable in solution; however, they readily decompose photochemically at wavelengths less than 550 nm.¹¹ Therefore, room light was filtered through a Kodak 1A filter that transmits light only at wavelengths greater than 580 nm.

Ruthenium Ammine Complexes. The starting material for the ruthenium complexes was $Ru(NH_3)_6Cl_3$ (Johnson Matthey, Inc.) purified by reported methods.⁸ The $Ru(NH_3)_6^{2+}$ solution was prepared by anaerobic reduction of the corresponding Ru(III) complex using the flow-through electrolysis cell described above. The solutions were purged continuously with argon. The concentration of Ru(II) was

Table I. Spectral and Electrochemical Data for the Copper and Ruthenium Complexes

complex	λ_{max} , nm	ϵ , $M^{-1} cm^{-1}$	E° , V ^a	ref
$Cu^{III}(H_{-3}Aib_3a)$	364	6870	0.37	b
$Cu^{III}(H_{-3}G_2AibG)^-$	366	8190	0.52	b
$Cu^{III}(H_{-3}V_4)^-$	365	~7000	0.52	1
$Cu^{III}(H_{-3}A_3G)^-$	365	7640	0.53	b
$Cu^{III}(H_{-3}G_4)^-$	365	7400 ^c	0.63	c, 1
$Cu^{III}(H_{-2}Aib_3)$	395	5200 ^b	0.66	b
$Ru(NH_3)_6^{2+}$	400	30		8
$Ru(NH_3)_6^{3+}$	320	100	0.065	8
$Ru(NH_3)_5py^{2+}$	407	7760		13
$Ru(NH_3)_5py^{3+}$	d		0.310 ^b	
$Ru(NH_3)_5pic^{2+}$	397	7700		e
$Ru(NH_3)_5pic^{3+}$	d		0.265 ^b	

^a Formal electrode potentials vs. NHE at $\mu = 0.1$ M ($NaClO_4$), 25.0 °C. ^b This work. ^c Anast, J. M.; Margerum, D. W. *Inorg. Chem.* 1981, 20, 2319. ^d No significant visible absorbance.

^e Chalsson, D. A.; Hintze, R. E.; Stuermer, D. H.; Peterson, J. D.; McDonald, D. P.; Ford, P. C. *J. Am. Chem. Soc.* 1972, 94, 6665.

determined by the change in absorbance of the Cu(III) solution upon completion of the reaction.

Pentammine(pyridine)ruthenium(II) perchlorate, $[Ru(NH_3)_5py](ClO_4)_2$, was prepared by the method of Ford et al.¹³ The picoline (4-methylpyridine) derivative, $[Ru(NH_3)_5pic](ClO_4)_2$, was prepared in a similar manner except the reaction time for addition of the substituted pyridine was decreased from 30 to 3 min to improve the yields. The concentrations of the Ru(II) and Cu(III) complexes were determined spectrophotometrically with a Cary 14 spectrophotometer. Spectroscopic and electrochemical data for the complexes are given in Table I. The formal reduction potential of $[Ru(NH_3)_5pic]^{3+,2+}$ was determined by cyclic voltammetry to be 0.265 ± 0.005 V vs. NHE.

Kinetic Measurements. The reaction rates were measured with a thermostated (± 0.1 °C) Durrum stopped-flow spectrophotometer. The ionic strength was held at $\mu = 0.10$ M ($NaClO_4$). On-line digital-data acquisition and data workup were carried out by a Hewlett-Packard 2108 minicomputer. Each pseudo-first-order rate constant, with Cu(II) the excess reagent, is the result of an ensemble of three data sets, and the reported rate constant is an average of at least five determinations. Second-order equal conditions were used in the temperature-dependence studies from 8.0 to 43.2 °C. The cross-reactions between Cu(III) and Cu(II) peptides were carried out in sufficiently basic media to ensure that the fully deprotonated Cu(II) complex was the major species. Under these conditions, the rate law in eq 1 was found. The reactions were monitored by observing the

$$\frac{d[Cu^{III}(H_{-3}L)]}{dt} = k[Cu^{III}(H_{-2}Aib_3)][Cu^{II}(H_{-3}L)] \quad (1)$$

formation of the $Cu^{III}(H_{-3}L)$ species at 365 nm. The fully deprotonated Cu(II) peptide complex is required for oxidation to the corresponding Cu(III) complex.¹ Therefore, the second-order rate constants were corrected for the equilibrium shown in eq 2.



The reactions between Cu(III) and Ru(II) were monitored by observing the loss of absorbance at the λ_{max} of the Cu(III) complex used. Pseudo-first-order conditions were used with excess Ru(II) for the reactions of $Cu^{III}(H_{-3}Aib_3a)$ with $Ru(NH_3)_5py^{2+}$ and with $Ru(NH_3)_5pic^{2+}$. Excess Cu(III) was used for the reaction of $Cu^{III}(H_{-3}Aib_3a)$ with $Ru(NH_3)_6^{2+}$. Second-order unequal concentrations were used for other reactions. All reactions fit the rate expression in eq 3.

$$-\frac{d[Cu(III)]}{dt} = k[Cu(III)][Ru(II)] \quad (3)$$

Electrochemical Measurements. Formal potentials, E° , were determined by cyclic voltammetry at a glassy-carbon or a carbon-paste

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Table II. Rate Data for the Reactions of $\text{Cu}^{\text{III}}(\text{H}_2\text{Aib}_3)$ with $\text{Cu}^{\text{II}}(\text{H}_3\text{L})$ Complexes^a

L	$\log K_{\text{H}}$	$10^5 [\text{Cu}^{\text{II}}(\text{H}_3\text{L})], \text{M}$	pH	$k_{\text{obsd}}, \text{s}^{-1}$	$10^{-5}k, \text{M}^{-1} \text{s}^{-1} \text{ }^b$
G_2AibG	8.11 ^c	1.00	10.4	3.74 ± 0.17	3.79 ± 0.06
		2.00	10.4	7.86 ± 0.20	
		5.00	10.4	20.2 ± 0.4	
		15.0	10.4	57.1 ± 0.7	
G_4	9.15 ^d	4.50	10.12	2.73 ± 0.08	0.651 ± 0.005
		9.00	10.11	5.59 ± 0.04	
		45.0	10.07	28.6 ± 0.5	
		89.0	10.08	57.8 ± 1.2	
V_4	10 ^e	1.0	10.01	1.19 ± 0.03	2.35 ± 0.05
		5.0	10.15	5.84 ± 0.60	
		10.0	10.16	14.2 ± 0.70	
		5.5	10.51	8.31 ± 0.13	
		8.0	10.49	12.9 ± 0.7	
		10.5	10.45	17.9 ± 0.9	
		26.5	10.49	46.3 ± 2.6	
A_3G	9 ^e	1.00	10.54	3.30 ± 0.03	3.03 ± 0.05
		2.00	10.53	9.08 ± 0.26	
		5.00	10.52	15.1 ± 0.4	
Aib_3a^f	7.97 ^c	1.8	9.61		61.1 ± 1.0
		0.36	9.61		55.6 ± 0.5

^a $[\text{Cu}^{\text{III}}\text{Aib}_3] = \sim 2 \times 10^{-6} \text{ M}$; $\mu = 0.1 \text{ M}$ (NaClO_4); 0.01 M carbonate buffer; 25.0 °C. ^b Rate constant is corrected for eq 2. ^c Reference 11. ^d Nancollas, G. N.; Poulton, D. J. *Inorg. Chem.* 1969, 8, 680. ^e Estimated from spectrophotometric pH data. ^f Second-order equal kinetics ($[\text{Cu}(\text{III})] = [\text{Cu}(\text{II})]$).

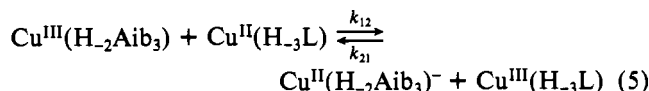
electrode using a Bioanalytical Systems CV-1A instrument. The midpoint potential for the quasi-reversible ($\Delta E_p = 70\text{--}100 \text{ mV}$) cyclic voltammograms was taken as the formal potential, with the diffusion coefficients for the oxidized and reduced species assumed to be equal. The midpoint potential did not depend upon the peak separation. The formal potentials were determined in 0.1 M NaClO_4 at 25.0 ± 0.1 °C and at a pH sufficiently basic that the fully deprotonated $\text{Cu}(\text{II})$ complex is the only copper complex present.

The entropy change for the $\text{Cu}^{\text{III,II}}(\text{H}_3\text{Aib}_3\text{a})^{0,-}$ and the $\text{Cu}^{\text{III,II}}(\text{H}_3\text{G}_2\text{AibG})^{-2,-}$ redox couples was determined by cyclic voltammetry in the nonisothermal cell configuration.² The saturated NaCl calomel reference electrode was thermostated at 25.0 ± 0.1 °C and connected to the sample cell by means of a saturated NaCl agar bridge. The sample cell was thermostated over the temperature range 10–40 °C. The entropy change for the redox couple, $\Delta S_{\text{rc}}^\circ$, is calculated from the variation of $E^{\circ'}$ with temperature according to eq 4.² The $E^{\circ'}$ values could be determined with a precision of $\pm 5 \text{ mV}$.

$$\left(\frac{dE^{\circ'}}{dt}\right)_{\text{noniso}} = \frac{\Delta S_{\text{rc}}^\circ}{nF} \quad (4)$$

Results and Discussion

Reactions of $\text{Cu}^{\text{III}}(\text{H}_2\text{Aib}_3)$ with $\text{Cu}(\text{II})$ -Peptide Complexes. The $\text{Cu}^{\text{III}}(\text{H}_2\text{Aib}_3)$ complex has a sufficiently high reduction potential to oxidize the triply deprotonated peptide complexes of copper(II), eq 5. The rate constants for five different



$\text{Cu}(\text{II})$ complexes are reported in Table II. In each case, the rate varies linearly with the concentration of $\text{Cu}^{\text{II}}(\text{H}_3\text{L})$, as in eq 1.

The reactions of $\text{Cu}(\text{III})$ peptides with $\text{Cu}(\text{II})$ peptides were used to determine the electron-exchange rate for the $\text{Cu}(\text{III, II})$ -peptide couple by applying the Marcus correlation,¹⁴ eq 6 and 7, where k_{11} and k_{22} are the rate constants for the

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \quad (6)$$

$$\log f = (\log K_{12})^2 / [4 \log (k_{11}k_{22}/Z^2)] \quad (7)$$

self-exchange reactions, k_{12} is the rate constant for the cross-exchange reaction, K_{12} is the equilibrium constant for the cross-reaction, and Z is the bimolecular collision frequency

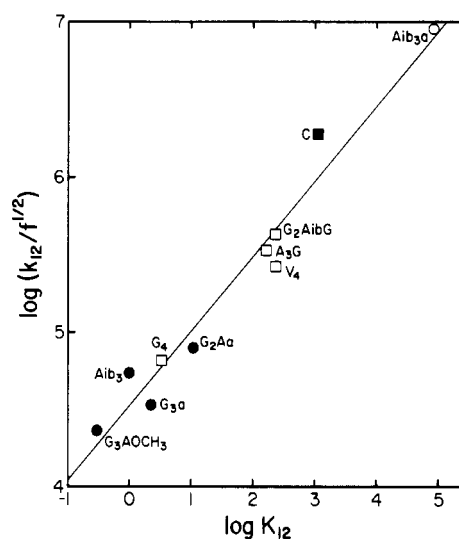


Figure 1. Marcus correlation for the reaction of $\text{Cu}^{\text{III}}(\text{H}_2\text{Aib}_3)$ with $\text{Cu}^{\text{II}}(\text{H}_3\text{L})$ complexes. The solid line is the calculated fit: $\log(k_{12}/f^{1/2}) = (0.49 \pm 0.04) \log K_{12} + (4.53 \pm 0.08)$. The symbols represent the charge of the $\text{Cu}^{\text{III,II}}(\text{H}_3\text{L})$ couple: 0, 1- (circles); 1-, 2- (squares). The filled symbols are data taken from ref 6 except that for C, which was reported in 1.0 M NaClO_4 at 25 °C in ref 22. The remaining data are given in Table III. All rate constants given are for $\mu = 0.10 \text{ M}$ (NaClO_4) at 25 °C except that for C.

taken to be $10^{11} \text{ M}^{-1} \text{ s}^{-1}$. Figure 1 shows an excellent Marcus correlation ($\log(k_{12}/f^{1/2})$ vs. $\log K_{12}$) for the $\text{Cu}(\text{III})$ - $\text{Cu}(\text{II})$ cross-reactions. The slope of the correlation, 0.49 ± 0.04 , agrees well with the theoretical value of 0.5. The previously reported data⁷ together with the data presented here reflect consistency in the $\text{Cu}(\text{III, II})$ -peptide self-exchange rate constants. The value of the self-exchange rate constant can be calculated from the intercept of the correlation, which is equal to $0.5 \log(k_{11}k_{22})$. In this case, the self-exchange of $\text{Cu}^{\text{III,II}}(\text{H}_2\text{Aib}_3)$ is known,⁷ $k_{11} = 5.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, so that the intercept value of 4.53 ± 0.08 yields a $\text{Cu}^{\text{III,II}}(\text{H}_3\text{L})$ self-exchange rate constant of $2.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

It is interesting that the charged couples, $\text{Cu}^{\text{III,II}}(\text{H}_3\text{L})^{1,-,2,-}$, fall on the same correlation as the neutral couples, $\text{Cu}^{\text{III,II}}(\text{H}_3\text{L})^{0,1-}$. In each cross-reaction, eq 5, one couple is always $\text{Cu}^{\text{III,II}}(\text{H}_2\text{Aib}_3)^{0,1-}$ with neutral $\text{Cu}^{\text{III}}(\text{H}_2\text{Aib}_3)$ being the reactant. The second couple has either a 1-, 2- or 0, 1- charge

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Table III. Cross-Reaction Rate Constants and Self-Exchange Rate Constants for the Cu^{III,II}(H₃L) Couple Determined from the Electron-Transfer Reaction with Cu^{III}(H₂Aib₃)^{a,b}

couple	10 ⁻⁵ k ₁₂ ^c	r ^{II} , Å	r ^{III} , Å	w ₂₂ ^d	w ₂₁ ^d	10 ⁻⁴ k ₂₂ ^{c,e}	10 ⁻⁴ k ₂₂ ^{cor,c,f}
Cu ^{III,II} (H ₃ Aib ₃ a) ^{0,-}	58	4.7	4.3	0	0	2.2	2.2
Cu ^{III,II} (H ₃ G ₂ AibG) ^{-2,-}	3.79	4.7	3.6	0.55	0.27	0.85	2.1
Cu ^{III,II} (H ₃ V ₄) ^{-2,-}	2.35	5.2	5.2	0.39	0.20	0.39	0.75
Cu ^{III,II} (H ₃ A ₃ G) ^{-2,-}	3.03	4.9	4.1	0.49	0.24	0.83	1.9
Cu ^{III,II} (H ₃ G ₄) ^{-2,-}	0.651	4.7	3.6	0.55	0.26	1.5	3.7
							av 2 ± 1

^a μ = 0.10 M (NaClO₄), 25.0 °C. ^b Subscript 1 refers to the Cu^{III,II}(H₂Aib₃)^{0,-} couple; subscript 2 refers to the Cu^{III,II}(H₃L) couple; w₁₁ = w₁₂ = 0. ^c Units are M⁻¹ s⁻¹. ^d Units are kcal mol⁻¹. ^e Using k₁₁ = 5.5 × 10⁴ M⁻¹ s⁻¹ and eq 8-12. ^f Using eq 13.

so that the reactant/product charges are either 0, 2-/1-, 1- or 0, 1-/1-, 0 respectively. In the 0, 2-/1-, 1- cross-reaction the driving force for the reaction is decreased by an unfavorable electrostatic interaction. Thus, the 1-, 2- couples should appear to react more slowly when compared with the 0, 1- couples. Since the 0, 1- and the 1-, 2- couples fall on the same log (k₁₂/f^{1/2}) vs. log K₁₂ line in Figure 1, the electrostatic effects must be small. These effects are expected to be minimal because of the magnitudes of the charges involved. In order to evaluate the self-exchange rate constants for the 1-, 2- couples from the observed cross-reaction data, corrections were made for the electrostatic effects as follows:¹⁵

$$\Delta G_{12}^* = w_{12} + \frac{\Delta G_{11}^* - w_{11} + \Delta G_{22}^* - w_{22} + \Delta G_r^\circ(1 + \alpha)}{2} \quad (8)$$

$$\alpha = \frac{\Delta G_r^\circ}{4(\Delta G_{11}^* - w_{11} + \Delta G_{22}^* - w_{22})} \quad (9)$$

$$\Delta G_r^\circ = \Delta G_{12}^\circ + w_{21} - w_{12} \quad (10)$$

The free energy terms, ΔG*, were calculated from the experimentally determined rate constants by eq 11. The work

$$\Delta G^* = -RT \ln(k/Z) \quad (11)$$

terms, w, were evaluated according to the Debye-Hückel theory,¹⁶ eq 12, for aqueous solutions at 25 °C and μ = 0.1

$$w = \frac{4.24z_1z_2}{\bar{r}(1 + 0.104\bar{r})} \quad (12)$$

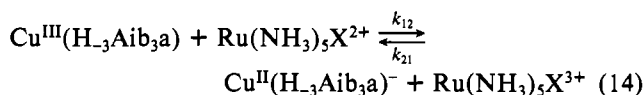
M, where \bar{r} is the approach distance taken as the radii of the two approaching molecules of charges z₁ and z₂. The radii of the copper-peptide complexes have been estimated⁵ by using CPK space-filling models.⁹ The reaction free energy change, ΔG₁₂⁰, was calculated from the formal electrode potentials given in Table I. The calculations used k₁₁ = 5.5 × 10⁴ M⁻¹ s⁻¹ and the experimentally determined k₁₂ value and were iterated until a consistent value of k₂₂ was obtained. Table III summarizes the results of the treatment. Indeed, the work term, w₂₁, that decreases the driving force of the reaction, ΔG_r⁰, for the Cu^{III,II}(H₃L)^{-2,-} couple is small. To compare the self-exchange rate constants for the Cu^{III,II}(H₃Aib₃a)^{0,-} couple and the other Cu^{III,II}(H₃L)^{-2,-} couples, a self-exchange rate constant, k₂₂^{cor}, has been calculated according to eq 13,¹⁵

$$k_{22}^{\text{cor}} = Z e^{-(\Delta G_{22}^* - w_{22})/RT} \quad (13)$$

which corrects for the work required to bring the 1-, 2- species together in the self-exchange reaction. The average value for k₂₂^{cor} is (2 ± 1) × 10⁴ M⁻¹ s⁻¹ for the Cu^{III,II}(H₃L) complexes, which is in good agreement with the self-exchange rate constant calculated from the intercept of the Marcus plot in Figure 1. In addition, the average value of k₂₂^{cor} differs only by a factor of 2.8 from the directly observed value of 5.5 × 10⁴ M⁻¹ s⁻¹ for the Cu^{III,II}(H₂Aib₃) complex. The self-exchange rate

constants are very similar for the Cu(III, II)-peptide complexes in this study when allowance is made for the differences in charge on the various couples. In contrast, a detailed study of the electron-transfer rates for Ni(III, II) peptides¹⁷ suggests a dependence of the self-exchange rate constants on the structure of peptide ligand even after correction for electrostatic effects.

Electron Transfer between Cu(III) Peptides and Ru(NH₃)₅X²⁺. Because of the low formal reduction potential for Cu^{III}(H₃Aib₃a), the rate of the electron-transfer reaction for Ru(NH₃)₅py²⁺, according to eq 14, was sufficiently slow to



confirm the concentration dependence of Ru(II) given in eq 3 by stopped-flow methods. The rate was independent of acid concentration between pH 4.8 and 5.7. The resolved second-order rate constant, k₁₂, for Ru(NH₃)₅py²⁺ was (1.04 ± 0.02) × 10⁶ M⁻¹ s⁻¹ in 0.10 M NaClO₄ at 25.0 °C. Reactions of Cu^{III}(H₃G₂AibG)⁻, Cu^{III}(H₃A₃G)⁻, and Cu^{III}(H₂Aib₃) with Ru(NH₃)₅py²⁺ were extremely rapid and required the use of low concentrations of both Cu(III) and Ru(II). An integrated rate equation for second-order unequal-concentration conditions was used. The resolved rate constants (M⁻¹ s⁻¹ at 25.0 °C in 0.1 M NaClO₄) for the reactions with Ru(NH₃)₅py²⁺ are (6.2 ± 0.7) × 10⁷ for Cu^{III}(H₃G₂AibG)⁻, (1.01 ± 0.09) × 10⁸ for Cu^{III}(H₃A₃G)⁻, and (1.5 ± 0.2) × 10⁸ for Cu^{III}(H₂Aib₃).

The reactions of Ru(NH₃)₅pic²⁺ were compared with those of Ru(NH₃)₅py²⁺ to test whether the methyl group in the 4-position of the pyridine ring would affect the rate of reaction with Cu(III) where edge-on contact of the aromatic ring with the empty Cu(III) axial site may be possible. The reaction of Ru(NH₃)₅pic²⁺ with Cu^{III}(H₃Aib₃a) was slow enough to determine the concentration dependence, and the rate law in eq 3 was verified. The data and the resolved rate constant, (1.82 ± 0.12) × 10⁶ M⁻¹ s⁻¹ at 25 °C in 0.10 M NaClO₄, are reported in Table IV.

To ensure that the pyridine ring does not interact with the Cu(III), the reaction in eq 14 was studied for Ru(NH₃)₆²⁺. The ruthenium(II) hexaammine complex contains no bridging or conducting ligands; therefore, the reaction is expected to proceed exclusively by an outer-sphere mechanism. The reaction was difficult to observe due to the rapid rate and the small molar absorptivity change between the products and reactants at 365 nm relative to the pyridyl derivatives already discussed. The reaction also was complicated by the instability of the Ru(II) complex. The latter fact made the study of the reaction under second-order conditions troublesome because the Ru(II) concentration changed with every kinetic determination. Hence, the reaction was conducted under pseudo-first-order conditions with excess Cu(III). The rapid rates and the small changes in the absorbance are very near the limit

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Table IV. Rate Data for the Reactions of Cu(III)-Peptide Complexes with Ruthenium(II) Ammine Complexes^a

reacn	10 ⁶ [Cu ^{III}], M	10 ⁶ [Ru ^{II}], M	k _{obsd} , s ⁻¹	10 ⁻⁷ k, M ⁻¹ s ⁻¹
Cu ^{III} (H ₋₃ Aib ₃ a) + Ru(NH ₃) ₅ py ²⁺	4.0	25.5	26.3 ± 0.9	0.104 ± 0.002
	4.0	52.0	57 ± 1	
	4.0	102	105 ± 9	
	4.0	160	168 ± 7	
	4.0	52.0	60 ± 1	
	4.0	50.5	60 ± 3	
Cu ^{III} (H ₋₃ G ₂ AibG) ⁻ + Ru(NH ₃) ₅ py ²⁺	0.45	4.05	253 ± 30	0.115 ^b
Cu ^{III} (H ₋₃ Aib ₃) + Ru(NH ₃) ₅ py ²⁺	0.50-0.63	1.51-1.68		0.119 ^c
Cu ^{III} (H ₋₃ A ₃ G) ⁻ + Ru(NH ₃) ₅ py ²⁺	0.68-0.78	1.69-1.78		15 ± 2 ^{d,e}
Cu ^{III} (H ₋₃ Aib ₃ a) + Ru(NH ₃) ₅ pic ²⁺	3.0	21.8	43.7 ± 0.8	10.1 ± 0.9 ^{d,f}
	3.0	39.0	84.6 ± 1.6	
	3.0	61.2	125 ± 9	
	3.0	92.8	175 ± 3	
Cu ^{III} (H ₋₃ Aib ₃ a) + Ru(NH ₃) ₆ ²⁺	12.3-15.8	0.51-1.51	177-251	1.5 ± 0.1 ^h

^a μ = 0.10 (M NaClO₄); 0.01 M acetate buffer; pH 5.2; 25.0 °C. ^b pH 4.8. ^c pH 5.7. ^d Second-order unequal-concentration integrated rate expression. ^e Five sets of reactions. ^f Six sets of reactions. ^g Based on the slope in a linear regression. ^h Nine sets of reactions.

Table V. Comparison of Observed^a and Calculated Rate Constants for Electron Transfer Using the Marcus Theory

reacn	k ₁₁ , M ⁻¹ s ⁻¹	k ₂₂ , M ⁻¹ s ⁻¹	w, kcal				k ₁₂ (obsd) ^b , M ⁻¹ s ⁻¹	k ₁₂ (calc) ^c , M ⁻¹ s ⁻¹
			w ₁₁	w ₂₂	w ₁₂	w ₂₁		
Cu ^{III} (H ₋₃ Aib ₃ a) + Ru(NH ₃) ₆ ²⁺ ^c	2.2 × 10 ⁴	4.0 × 10 ⁵ ^d	0	2.29	0	-0.87	1.5 × 10 ⁷	2.3 × 10 ⁷
Cu ^{III} (H ₋₃ Aib ₃ a) + Ru(NH ₃) ₅ pic ²⁺ ^e	2.2 × 10 ⁴	1.1 × 10 ⁵ ^f	0	1.80	0	-0.78	1.8 × 10 ⁶	2.9 × 10 ⁶
Cu ^{III} (H ₋₃ Aib ₃ a) + Ru(NH ₃) ₅ py ²⁺ ^g	2.2 × 10 ⁴	1.1 × 10 ⁵ ^h	0	1.87	0	-0.79	1.0 × 10 ⁶	1.4 × 10 ⁶
Cu ^{III} (H ₋₃ G ₂ AibG) ⁻ⁱ + Ru(NH ₃) ₅ py ²⁺	8.5 × 10 ³	1.1 × 10 ⁵	0.55	1.87	-0.65	-1.59	6.2 × 10 ⁷	6.0 × 10 ⁷
Cu ^{III} (H ₋₃ A ₃ G) ⁻ⁱ + Ru(NH ₃) ₅ py ²⁺	8.3 × 10 ³	1.1 × 10 ⁵	0.49	1.87	-0.59	-1.54	1.0 × 10 ⁸	5.9 × 10 ⁷
Cu ^{III} (H ₋₂ Aib ₃) + Ru(NH ₃) ₅ py ²⁺	5.5 × 10 ⁴	1.1 × 10 ⁵	0	1.87	0	-0.79	1.5 × 10 ⁸	2.2 × 10 ⁸

^a μ = 0.10 M (NaClO₄) at 25 °C. ^b Calculated by using eq 8-12. ^c Radii of the Ru(III, II) = 3.3 Å.¹⁶ ^d Reference 8. ^e Radii of the Ru(III, II) = 3.9 Å, based on calculations similar to those given in ref 16. ^f Assumed equal to the value for the pyridine derivative; similar to the rationale given in ref 9. ^g Radii of the Ru(III, II) = 3.8 Å.¹⁶ ^h Reference 9; corrected to μ = 0.1 M by the Debye-Hückel treatment. ⁱ Radii of Cu(III, II) given in Table III.

of the stopped-flow method. The resolved rate constant is (1.5 ± 0.1) × 10⁷ M⁻¹ s⁻¹ in 0.1 M NaClO₄ at 25.0 °C.

Mechanism of Electron Transfer. The rate constants for electron transfer between Cu(III)-peptide complexes and ruthenium(II) amines are compared to predictions based on the Marcus theory. Electrostatic corrections are needed since the self-exchange couples have different signs and magnitudes of charge. The calculated rate constants are reported in Table V and are within a factor of 2 of the observed rate constants. The high degree of correlation shown in Figure 2 agrees with the Marcus theory for an outer-sphere mechanism of electron transfer. The lack of rate enhancement for the reactions of Ru(NH₃)₅py²⁺ and Ru(NH₃)₅pic²⁺ with Cu(III) peptides indicates that pyridine-ring overlap and conduction is not important for electron transfer to Cu(III) peptides. This was checked because of the unusual behavior exhibited by the tris(1,10-phenanthroline)cobalt(II)¹⁸ and bis(2,9-dimethyl-1,10-phenanthroline)copper(I)¹⁹ complexes in earlier electron-transfer studies with Cu(III) peptides. The Cu(III, II)-peptide self-exchange rate constants (with values in the vicinity of 10⁴ M⁻¹ s⁻¹) resolved from the Cu^{III}(H₋₂Aib₃)-Cu^{II}(H₋₃L) cross reactions are appropriate for predicting other cross-reaction rates that proceed by an outer-sphere mechanism. Hence, major deviations from these predictions can be used as a basis for exploring other mechanisms such as the inner-sphere bridging pathways proposed for the IrCl₆³⁻ and Fe(CN)₆⁴⁻ reactions with Cu(III)-peptide complexes.

Temperature Dependences of Electron Transfer. The reactions in eq 14 for X = py and NH₃ were studied as a function of temperature. The experimental activation parameters are ΔH^{*} = 1.8 ± 0.6 kcal mol⁻¹, ΔS^{*} = -25 ± 2 cal K⁻¹ mol⁻¹ for Cu^{III}(H₋₃Aib₃a) + Ru(NH₃)₅py²⁺ and ΔH^{*} =

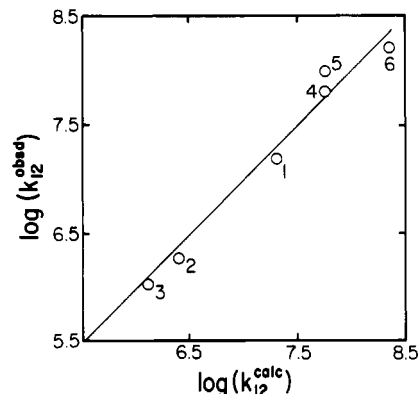


Figure 2. Plot of the logarithm of the observed rate constant vs. the logarithm of the calculated rate constant using eq 8-19 for the reactions of copper(III)-peptide complexes with ruthenium(II) ammine complexes. The reaction numbers correspond to those given in Table VI.

1.5 ± 0.3 kcal mol⁻¹, ΔS^{*} = -21 ± 2 cal K⁻¹ mol⁻¹ for Cu^{III}(H₋₃Aib₃a) + Ru(NH₃)₆²⁺. The rate data are listed in Table VI.

The activation parameters for outer-sphere electron-transfer reactions can be calculated by using eq 15-19.²⁰ The sub-

$$\Delta H_{12}^* = 0.5(\Delta H_{11}^* + \Delta H_{22}^*)(1 - 4\beta^2) + 0.5\Delta H_{12}^\circ(1 + 2\beta) \quad (15)$$

$$\Delta H^* = \Delta H^* - 0.5RT \quad (16)$$

$$\Delta S_{12}^* = 0.5(\Delta S_{11}^* + \Delta S_{22}^*)(1 - 4\beta^2) + 0.5\Delta S_{12}^\circ(1 + 2\beta) \quad (17)$$

$$\Delta S^* = \Delta S^* + R \ln(hZ/k_B T) - 0.5R \quad (18)$$

$$\beta = \Delta G_{12}^\circ / 4(\Delta G_{11}^* + \Delta G_{22}^*) \quad (19)$$

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Table VI. Temperature Dependence for the Rate of Reaction between $\text{Cu}^{\text{III}}(\text{H}_3\text{Aib}_3\text{a})$ and Ruthenium(II) Amines^a

reacn	T, °C	10 ⁶ [Cu ^{III}], M	10 ⁶ [Ru ^{II}], M	k _{obsd} , s ⁻¹	10 ⁻⁵ k, M ⁻¹ s ⁻¹
Ru(NH ₃) ₅ py ²⁺	9.7	3.99	45.8	34.8 ± 1.6	7.60 ± 0.35
	15.9	3.99	44.1	42.6 ± 1.8	9.66 ± 0.41
	20.5	3.99	45.0	42.5 ± 3.3	9.44 ± 0.73
	26.9	3.99	47.5	50.1 ± 2.1	10.5 ± 0.4
	32.9	3.99	47.6	51.2 ± 2.2	10.8 ± 0.5
Ru(NH ₃) ₆ ²⁺	8.4	12.9–15.3	0.94–1.36	159–208	123 ± 8 ^b
	11.9	14.2–16.0	0.11–2.00	184–208	129 ± 7 ^b
	15.9	13.6–14.9	0.77–1.28	171–217	138 ± 8 ^c
	20.6	13.6–16.4	0.60–2.50	196–253	149 ± 8 ^d
	25.0		see Table IV		150 ± 10

^a $\mu = 0.10 \text{ M}$ (NaClO₄); 0.01 M acetate buffer; pH 5.2. ^b Seven sets of reactions. ^c Five sets of reactions. ^d Eight sets of reactions.

Table VII. Temperature Dependence of the Rate of Reaction between $\text{Cu}^{\text{III}}(\text{H}_2\text{Aib}_3)$ and $\text{Cu}^{\text{II}}(\text{H}_3\text{Aib}_3\text{a})^{-}$ ^a

T, °C	10 ⁵ [Cu], M	k _{obsd} , s ⁻¹	10 ⁻⁶ k ₁₂ , M ⁻¹ s ⁻¹
8.0	2.5	118 ± 10	4.72 ± 0.41
8.7	2.5	122 ± 8	4.88 ± 0.33
12.5	2.5	150 ± 21	6.00 ± 0.85
16.4	2.5	182 ± 5	7.28 ± 0.25
19.0	2.5	210 ± 28	8.40 ± 1.1
25.0	1.8	110 ± 18	6.11 ± 1.0
25.0	0.36	20 ± 2	5.56 ± 0.56
25.4	2.5	135 ± 2	5.40 ± 0.08
31.9	2.5	204 ± 45	8.16 ± 1.8
39.9	2.5	269 ± 75	10.8 ± 3.0
43.2	2.5	239 ± 3	9.56 ± 0.35

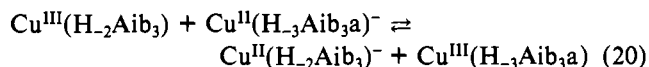
$$\Delta H_{12}^{\ddagger} = 2.6 \pm 0.9 \text{ kcal mol}^{-1}$$

$$\Delta S_{12}^{\ddagger} = -18 \pm 4 \text{ cal K}^{-1} \text{ mol}^{-1}$$

^a Second-order equal conditions; $\mu = 0.1 \text{ M}$ (NaClO₄); 0.01 M carbonate; pH 9.5.

scripts 11, 22, and 12 refer to the two self-exchange reactions and to the cross-reaction, respectively. The values of ΔS_{12}° were calculated from the entropy change of the electrode reactions ($\Delta S_{\text{rc}}^{\circ}$) for both reactant couples. The values of $\Delta S_{\text{rc}}^{\circ}$ for $\text{Cu}^{\text{III,II}}(\text{H}_3\text{Aib}_3\text{a})^{0,-}$ and $\text{Cu}^{\text{III,II}}(\text{H}_3\text{G}_2\text{AibG})^{1,-2-}$ were determined from eq 4 to be $-11.6 \pm 0.3 \text{ cal K}^{-1} \text{ mol}^{-1}$ and $-15.3 \pm 0.6 \text{ cal K}^{-1} \text{ mol}^{-1}$, respectively.

Enthalpy and Entropy of Activation. The activation parameters for the electron cross-exchange reaction given in eq 20 have been determined from the temperature dependence



of the reaction rate constant as reported in Table VII. The values $\Delta H_{12}^{\ddagger} = 2.6 \pm 0.9 \text{ kcal mol}^{-1}$ and $\Delta S_{12}^{\ddagger} = -18 \pm 4 \text{ cal K}^{-1} \text{ mol}^{-1}$ were calculated from the Eyring equation. By use of eq 11 and 15–19, the activation parameters, ΔH_{22}^{\ddagger} and ΔS_{22}^{\ddagger} , for the self-exchange reaction of $\text{Cu}^{\text{III,II}}(\text{H}_3\text{Aib}_3\text{a})^{0,-}$ have been resolved from ΔH_{12}^{\ddagger} and ΔS_{12}^{\ddagger} and the activation parameters for the $\text{Cu}^{\text{III,II}}(\text{H}_2\text{Aib}_3)^{0,-}$ couple ($\Delta H_{11}^{\ddagger} = 7.0$

$\pm 0.5 \text{ kcal mol}^{-1}$ and $\Delta S_{11}^{\ddagger} = -13 \pm 2 \text{ cal K}^{-1} \text{ mol}^{-1}$).⁷ The values obtained for the $\text{Cu}^{\text{III,II}}(\text{H}_3\text{Aib}_3\text{a})^{0,-}$ couple are $\Delta H_{22}^{\ddagger} = 5 \pm 2 \text{ kcal mol}^{-1}$ and $\Delta S_{22}^{\ddagger} = -19 \pm 9 \text{ cal K}^{-1} \text{ mol}^{-1}$. The error limits given for the $\text{Cu}^{\text{III,II}}(\text{H}_3\text{Aib}_3\text{a})^{0,-}$ electron self-exchange activation parameters are obtained through propagation of the error in the measured activation parameters for the cross-exchange reaction and the $\text{Cu}^{\text{III,II}}(\text{H}_2\text{Aib}_3)^{0,-}$ self-exchange reaction. Within the uncertainty of the measurements, the activation parameters for electron self-exchange for $\text{Cu}^{\text{III,II}}(\text{H}_2\text{Aib}_3)^{0,-}$ and $\text{Cu}^{\text{III,II}}(\text{H}_3\text{Aib}_3\text{a})^{0,-}$ are the same as expected for complexes of such similar structure and charge type.

Since the activation parameters for the electron cross-exchange reactions of $\text{Cu}^{\text{III}}(\text{H}_3\text{Aib}_3\text{a})$ with $\text{Ru}(\text{NH}_3)_6^{2+}$ and $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$ have been determined and the individual self-exchange values are known, the calculated activation parameters for the cross-reactions (obtained from eq 15–19) can be compared with the experimentally observed numbers. This is informative since two different sets of ΔH_{11}^{\ddagger} and ΔS_{11}^{\ddagger} have been determined for the $\text{Ru}(\text{NH}_3)_6^{3+,2+}$ couple.^{8,16} The agreement between the observed and calculated entropy and enthalpy for the $\text{Cu}^{\text{III}}(\text{H}_3\text{Aib}_3\text{a})$ and $\text{Ru}(\text{NH}_3)_6^{2+}$ electron-exchange reaction is better when the activation parameters, $\Delta H^{\ddagger} = 10 \text{ kcal mol}^{-1}$ and $\Delta S^{\ddagger} = -11 \text{ cal K}^{-1} \text{ mol}^{-1}$, determined by Meyer and Taube⁸ for the $\text{Ru}(\text{NH}_3)_6^{3+,2+}$ and $\text{Ru}(\text{ND}_3)_6^{3+,2+}$ cross-reaction, are used as shown in Table VIII.

Upon closer inspection of the activation parameters observed and calculated for the $\text{Cu}^{\text{III}}(\text{H}_3\text{Aib}_3\text{a})$ and $\text{Ru}(\text{NH}_3)_6^{2+}$ or $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$ reactions, the small magnitude of ΔH^{\ddagger} appears to be a reflection of the overall negative value of ΔH_{12}° . On the other hand, the rather large negative values of ΔS^{\ddagger} observed suggest extensive outer-sphere reorganization. The ΔS^{\ddagger} values for the self-exchange reactions for the couples involved in each of the cross-reactions are negative and can be related to the observed ΔS_{12}^{\ddagger} values. Change in the number of coordinated waters has been proposed to account for the negative ΔS^{\ddagger} for the Cu(III, II)–peptide self-exchange process⁷ while for the $\text{Ru}^{3+,2+}$ complexes concentration of charge in the collision complex has been suggested to account for the negative ΔS^{\ddagger} values observed.²¹ The transition state for the

Table VIII. Comparison of Observed and Calculated Activation Parameters Using the Marcus Theory^a

reacn	$\Delta S_{\text{rc}}^{\circ}$ ^{b,c}	ΔS_{12}° ^b	ΔH_{12}° ^d	ΔH^{\ddagger} ^d	ΔS^{\ddagger} ^b	ΔH_{12}^{\ddagger} ^e (obsd) ^d	ΔH_{12}^{\ddagger} ^e (calcd) ^d	ΔS_{12}^{\ddagger} ^e (obsd) ^b	ΔS_{12}^{\ddagger} ^e (calcd) ^b
Ru(NH ₃) ₆ ^{3+,2+}	19 ^e			10 ^f	-11 ^f				
Ru(NH ₃) ₅ py ^{3+,2+}	19 ^e			4.5 ^g	-27 ^g				
Ru(NH ₃) ₅ py ^{3+,2+}	16 ^h			2.9 ⁱ	-23 ⁱ				
$\text{Cu}^{\text{III,II}}(\text{H}_3\text{Aib}_3\text{a})^{0,-}$	-12			5	-19				
$\text{Cu}^{\text{III}}(\text{H}_3\text{Aib}_3\text{a}) + \text{Ru}(\text{NH}_3)_6^{2+}$		-31	-16			1.5	0.7 ^j	-21	-27 ^j
$\text{Cu}^{\text{III}}(\text{H}_3\text{Aib}_3\text{a}) + \text{Ru}(\text{NH}_3)_5\text{py}^{2+}$		-31	-16			1.5	-2.1 ^k	-21	-35 ^k
$\text{Cu}^{\text{III}}(\text{H}_2\text{Aib}_3) + \text{Ru}(\text{NH}_3)_5\text{py}^{2+}$		-28	-10			1.8	-1.0	-25	-34

^a $\mu = 0.1 \text{ M}$ (NaCl₄), unless otherwise indicated. ^b Units are cal K⁻¹ mol⁻¹. ^c $\Delta S_{\text{rc}}^{\circ} = \Delta S_{\text{rc}}^{\text{ox}} - \Delta S_{\text{rc}}^{\text{red}}$. ^d Units are kcal mol⁻¹. ^e Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* 1979, 101, 1131. ^f Reference 8; $\mu = 0.013 \text{ M}$. ^g Reference 16. ^h Reference 21. ⁱ Reference 9; $\mu = 1 \text{ M}$. ^j Activation parameters calculated by using values for $\text{Ru}(\text{NH}_3)_6^{3+,2+}$ from ref 8 and eq 15–19. ^k As for *j* except the values for $\text{Ru}(\text{NH}_3)_6^{3+,2+}$ were from ref 9.

cross-reactions appear to contain contributions from each. The partial development of the product charges $3+$, $1-$ leading to increased solvent organization and the coordination of axial water to the copper complex would give rise to the observed negative ΔS^\ddagger values. It is interesting that the majority of the entropy change for each reaction is encountered in the activation steps prior to electron transfer.

Conclusions

The reactions of $\text{Cu}^{\text{III}}(\text{H}_2\text{Aib}_3)$ with several $\text{Cu}^{\text{II}}(\text{H}_3\text{L})$ complexes show an excellent Marcus correlation and indicate an average self-exchange rate constant (corrected for electrostatic work terms) of $(2 \pm 1) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Cu}^{\text{III,II}}(\text{H}_3\text{L})$. The exchange rate constants can be used to predict accurately the rates of electron transfer between Cu^{III} -peptide complexes and ruthenium(II) ammine complexes from the Marcus theory for outer-sphere reactions. The reactions of $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$ and $\text{Ru}(\text{NH}_3)_5\text{pic}^{2+}$ show no evi-

dence of any special pyridyl-ring interaction by which facile electron conduction can occur.

The absence of bridging ligands on the Ru^{II} complexes, the substitution rate constants of the complexes involved, and the adherence of the reactions to the Marcus theory suggest that Cu^{III} peptides undergo electron transfer with Ru^{II} complexes by an outer-sphere mechanism. This is in contrast to the inner-sphere reactions reported for IrCl_6^{3-4} and $\text{Fe}(\text{CN})_6^{4-5}$. Thus, the reaction partner in cross-reactions with Cu^{III} , Ru^{II} -peptide complexes determines whether the reactions proceed by an inner-sphere or an outer-sphere mechanism.

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Registry No. I, 69990-31-4; II, 82495-22-5; $\text{Cu}^{\text{II}}(\text{H}_3\text{Aib}_3\text{a})^-$, 85926-43-8; $\text{Cu}^{\text{II}}(\text{H}_3\text{G}_2\text{AibG})^{2-}$, 85926-41-6; $\text{Cu}^{\text{III}}(\text{H}_3\text{G}_2\text{AibG})^-$, 82495-23-6; $\text{Cu}^{\text{II}}(\text{H}_3\text{V}_4)^{2-}$, 62959-94-8; $\text{Cu}^{\text{III}}(\text{H}_3\text{V}_4)^-$, 62959-93-7; $\text{Cu}^{\text{II}}(\text{H}_3\text{A}_3\text{G})^{2-}$, 85926-42-7; $\text{Cu}^{\text{III}}(\text{H}_3\text{A}_3\text{G})^-$, 82495-25-8; $\text{Cu}^{\text{II}}(\text{H}_3\text{G}_4)^{2-}$, 57603-18-6; $\text{Cu}^{\text{III}}(\text{H}_3\text{G}_4)^-$, 57692-61-2; $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$, 19052-44-9; $\text{Ru}(\text{NH}_3)_5\text{pic}^{2+}$, 21360-09-8; $\text{Ru}(\text{NH}_3)_5\text{pic}^{2+}$, 19482-30-5.

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Early Stages of the Hydrolysis of Chromium(III) in Aqueous Solution. 1. Characterization of a Tetrameric Species

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The first few members of the series of hydrolytic polymers of Cr^{III} , formed upon addition of hydroxide ion (<1 equiv) to the chromium(III) aqua ion, were separated on Sephadex SP C-25. Elution with sodium perchlorate (0.5–4 M) gave fractions containing $\text{Cr}^{3+}(\text{aq})$, $\text{Cr}_2(\text{OH})_2^{4+}(\text{aq})$, $\text{Cr}_3(\text{OH})_4^{5+}(\text{aq})$, and $\text{Cr}_4(\text{OH})_6^{6+}(\text{aq})$, respectively. Two higher polymers, presumably pentamer and hexamer, were eluted with 4 M LiClO_4 . The pK_a values of the first oligomers were determined ($I = 1 \text{ M}$ (NaClO_4) at 25°C) from pH titrations: 4.29, 6.1 (monomer); 3.68, 6.04 (dimer); 4.35, 5.63, 6.0 (trimer); 2.55, 5.08 (tetramer). The visible spectra of the monomer, dimer, and trimer agree with those given in the literature, and $\text{Cr}_4(\text{OH})_6^{6+}$ has $\lambda_{\text{max}} = 426 \text{ nm}$ ($\epsilon = 30.3$) and 580 nm ($\epsilon = 15.6$). The spectrum of the hexamer is very similar to that of the trimer. The tetramer is most conveniently synthesized by adding hydroxide ion to solutions of the pure dimer, but in acidic solution it cleaves rapidly and almost exclusively into monomer and trimer. The order of robustness (in acidic solution) and stability is dimer $<$ trimer $>>$ tetramer. The above observations agree best with a trimer consisting of a trigonal array of the three chromium ions sharing a common hydroxide bridge (2). The properties of the tetramer, $\text{Cr}_4(\text{OH})_6^{6+}$, suggest that the fourth chromium center may be bound through OH bridges to two of the chromium ions of a trimer unit (3a). On deprotonation, intramolecular condensation is proposed to give $\text{Cr}_4\text{O}(\text{OH})_5^{5+}$ (3b) with a central tetracoordinated oxo ligand. Reaction of ^{51}Cr -labeled monomer with excess deprotonated trimer afforded labeled tetramer, which was isolated and cleaved with acid to give equal amounts of label in the monomer and trimer. The tetramer thus contains two equivalent metal centers, consistent with the proposed structures of the tetramer and trimer.

Introduction

The hydrolysis of metal ions is a fundamental process occurring in natural waters and ore formation and also in biological systems. The knowledge even of the early stages of hydrolytic polymerization is still sketchy because formation of significant amounts of soluble oligomers is usually prevented by precipitation of insoluble hydroxo- and hydroxo-oxo-metal phases.¹ This does not hold for chromium(III) owing to its kinetic robustness. Furthermore, the hydrolytic polymerization of Cr^{III} is not complicated by redox processes and structural assignments can be made by relying on the almost exclusive and constant octahedral coordination of Cr^{III} centers.

Indeed, the study of the hydrolytic polymerization of chromium(III) started as early as 1908,² when Bjerrum pos-

tulated the presence of a dimeric species from pH titration experiments. Although no unambiguously characterized crystalline sample of this dimeric species has yet been obtained,³ it has been studied extensively in solution³⁻⁸ and its configuration $((\text{H}_2\text{O})_4\text{Cr}(\text{OH})_2\text{Cr}(\text{OH})_4^{4+})$ (1) has been established.⁹ A trimeric complex, $\text{Cr}_3(\text{OH})_4^{5+}$, was obtained

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