32354-82-8; $Ni(CO)_2$(diars), 69204-58-6; $Ni(CO)_2$(DAS), 32355-21-8.

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Electron-Transfer Reactions of Copper(III)–Peptide Complexes with Hexachloroiridate(III)

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Oxidation–reduction reactions involving the peptide complexes of copper(III) and copper(II) provide the first opportunity to determine the speed of electron-transfer reactions between these oxidation states as well as providing an example of electron transfer between two predominantly square-planar complexes. Although the reactions between $IrCl_6^{3-}$ and copper(III)–peptides are uphill electron transfers, the reactions can be forced in this direction by taking advantage of the relatively rapid reaction of acids with the copper(II)–peptides compared to the analogous reactions of the copper(III)–peptides. Application of Marcus' theory for outer-sphere electron transfer to the neutral copper(III)–peptides permits calculation of an apparent self-exchange rate constant for the copper(III)–copper(II) species as 7×10^7 M^{-1} s^{-1} (25.0 °C, 0.1 M ionic strength). An alternative mechanism with electron transfer via a chloride bridge between iridium and copper also is possible.

Introduction

Copper(III)–deprotonated-peptide complexes are readily prepared by chemical or electrochemical oxidation and are moderately stable in aqueous media.[1-4] The copper(III)–peptides have intense charge-transfer bands in the vicinity of 250 and 365 nm. The complexes have no ESR spectra, and they are very slow to undergo ligand substitution reactions. Their properties are characteristic of low-spin, d^8, square-planar complexes. Although crystal structures of the copper(III)–peptide complexes have not been obtained, the crystal structure of the triply deprotonated tetraglycine complex of copper(II), $Cu^{II}(H_{-3}G_4)^{2-}$, has been determined.[5] This d^9 complex has four nitrogens coordinated to copper in a nearly square-planar arrangement with Cu–N distances of 2.03 Å (for the amine) and 1.91–1.94 Å (for the deprotonated peptides). The crystal structure of a related complex, *o*-phenylenebis(biuretato)cuprate(III), has been determined.[6] The copper atom is surrounded by an approximately planar arrangement of four nitrogen atoms with short Cu–N distances (1.82–1.89 Å).

Oxidation–reduction reactions involving the peptide complexes of copper(II) and copper(III) provide the first opportunity to determine the speed of electron-transfer reactions between these oxidation states as well as providing an example of electron transfer between two predominantly square-planar complexes. The $Ir^{IV}Cl_6^{2-}$–$Ir^{III}Cl_6^{3-}$ redox couple was chosen to study the electron-transfer characteristics of the $Cu^{III,II}$ systems because the iridium complexes are known to undergo outer-sphere electron-transfer reactions with a variety of compounds[7] and because the self-exchange rate constant has been evaluated.[8] Both of these iridium complexes have very slow substitution reactions.[9] Copper(III)–peptides are formed by $IrCl_6^{2-}$ oxidation of the corresponding copper(II) complexes,[1,2] but the reactions are too fast to measure by stopped-flow techniques.[10,11] This difficulty has been circumvented by measuring the rates of the reverse reactions between $IrCl_6^{3-}$

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Table I. Summary of Peptide Complexes and Thermodynamic Data

copper-peptide	E°,[a] V	copper-peptide	E°,[a] V
	Neutral Cu(III) Complexes		
A_3	−0.08	G_3a	−0.25
leu_3	−0.12	VG_2a	−0.28
G_3AOCH_3	−0.19[b]	G_2Aa	−0.29
G_4a	−0.21	PG_2a	−0.29[b]
	Uninegative Cu(III) Complexes		
G_5	−0.23	AG_3	−0.28
G_4A	−0.23	A_4	−0.29
G_4	−0.26	V_4	−0.38

[a] E° values are for $Cu^{III}(H_{-x}L) + IrCl_6^{3-} \rightleftarrows Cu^{II}(H_{-x}L)^- + IrCl_6^{2-}$. [b] The potentials for the $Cu^{III,II}(H_{-3}G_3AOCH_3)^{0,1-}$ and $Cu^{III,II}(H_{-2}PG_2a)^{0,1-}$ couples were determined under the same conditions as those of ref 2. $E^\circ = 0.70$ V vs. NHE; $\Delta(mV) = 100$ for G_3AOCH_3 and $E^\circ = 0.60$ V vs. NHE $\Delta(mV) = 107$ for PG_2a.

and copper(III)–peptides. Although the latter reactions are uphill electron transfers, it is possible to force the reactions in this direction by taking advantage of the rapid reactions of acids with the copper(II)–peptides[11-14] compared to the relatively sluggish reactions of acids with the copper(III)–peptides. This permits the rate constants to be determined for the oxidation of $IrCl_6^{3-}$ by a variety of copper(III)–peptides, with a wide range of electrode potentials.[2] The results show very rapid electron transfers between the copper and iridium centers and indicate a large value for the self-exchange rate constant for copper(III)–peptides and copper(II)–peptides.

Experimental Section

The peptides used to form the copper complexes are listed in Table I. The following abbreviations are used for the amino acid residues (L isomers) of the peptides: glycyl, G; alanyl, A; valyl, V; leucyl, leu; prolyl, P; G_3a is glycylglycylglycylamide, etc. Most of the peptides were obtained from Biosynthetika except for G_3AOCH_3, G_3a, and VG_2a which were obtained from Vega-Fox and G_4a and G_2Aa which were obtained from Cyclo Chemical Co. The standard redox potentials for the reactions of each of the copper(III)–peptide complexes with $IrCl_6^{3-}$ are also included in Table I. The potentials were calculated using 0.892 V vs. NHE for the $IrCl_6^{2-}$–$IrCl_6^{3-}$ couple[1] and potentials for the copper(II, III)–peptide couples reported elsewhere.[2]

Millimolar solutions of the copper(II) complexes were prepared by the reaction of solutions of $Cu(ClO_4)_2$ with peptides in 5–10% excess. The pK_a values of these complexes[3] are such that the fully deprotonated form predominates at pH >10 for the tetrapeptides and tripeptide amides and at pH >8.0 for the tripeptides. Thus the pH of the freshly prepared solutions of tetrapeptides or tripeptide amides was raised to 10.5, and the pH of the tripeptide solutions was raised to 8.5. Oxidation to the corresponding copper(III) complexes was accomplished electrochemically using a flow system in which the electrode arrangement included a graphite powder working electrode packed in a porous glass column, wrapped externally with a platinum wire electrode.[15] The resulting solutions were diluted (1×10^{-5} M) and their ionic strength was adjusted to 0.10 M with $NaClO_4$ (prepared from Na_2CO_3 and $HClO_4$).

Crystalline sodium hexachloroiridate(III) was prepared by the method of Poulsen.[16] The iridium content of the solid was determined by oxidation with $Cl_2(g)$ followed by either spectrophotometric determination of $IrCl_6^{2-}$ or potentiometric titration with $Fe(CN)_6^{4-}$. Solutions of $IrCl_6^{3-}$ (8×10^{-4} M) were prepared from the solid not more than 1 h before each kinetic determination and were buffered with 0.10 M acetic acid at pH values between 4.0 and 6.0. The ionic strength of the buffered $IrCl_6^{3-}$ solutions was adjusted to 0.10 M with $NaClO_4$, allowing for contributions from the buffer salt at each pH.

The amount of $IrCl_6^{2-}$ present in the $IrCl_6^{3-}$ solutions was shown to be negligible. The amount of $IrCl_6^{2-}$ (λ_{max} 490 nm, ϵ 4075 M^{-1} cm^{-1}) present in the $IrCl_6^{3-}$ solutions was established spectrophotometrically by obtaining the absorbance at 490 nm before and after the addition of a large excess of ascorbic acid. The absorbance differences obtained indicated that less than 5×10^{-8} M $IrCl_6^{2-}$ was present in 8×10^{-4} M $IrCl_6^{3-}$ solutions corresponding to a relative impurity of less than 0.01%.

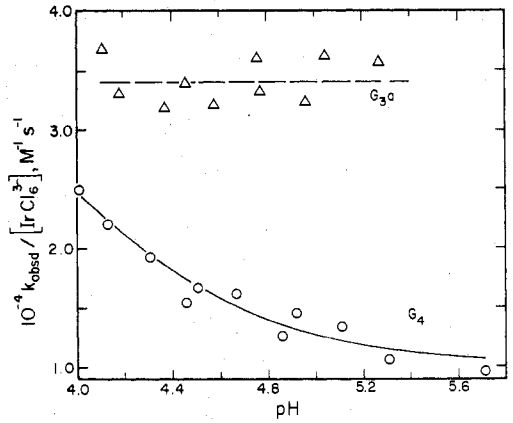

Figure 1. Effect of pH on the reactions of $Cu^{III}(H_{-3}G_3a)$ and of $Cu^{III}(H_{-3}G_4)^-$ with $IrCl_6^{3-}$ (25.0 °C, 0.1 M $NaClO_4$).

Reactions were monitored by a computer-interfaced stopped-flow[17] spectrophotometer thermostated at 25.0 °C. The decay of the copper(III)–peptide was observed by following the absorbance at 365 nm where $-d[Cu(III)]/dt = k_{obsd}[Cu(III)]$, $[IrCl_6^{3-}] >> [Cu(III)]$, and k_{obsd} is a pseudo-first-order rate constant dependent on $[IrCl_6^{3-}]$. Formation of $IrCl_6^{2-}$ at 490 nm also was monitored and gave equivalent rate constants.

The pH of each reaction mixture was determined on a Radiometer 26 pH meter equipped with a Radiometer G2222C glass electrode and a Radiometer K4112 reference electrode. A titration of 0.100 M $HClO_4$ with 0.100 M NaOH containing 0.100 M $NaClO_4$ as suggested by Irving, Miles, and Pettit[18] was employed to determine the pH correction for these electrodes at $\mu = 0.10$ M. The expression obtained for use under these conditions was $-\log [H^+] = pH_{obsd} + 0.06$.

Results

The reactions observed between the copper(III)–peptides and $IrCl_6^{3-}$ can be represented as shown in eq 1 and 2. The

$$Ir^{III}Cl_6^{3-} + Cu^{III}(H_{-x}L) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ir^{IV}Cl_6^{2-} + Cu^{II}(H_{-x}L)^- \quad (1)$$

$$Cu^{II}(H_{-x}L)^- \xrightarrow[\text{acid}]{k_D} Cu^{II}(aq) + HL \quad (2)$$

reduction of the copper(III)–peptides in eq 1 is thermodynamically unfavorable as shown in Table I. However, when the reactions are carried out in acidic media the $Cu^{II}(H_{-x}L)^-$ produced by the redox reaction rapidly dissociates to aquocopper(II) and protonated peptides. This rapid acid dissociation pulls the unfavorable redox reaction uphill.

Reaction Orders of Reactants. When the absorbance, A, at 365 nm was monitored, excellent linearity was obtained for plots of $\log (A - A_\infty)$ vs. time if the reactions were carried out with excess $IrCl_6^{3-}$ and at constant pH less than 4.5. Therefore, the reactions were first order in $Cu^{III}(H_{-x}L)$. The k_{obsd} values for the neutral copper(III) complexes are given in Table II where the standard deviation results from at least three separate runs.

Data for $Cu^{III}(H_{-3}G_3a)$ in Table II show the dependence of k_{obsd} on the $IrCl_6^{3-}$ concentration at $[H^+] = 1.82 \times 10^{-5}$ M. This dependence is given in eq 3, where k_1 is $(3.1 \pm 0.3) \times 10^4$ M^{-1} s^{-1} and the correlation coefficient, r^2, for the least-squares fit was 0.98.

$$k_{obsd} = k_1[Ir^{III}Cl_6^{3-}] \quad (3)$$

For the neutral copper(III)–peptides, k_{obsd} showed only a slight dependence on hydrogen ion concentration as seen in Table II and Figure 1. Thus, k_1, the rate constant for the reduction of copper(III)–peptide by $Ir^{III}Cl_6^{3-}$, was obtained by averaging the k_{obsd} values and dividing by the $IrCl_6^{3-}$

Table II. Neutral Copper(III)–Peptide Complexes[a]

peptide	$10^5[H^+]$, M	$10^4[IrCl_6^{3-}]$, M	k_{obsd}, s^{-1}	$10^{-4}k_1$, M^{-1} s^{-1}	$10^{-8}k_{-1}$, M^{-1} s^{-1}
A_3	5.50	3.99	237 (±7)		
	1.10		197 (±25)[b]	av 54 (±5)	0.12
leu_3	5.50	3.99	201 (±6)		
	2.75		210 (±5)[b]		
	1.74		200 (±6)[b]	av 51 (±3)	0.55
G_3AOCH_3	7.76	3.96	39.7 (±0.9)		
	4.57		37 (±1)		
	2.95		35.5 (±0.8)		
	1.91		35 (±1)[b]	av 9.3 (±0.3)	1.5
G_4a	7.59	3.71	36.7 (±0.6)		
	5.01		36 (±1)		
	3.16		38 (±1)		
	2.00		39 (±2)[b]	av 10.1 (±0.5)	3.6
G_3a	13.8	3.60	15.3 (±0.1)		
	7.76		13.2 (±0.1)		
	3.47		12.2 (±0.2)		
	1.74		13.0 (±0.1)[b]		
	0.912		13.0 (±0.2)[b]		
	0.537		12.8 (±0.3)[b]		
	6.60	3.52	11.6 (±0.2)		
	4.27		11.2 (±0.1)		
	2.63		11.3 (±0.1)		
	1.70		11.7 (±0.2)[b]		
	1.10		11.4 (±0.3)[b]	av 3.4 (±0.1)	5.8
G_3a	1.82	1.53	5.6 (±0.2)[b]		
	1.82	3.06	12.2 (±0.2)[b]		
	1.82	4.60	17.5 (±0.8)[b]		
	1.82	7.65	25 (±1)[b]	av 3.1 (±0.3)	
VG_2a	7.59	3.71	3.8 (±0.2)		
	5.01		3.7 (±0.1)		
	3.16		3.19 (±0.06)		
	2.00		3.1 (±0.1)[b]	av 0.93 (±0.03)	5.1
G_2Aa	8.51	3.67	3.59 (±0.04)		
	5.50		3.30 (±0.06)		
	3.31		3.4 (±0.1)		
	2.14		3.27 (±0.05)[b]		
	1.26		3.3 (±0.1)[b]		
	0.832		3.3 (±0.1)[b]	av 0.92 (±0.03)	7.5
PG_2a	7.76	3.96	2.25 (±0.03)		
	4.57		2.30 (±0.03)		
	2.95		2.12 (±0.07)		
	0.724		2.2 (±0.1)[b]	av 0.58 (±0.1)	4.7

[a] $T = 25.0$ °C, $\mu = 0.1$ M ($NaClO_4$ + OAc^-), $[HOAc]_T = 0.05$ M, and $[Cu^{III}(H_{-x}L)] \approx 10^{-5}$ M. [b] Initial rate.

Table III. Acid Dissociation Rate Constants for $Cu^{II}(H_{-x}L)$ and the Rate Determining Step Ratio vs. pH

peptide	pH	10^4k_D, s^{-1}	$k_D/(k_{-1} \times [IrCl_6^{2-}])$[a]
G_4	3.0	18.1	72
	3.5	7.02	28
	4.0	3.32	13
	4.5	1.62	6.5
	5.0	0.809	3.3
	5.5	0.287	1.2
A_3	3.0	0.684	38
	3.5	0.324	18
	4.0	0.198	11
	4.5	0.115	6.4
	5.0	0.0566	3.1

[a] For $[IrCl_6^{2-}] = 10^{-5}$ M, $k_{-1} = 2.5 \times 10^8$ M^{-1} s^{-1} for G_4 and $k_{-1} = 1.8 \times 10^7$ M^{-1} s^{-1} for A_3.

concentration. For the $Cu^{III}(H_{-3}G_3a)$ case, k_1 obtained from an average of the k_{obsd} values was in good agreement with the k_1 obtained from the slope of the k_{obsd} vs. $IrCl_6^{3-}$ concentration plot.

The lack of a hydrogen ion dependence above pH 4 is expected because appreciable protonation of the copper(III)–tripeptides and tripeptide amides should not occur until pH ~3 by analogy with $Ni^{II}(H_{-2}G_3)^-$ [19] and $Ni^{II}(H_{-3}G_3a)^-$.[20]

Evidence That Reduction of Copper(III)–Peptide by $IrCl_6^{3-}$ is the Rate-Determining Step. The rate of acid decomposition of $Cu^{III}(H_{-3}G_4)^-$ [10] is much slower than the rate of acid dissociation of $Cu^{II}(H_{-3}G_4)^{2-}$.[11] Slow substitution is characteristic of low-spin, d^8, square-planar complexes, and self-redox is observed for the copper(III) complexes rather than substitution reactions. The acid decomposition (self-redox) of $Cu^{III}(H_{-3}G_4)^-$ has first-order rate constants of 6.3×10^{-4} s^{-1} at pH 4 and of 2.0×10^{-4} s^{-1} at pH 5.[10] The reaction of $Cu^{III}(H_{-3}G_4)^-$ with $Ir^{III}Cl_6^{3-}$ (2.92×10^{-4} M) is approximately 10^4 s^{-1} faster with pseudo-first-order rate constants of 7.3 s^{-1} at pH 4 and 3.3 s^{-1} at pH 5.

The acid dissociation properties of the copper(II)–tetraglycine complex, $Cu^{II}(H_{-3}G_4)^{2-}$, are summarized in eq 4 and 5, where $k_H = 1.6 \times 10^8$ M^{-1} s^{-1}, $k_{HX} = 3.8 \times 10^5$ M^{-1} s^{-1} for acetic acid, $k_{H_2O} = 16$ s^{-1}, and K_a is the acid dissociation constant for HX (2.24×10^{-5} for acetic acid).[11]

$$-d[Cu^{II}(H_{-3}G_4)^{2-}]/dt = k_D[Cu^{II}(H_{-3}G_4)^{2-}] \quad (4)$$

$$k_D = k_{H_2O} + k_H[H^+] + \frac{k_{HX}[HX]_T[H^+]}{K_a + [H^+]} \quad (5)$$

The conditions for which the redox reaction will be the rate-determining step for the reactions in eq 1 and 2 can now be evaluated. For the reaction of $Cu^{III}(H_{-3}G_4)^-$ with $IrCl_6^{3-}$, eq 6 is obtained if it is assumed that a steady-state concen-

$$k_{obsd} = \frac{k_1k_D[IrCl_6^{3-}]}{k_{-1}[IrCl_6^{2-}] + k_D} \quad (6)$$

Table IV. Iridium(IV) Inhibition of the Observed Rate Constant[a]

Cu(III)-peptide	10^5 [H$^+$], M	$10^4 \times$ [$IrCl_6^{3-}$], M	$10^5 \times$ [$IrCl_6^{2-}$], M	k_{obsd}, s^{-1}
G_4	1.15	3.93	0	6.18 (±0.08)[b]
			0.346	4.8 (±0.1)[b]
			0.691	4.3 (±0.1)[b]
			1.38	3.4 (±0.1)[b]
			2.07	2.61 (±0.05)[b]
			2.76	2.21 (±0.01)[b]
	11.0	3.93	0	14.2 (±0.3)
			0.691	11.6 (±0.3)
			2.07	8.7 (±0.2)
A_4	1.15	3.93	0	0.52 (±0.01)[b]
			0.691	0.401 (±0.008)[b]
			1.38	0.346 (±0.01)[b]
			2.07	0.287 (±0.007)[b]

[a] $T = 25.0$ °C, $\mu = 0.1$ M ($NaClO_4$ + OAc^-), $[HOAc]_T = 0.05$ M, and [Cu(III)L] $\leq 10^{-5}$ M. [b] Initial rate.

tration of $Cu^{II}(H_{-3}G_4)^{2-}$ is present. The requirement for $k_{obsd} = k_1[IrCl_6^{3-}]$ is that $k_D >> k_{-1}[IrCl_6^{2-}]$. Thus linear plots of log $(A - A_\infty)$ vs. time are expected only if $k_D >> k_{-1}[IrCl_6^{2-}]$ because the $IrCl_6^{2-}$ concentration is changing during the reaction. This is the case for $Cu^{III}(H_{-3}G_4)^-$ up to pH 4.5. Above this pH, initial rate data were used because the reactions deviated from first order if followed to completion.

The acid dissociation characteristics of the copper(II)–trialanine complex, $Cu^{II}(H_{-2}A_3)^-$, also have been determined.[21] The acid dissociation rate constant is of the same form as eq 5, where $k_H = 5.1 \times 10^6$ M^{-1} s^{-1}. The rate constant for acetic acid catalyzed dissociation, k_{HX}, can be estimated using the value 3.4×10^4 M^{-1} s^{-1} determined for the similar complex $Cu^{II}(H_{-2}G_3)^-$.[22]

Table III shows a calculation of k_D as a function of pH as well as the ratio $k_D/k_{-1}[IrCl_6^{2-}]$ for the reaction of $IrCl_6^{3-}$ with $Cu^{III}(H_{-3}G_4)^-$ and $Cu^{III}(H_{-2}A_3)$. The concentration of $IrCl_6^{2-}$ used for the calculations is 10^{-5} M corresponding to the initial concentration of copper(III)–peptide, and the k_{-1} values employed are explained later. The ratio given in Table III is calculated for the worst case near the end of the reaction where the maximum concentration of $IrCl_6^{2-}$ is produced. As Table III indicates, initial rate data are needed to meet the requirement that $k_D >> k_{-1}[IrCl_6^{2-}]$ at pH 4.5 and above.

Another verification of the mechanism shown in eq 1 and 2 is the dependence of the rate on the concentration of $IrCl_6^{2-}$. This dependence was determined for $Cu^{III}(H_{-3}G_4)^- + IrCl_6^{3-}$ at pH 4.0 and 5.0 and for $Cu^{III}(H_{-3}A_4)^- + IrCl_6^{3-}$ at pH 5.0. Table IV shows the change in k_{obsd} as a function of the concentration of $IrCl_6^{2-}$. If eq 6 for k_{obsd} is correct, then a plot of $1/k_{obsd}$ vs. the concentration of $IrCl_6^{2-}$ should be linear. Figure 2 shows that such a plot for $Cu^{III}(H_{-3}G_4)^-$ is linear at both pH 4.0 and 5.0. Similar behavior is observed for $Cu^{III}(H_{-3}A_4)^-$. The intercepts of the k_{obsd} vs. concentration of $IrCl_6^{2-}$ plots at both pH values and for both peptides are in reasonable agreement with the k_{obsd} values in Table V. The slopes of the plots in Figure 2 correspond to $k_{-1}/(k_1k_D[IrCl_6^{3-}])$ and have numerical values of $(9.4 \pm 0.5) \times 10^3$ M^{-1} s at pH = 5.0 and $(2.2 \pm 0.1) \times 10^3$ M^{-1} s at pH = 4.0. Since k_D has been calculated as shown in Table III, the ratio k_{-1}/k_1 can be determined directly giving a measure of the equilibrium constant for the electron-transfer step. From Table I, the $E°$ for $Cu^{III}(H_{-3}G_4)^- + IrCl_6^{3-}$ has been previously evaluated as −0.26 V using cyclic voltammetry. The slopes of the $IrCl_6^{2-}$ inhibition plots give −0.265 V at pH 5.0 and −0.263 V at pH 4.0.

Thus, it is concluded that the reduction of copper(III)–peptide by $IrCl_6^{3-}$ is the rate-determining step for the reactions of $Cu^{III}(H_{-3}G_4)^-$, $Cu^{III}(H_{-3}A_4)^-$, and $Cu^{III}(H_{-2}A_3)$ with $IrCl_6^{3-}$. It is assumed from these considerations that this reduction is

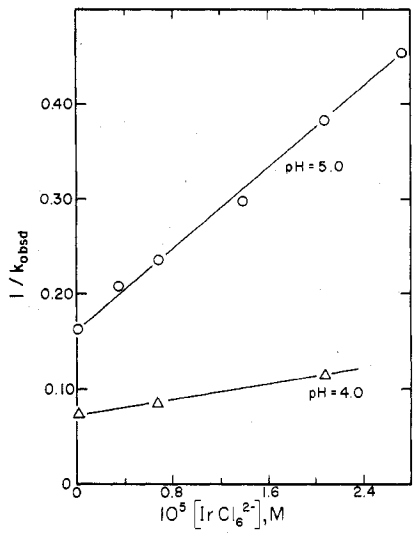

Figure 2. Dependence of the reciprocal of the observed rate constant for the reaction of $Cu^{III}(H_{-3}G_4)^-$ with $IrCl_6^{3-}$ on the $IrCl_6^{2-}$ concentration showing the inhibition of the overall reaction by iridium(IV).

the rate-determining step for the reactions of the other copper(III)–peptides summarized in Tables II and V, all of which exhibited similar behavior.

pH Dependence for Uninegative Complexes. From eq 1 and 2 and Table III, it can be seen that the contribution of reaction 2 to the rate expression should be smallest at low pH. Hence no pH dependence would be expected when k_D is large. However, data in Table V show that k_{obsd} increases with acidity for the uninegative Cu(III) complexes of the peptides G_4, AG_3, A_4, and V_4. This effect is illustrated in Figure 1 where the $k_{obsd}/[IrCl_6^{3-}]$ is plotted as a function of pH for $Cu^{III}(H_{-3}G_4)^- + IrCl_6^{3-}$.

The dependence of k_{obsd} on hydrogen ion concentration for the uninegatively charged copper(III) complexes of G_4, AG_3, A_4, and V_4 can be accounted for by assuming that protonation of the copper complex occurs and that both the protonated and unprotonated Cu(III) species react with $IrCl_6^{3-}$. Thus, the reactions in eq 7–9 are occurring as well as those in eq

$$Cu^{III}(H_{-x}L)^- + H^+ \underset{}{\overset{K_H}{\rightleftharpoons}} Cu^{III}(H_{-x}L)H \quad (7)$$

$$Cu^{III}(H_{-x}L)H + IrCl_6^{3-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} IrCl_6^{2-} + Cu^{II}(H_{-x}L)H^- \quad (8)$$

$$Cu^{II}(H_{-x}L)H^- \xrightarrow[\text{acid}]{k_D'} Cu^{II}(aq) + HL \quad (9)$$

1 and 2. Assuming a steady state in both the $Cu^{II}(H_{-x}L)H^-$

Table V. Reaction of Uninegative Copper(III)–Peptide Complexes with Iridium(III)[a]

peptide	$10^5[H^+]$, M	$10^4[IrCl_6^{3-}]$, M	k_{obsd}, s^{-1}	$10^{-4}k_1$, M^{-1} s^{-1}	$10^{-8}k_{-1}$, M^{-1} s^{-1}
G_5	8.51	3.67	13.5 (±0.2)		
	5.50		12.5 (±0.3)		
	3.31		10.8 (±0.3)		
	2.14		11.9 (±0.6)[b]		
	1.26		11 (±1)[b]	av 3.3 (±0.2)	2.6
G_4A	9.77	4.16	14.6 (±0.2)		
	5.10		12.5 (±0.3)		
	2.40		12.0 (±0.5)[b]		
	0.955		10.2 (±0.3)[b]	av 3.0 (±0.2)	2.3
G_4	9.77	2.92	7.30 (±0.05)		
	3.47		4.50 (±0.05)		
	1.38		3.69 (±0.05)		
	0.490		3.1 (±0.1)[b]		
	0.195		2.8 (±0.1)[b]		
	7.41	4.25	9.4 (±0.3)		
	4.90		8.2 (±0.2)		
	3.09		7.1 (±0.2)		
	2.14		6.9 (±0.1)[b]		
	1.20		6.20 (±0.05)[b]		
	0.776		5.7 (±0.1)[b]	1.0 (±0.1)	2.5
AG_3	9.77	4.16	4.11 (±0.05)		
	5.01		3.00 (±0.04)		
	2.40		2.19 (±0.02)		
	0.955		1.69 (±0.05)[b]	0.31 (±0.1)	1.7
A_4	9.12	3.55	0.99 (±0.02)		
	6.46		0.86 (±0.01)		
	3.80		0.67 (±0.01)		
	2.40		0.65 (±0.01)[b]		
	1.38		0.47 (±0.01)[b]		
	0.912		0.43 (±0.01)[b]		
	0.589		0.35 (±0.01)[b]	0.075 (±0.005)	0.61
V_4	6.92	4.53	0.031 (±0.002)		
	4.47		0.023 (±0.001)		
	1.95		0.017 (±0.001)[b]		
	1.00		0.014 (±0.001)[b]		
	0.525		0.012 (±0.001)[b]	0.0020 (±0.0001)	0.54

[a] $T = 25.0$ °C, $\mu = 0.1$ M ($NaClO_4$ + OAc^-), $[HOAc]_T = 0.05$ M, and $[Cu^{III}(H_{-x}L)] \approx 10^{-5}$ M. [b] Initial rate.

species and the $Cu^{II}(H_{-x}L)^-$ species allows the derivation of the expression for k_{obsd} in eq 10.

$$k_{obsd} = \frac{[IrCl_6^{3-}]}{(1 + K_H[H^+])}\left[\frac{k_1k_D}{k_{-1}[IrCl_6^{2-}] + k_D} + \frac{k_2k_D'}{k_{-2}[IrCl_6^{2-}] + k_D'}\right] \quad (10)$$

If $k_D >> k_{-1}[IrCl_6^{2-}]$ and $k_D' >> k_{-2}[IrCl_6^{2-}]$, then eq 10 becomes

$$k_{obsd} = \left[\frac{k_1 + k_2K_H[H^+]}{1 + K_H[H^+]}\right][IrCl_6^{3-}] \quad (11)$$

The magnitude of k_D' for the outside protonated species is known to be greater than k_D for the unprotonated $Cu^{II}(H_{-x}L)^-$. Hence, a nonlinear regression analysis using eq 11 was employed to fit the pH profile in Figure 1. The solid line in Figure 1 is the result of the fit where $k_1 = 1.0 \times 10^4$ M^{-1} s^{-1}, $k_2 = 5 \times 10^4$ M^{-1} s^{-1}, and $K_H = (1 \pm 1) \times 10^4$ M^{-1} for $Cu^{III}(H_{-3}G_4)^-$. The value of K_H is consistent with the protonation constant for $Ni^{II}(H_{-3}G_4)^-$, where the outside protonated species is stabilized by internal hydrogen bonding[20] and with that for $Cu^{II}(H_{-2}glyglyhis)^-$ where the histidyl residue also provides stabilization via internal hydrogen bonding.[23]

Equation 11 also was used to resolve the pH data for the Cu(III) complexes of AG_3, A_4, and V_4. The K_H values obtained for these complexes were in reasonable agreement with that obtained for G_4. However, we are reporting only the k_1 values because they are of greatest interest to this study. The assignment of k_2 and K_H values is useful to resolve k_1 but falls short of explaining the full H^+ dependence because the k_{obsd} values continue to increase below pH 3. Hence there are undoubtedly other protonated species contributing to the redox reaction at lower pH.

The uninegatively charged Cu(III) complexes of G_4A and G_5 showed little or no dependence of k_{obsd} on hydrogen ion concentration as seen in Table V. These species are not expected to be appreciably protonated at pH values above 3, because their outside protonated species are less stabilized by internal hydrogen bonding.[20,23] Thus, k_1 for these species was obtained in the same manner as for the neutral complexes: by averaging the k_{obsd} values and dividing by the concentration of $IrCl_6^{3-}$.

Using the k_1 values obtained as described above, we calculated rate constants for the oxidation of the Cu(II) complexes by $IrCl_6^{2-}$ directly from the known $E°$ values for the individual reactions. These k_{-1} values are given in Tables II and V and are not far from the diffusion limit of (for a 5-Å distance of closest approach) approximately 10^9 M^{-1} s^{-1} for −1 and −2 charged reactants and 2×10^8 M^{-1} s^{-1} for −2 and −2 charged reactants.[24] These values are in agreement with the inability to observe the reactions using stopped-flow methods; however, they are within the range of a pulsed-flow method[25] and preliminary data by this technique agree with the magnitude of these rate constants.

Discussion

Because of the slow substitution character of both the $Cu^{III}(H_{-x}L)$ species and the $IrCl_6^{3-}$ species, an outer-sphere mechanism for electron transfer might be expected. Little is known, however, about the one-electron-transfer behavior of square-planar complexes, and this geometry also could permit

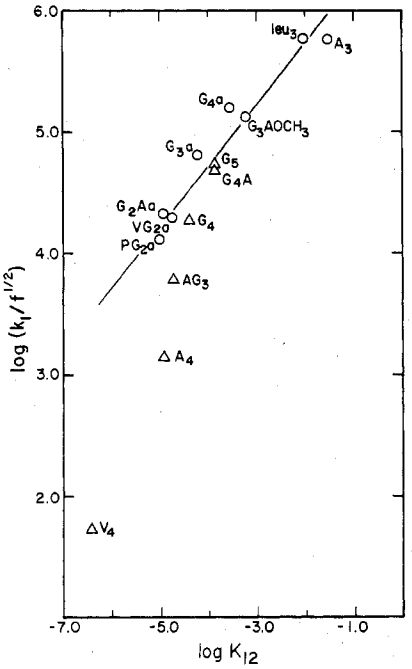

Figure 3. Marcus plot for the electron-transfer reaction between copper(III)–peptide complexes and $IrCl_6^{3-}$. The neutral Cu(III) complexes (○) fit the Marcus correlation while the negative Cu(III) complexes (△) do not.

electron transfer via an axial chloride bridge between iridium and copper. This possibility cannot be eliminated a priori.

The one-electron oxidation of $IrCl_6^{3-}$ by a copper(III)–peptide is given in eq 1. If an outer-sphere mechanism is assumed, the corresponding self-exchange reactions are given by eq 12 and 13. The self-exchange rate constant k_{11} for the

$$Ir^*Cl_6^{3-} + IrCl_6^{2-} \underset{}{\overset{k_{11}}{\rightleftharpoons}} Ir^*Cl_6^{2-} + IrCl_6^{3-} \quad (12)$$

$$Cu^{*III}(H_{-x}L)^{-n} + Cu^{II}(H_{-x}L)^{-(n+1)} \overset{k_{22}}{\rightleftharpoons} Cu^{*II}(H_{-x}L)^{-(n+1)} + Cu^{III}(H_{-x}L)^{-n} \quad (13)$$

iridium hexachloride couple has been determined[8] as 2.3×10^5 M^{-1} s^{-1}. According to the Marcus theory,[26] eq 14 and 15

$$k_1 = (k_{11}k_{22}K_{12}f)^{1/2} \quad (14)$$

$$\log f = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \quad (15)$$

give the relationship between the cross-reaction rate constant k_1, the two self-exchange rate constants k_{11} and k_{22}, and the equilibrium constant for the cross reaction K_{12}. Equations 14 and 15 apply if outer-sphere mechanisms are followed and the appropriate work terms are small or cancel.

Equation 14 implies that a plot of log $(k_1/f^{1/2})$ vs. log K_{12} should be linear with a slope of 0.50 and an intercept of 0.5 log $k_{11}k_{22}$. A plot of this type for the reactions of both the neutral and uninegative copper(III)–peptide complexes with $IrCl_6^{3-}$ is shown in Figure 3. The electron-transfer behavior of the neutral copper(III)–peptides follows the Marcus prediction. The solid line in Figure 3 is a linear least-squares fit of the data for the neutral complexes, and it has a slope of 0.46 ± 0.05, an intercept of 6.6 ± 0.2, and a correlation coefficient of 0.93. The f values calculated by successive approximations from eq 14 and 15 ranged from 0.19 for G_2Aa to 0.89 for A_3. The intercept corresponds to a self-exchange rate constant of 7×10^7 M^{-1} s^{-1} for the neutral copper(III)–peptide complexes.

Only a small number of examples of self-exchange rates larger than 10^7 M^{-1} s^{-1} are known.[27,28] Hence the copper(II, III)–peptides appear to belong to a select group of very effective electron-transfer agents with self-exchange rates near the diffusion limit. The efficiency of electron transfer in this system is also evidenced by the role of $Cu^{III}(H_{-3}G_4)^-$ as a redox catalyst in oxygen uptake by $Cu^{II}(H_{-3}G_4)^{2-}$.[4]

The uninegative copper(III)–peptide complexes of G_5, G_4A, and G_4 also follow the Marcus prediction as seen in Figure 3. Deviation from Marcus behavior is observed, however, as log K_{12} approaches −5 for the Cu(III) complexes of AG_3, A_4, and V_4. This deviation at large negative values of log K_{12} can be attributed in part to the behavior of the rates of the reverse reactions (the oxidation of the copper(II)–peptides by $IrCl_6^{2-}$), which approach the diffusion limit. A detailed consideration of limiting factors in copper(III)–peptide electron-transfer reactions will be presented later.[29]

Conclusions

The sluggish acid dissociation of trivalent copper–peptide complexes combined with the rapid acid dissociation of divalent copper–peptide complexes permits uphill oxidations of iridium(III) to iridium(IV) by copper(III) complexes. The redox reaction can be made to be the rate-determining step. The resulting rate constants for copper(III)–peptides with $IrCl_6^{3-}$ are quite large considering the unfavorable range of $E°$ values (from −0.09 to −0.38 V) for the electron-transfer step and the electron-exchange characteristics of the iridium complexes.[8] The neutral copper(III)–peptide complexes fit the Marcus correlation for outer-sphere electron-transfer processes and give a self-exchange rate constant of 7×10^7 M^{-1} s^{-1} for the $Cu^{III}(H_{-x}L)$–$Cu^{II}(H_{-x}L)^-$ couple. This large value for the self-exchange rate constant is remarkable because sizable changes in crystal field stabilization energy for two oxidation states often cause small self-exchange rate constants. Yet studies of the electrode potentials indicate that the relative gain in crystal field stabilization energy is an important factor in the overall thermodynamic stability of the copper(III)–peptide complexes.[2]

A chloride-bridging mechanism is a possible alternative to an outer-sphere mechanism. Thus, a chloride from $IrCl_6^{3-}$ could enter the inner sphere of copper(III) via an axial position and provide a pathway for electron transfer between iridium and copper. Marcus free energy correlations have been observed for inner-sphere reactions as well as for outer-sphere reactions, particularly in instances of weak inner-sphere coordination.[30-33] Copper(III) complexes would be expected to have primarily square-planar coordination with only weak axial interactions and hence they would satisfy the weak inner-sphere interaction property. However, the rapid reactions of copper(III)–peptides with $Co(phen)_3^{2-}$ show that a bridging ligand is not required for fast electron-exchange reactions.[34]

The more uphill reactions (log $K_{12} < -4$) of the uninegative copper(III)–peptide complexes deviate markedly from the Marcus correlation. It can be shown that this deviation is to be expected because the reverse rate in eq 1 reaches the diffusion limit as log K_{12} becomes more negative. Therefore the rate-limiting step in the forward direction is no longer the electron-transfer step itself and eq 14 is not valid. Instead the limiting step becomes the separation of the species after electron transfer. This could occur either for an outer-sphere mechanism or for a bridging mechanism, but it does add some weight to the latter possibility. Whichever mechanism holds, this work shows that the electron-transfer reactions of copper(III)–peptides can be extremely fast.

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Registry No. $Cu^{III}(H_{-2}A_3)$, 69042-71-3; $Cu^{III}(H_{-2}leu_3)$, 69042-72-4; $Cu^{III}(H_{-3}G_3AOCH_3)$, 69042-73-5; $Cu^{III}(H_{-3}G_4a)$, 68550-44-7; $Cu^{III}(H_{-3}G_3a)$, 62801-36-9; $Cu^{III}(H_{-3}VG_2a)$, 62801-40-5; Cu^{III}-

$(H_{-3}G_2Aa)$, 62801-38-1; $Cu^{III}(H_{-3}PG_2a)$, 24212-63-3; $Cu^{III}(H_{-3}G_5)^-$, 68550-43-6; $Cu^{III}(H_{-3}G_4A)^-$, 69042-74-6; $Cu^{III}(H_{-3}G_4)^-$, 57692-61-2; $Cu^{III}(H_{-3}AG_3)^-$, 69088-03-5; $Cu^{III}(H_{-3}A_4)^-$, 68628-66-0; $Cu^{III}(H_{-3}V_4)^-$, 62959-93-7; $IrCl_6^{3-}$, 14648-50-1; $IrCl_6^{2-}$, 16918-91-5.

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Oxidative Decarboxylation of Glyoxylate Ion by a Deprotonated-Amine Copper(III)–Peptide Complex

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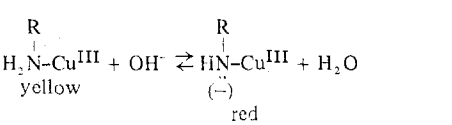
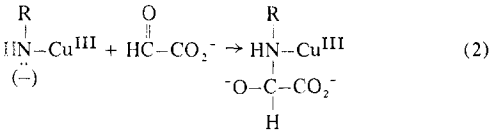
In basic solution copper(III) pentaglycine forms a species, $Cu(H_{-4}G_5)^{2-}$, which has three deprotonated-peptide groups and one deprotonated-amine group coordinated. Acting as a nucleophile, the deprotonated amine attacks glyoxylate ion followed by rapid electron-transfer and decarboxylation steps. The reaction stoichiometry is $2Cu^{III}(H_{-4}G_5)^{2-} + CHOCO_2^- + 2OH^- \rightarrow Cu^{II}(H_{-3}G_5)^{2-} + Cu^{II}(H_{-4}\text{-}N\text{-}fG_5)^{3-} + CO_3^{2-} + H_2O$, where half of the pentaglycine is converted to the *N*-formyl derivative (*N*-fG$_5$). The reaction is first order in the deprotonated-amine species and first order in glyoxylate ion with a rate constant of 1.1×10^6 M^{-1} s^{-1} for the dehydrated form of glyoxylate ion. The rate is pH dependent, with a maximum about pH 13. The rate decreases at higher pH due to the formation of the unreactive glyoxylate dianion. Pyruvate and phenylglyoxylate also react with $Cu^{III}(H_{-4}G_5)^{2-}$ and the relative reactivity is glyoxylate >> pyruvate >> phenylglyoxylate.

Introduction

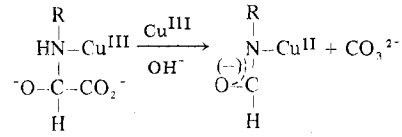
Copper(III)–peptide complexes[1] can be generated in good yield by chemical or electrochemical oxidation of copper(II)–peptide solutions.[2,3] Above pH 11 the normally yellow copper(III)–peptide solutions turn deep red. Rapid acidification restores the yellow color.[3] Spectral and electrochemical data indicate that reversible deprotonation of the coordinated amine terminus of the peptide[4] occurs (eq 1). Copper(III)–peptide complexes undergo self-redox reactions within a few minutes in strong base. However, the addition of reducing agents can destroy copper(III) more rapidly. When copper(III) pentaglycine is formed in the presence of millimolar concentrations of glyoxylate ion ($CHOCO_2^-$), the red species is immediately lost. Pyruvate ion ($CH_3COCO_2^-$) and phenylglyoxylate ion ($C_6H_5COCO_2^-$) are less reactive and require higher concentrations for rapid quenching to be observed. For the glyoxylate reaction, carbonate ion and *N*-formylpentaglycine are identified as products. It is proposed that the deprotonated-amine copper(III) species, acting as a nucleophile, attacks the carbonyl carbon of glyoxylate to form a carbinolamine species (eq 2). This species undergoes oxidative decarboxylation (eq 3) and reacts rapidly via electron transfer with a second copper(III)–pentaglycine complex to give the observed products.



(1)



(2)



(3)

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