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Inner-Sphere Oxidation of Ethylenediaminetetraacetatocobaltate(II) by Copper(III)–Imine–Oxime Complexes

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Abstract

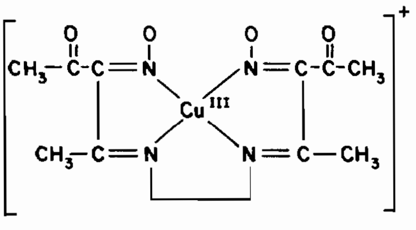
The oxidation of the Co^{II}–EDTA complex by the imine–oxime copper(III) complexes $[Cu^{III}(Enio)]^+$ and $[Cu^{III}(Pre)]^+$ {$EnioH_2$ = N,N^0-ethylenbis(isonitrosoacetylacetoneimine) and $PreH_2$ = N,N^0-propylenebis(isonitrosoacetylacetoneimine)} proceeds via rapid electron-transfer leading to the formation of long-lived intermediates which undergo slow conversion to the final products. It is believed that these intermediates arise from the coordination of one or both of the oxime oxygens to the cobalt(II) complex prior to electron-transfer. The kinetics of the fast step showed first-order dependence on each reactant concentration. The second-order rate constant varied with $[H^+]$ according to the eqn. (i):

$$k_2 = \frac{k_2{}^0 + k'[H^+]}{1 + K_1[H^+]} \qquad \text{(i)}$$

where $k_2{}^0$ and k' refer to the hydrogen-independent and hydrogen-dependent pathways respectively, and K_1 to the protonation constant of $[Co^{II}(EDTA)]^{2-}$. Composite activation parameters associated with $k_2{}^0$ and k' have been determined.

Introduction

Recently we reported that the trivalent oxidation state of copper was stabilized by imine–oxime ligands [1, 2]. Two copper(III) complexes, $[Cu^{III}(Enio)]^+$ (1), and $[Cu^{III}(Pre)]^+$ (2), were generated by chemical oxidation of the corresponding copper(II) complexes:



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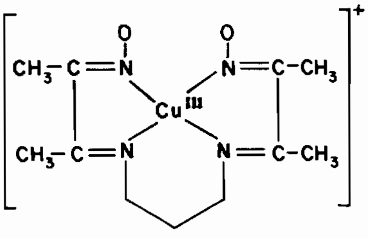

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These complexes were characterized by the loss of the ESR signals of the corresponding copper(II) complexes, ligand-to-metal (LTM) charge transfer spectra with high molar absorptivities, and redox capabilities with a number of reducing agents. Cyclic voltammograms of the copper(II) complexes also displayed quasi-reversible electrochemical behaviour with peak-to-peak separation indicative of one-electron transfer.

The kinetics of the oxidation of several substrates by copper(III)–peptide complexes were investigated, and all were found to be rapid [3]. Both outer-sphere and inner-sphere pathways were envisaged to be operative, depending on the nature of the reductant. Thus in the oxidation of both $IrCl_6{}^{3-}$ and $Fe(CN)_6{}^{4-}$ chloro- and cyano-bridging was invoked to account for the increase in the apparent self-exchange rate constant for $Cu^{III,II}(H_{-n}L)$ and the enhancement of the cross-reaction rate constant respectively [4, 5].

The kinetics of the oxidation of iodide ion by the copper(III)–imine–oxime complexes, (1) and (2), obeyed a rate law similar to that obtained for its oxidation by copper(III)–peptide complexes [6]. An inner-sphere mechanism may be proposed for the pathway that is first-order in iodide ion concentration. An association between iodide ion and copper(III) complexes is required to account for the pathway, showing second-order dependence on this reductant concentration.

The copper(III)–imine–oxime complexes (1) and (2) may react via an inner-sphere mechanism with one or both deprotonated oxime oxygens bridging the two reacting centres when the reductant is

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labile. The oxidation of $Co^{II}EDTA^{2-}$ by these two complexes, as will be shown later, proceeds *via* the formation of an intermediate in each reaction. The intermediates slowly convert to final products.

Experimental

The brown copper(II)–imine–oxime complex $[Cu^{II}(Enio)]$ was prepared from a 1:1 ratio of copper(II) acetate and (H_2Enio) in hot ethanol. The ligand $(EnioH_2)$, N,N′-ethylenebis(isonitrosoacetyleacetoneimine) was prepared by the method of Aly and El-said [7]. The copper(II)–imine–oxime complex $[Cu^{II}(PreH)]ClO_4 \cdot 2H_2O$, where $PreH_2$ = N,N′-propylenebis(isonitrosoacetylacetoneimine), was prepared and recrystallized according to the method of Addison *et al.* [8], and its purity was checked by elemental analysis.

The Cu(III) complexes were obtained in solution by oxidation of the corresponding Cu(II) complexes by using excess PbO_2. The oxidation was carried out in a buffer zone of pH 3.2 – 5.5. To obtain stable Cu(III) complexes in solution, PbO_2 was first mixed with the buffer before the addition of the Cu(II) complex. The mixture was left for 15 minutes, then filtered and used immediately. The $[Cu^{III}(Enio)]^+$ complex has an intense blue colour and absorbs at 581 nm ($\epsilon = 10^4$ M^{-1} cm^{-1}). The $[Cu^{III}(Pre)]^+$ is red and absorbs at 515 nm ($\epsilon = 1.25 \times 10^4$ M^{-1} cm^{-1}) at pH = 4.0. $Co^{II}(EDTA)^{2-}$ solutions were prepared by the mixing of solutions of $Co(NO_3)_2$ and EDTA. To ensure the formation of a 1:1 complex, EDTA was taken slightly in excess of what was required. The excess EDTA would also serve the double purpose of scavenging trace metals in solution. Buffer solutions were prepared from acetic acid and sodium acetate of ordinary grade. The ionic strengths of solutions were adjusted by sodium nitrate.

The kinetics of the oxidation of $[Co^{II}(EDTA)]^{2-}$ by Cu(III)–imine–oxime complexes were monitored spectrophotometrically by following the decrease in their absorption at 581 nm for $[Cu^{III}(Enio)]^+$ and 515 nm for $[Cu^{III}(Pre)]^+$. The spectrophotometer used was a Hi-Tech stopped-flow model SF-3L. The signal and the trigger pulse from the SF-3L were fed into a DL 901 transient recorder, where the information is stored in the memory in digital form and was displayed continuously on an oscilloscope. The transient recorder is interfaced with a Hewlett–Packard 9825B desktop calculator which was used to analyze the absorbance data. All kinetic runs were performed under pseudo-first-order conditions where $[Co^{II}] \geqslant 10[Cu^{III}]$. The pH of the reaction was measured by a Radiometer digital pH meter model PHM62. The effect of varying pH, temperature and ionic strength on the reactions rates were investigated.

It was observed that on mixing the cobalt(II) complex with either of the copper(III) complexes an intermediate was formed. Figures 1 and 2 show that in each case an intermediate was formed. The intermediate obtained in the case of $[Cu^{III}(Pre)]^+$ underwent a slow conversion to give hexacoordinated $[Co^{III}(EDTA)]^-$ as a final product, as evidenced from the absorption peak at 532 nm (Fig. 1). The shift from the 535 nm peak, known for $[Co^{III}(EDTA)]^-$, is probably due to absorption by the product $[Cu^{II}(PreH)]^+$. The intermediate of the $[Co^{II}(EDTA)]^{2-}/[Cu^{III}(Enio)]^+$ reaction was also slowly converted to give a hexacoordinated $[Co^{III}(EDTA)]^-$ complex (Fig. 2). The kinetics of the slow conversion of these intermediates were not investigated.

Results and Discussion

The results in Table I show that at fixed reaction conditions the order with respect to each copper(III) complex is one. This is indicated by the constancy of the magnitude of k_{obs} over a ten-fold variation of the concentrations of the two copper(III) complexes.

The order with respect to the $[Co^{II}(EDTA)]^{2-}$ complex concentration was obtained by varying its concentration while maintaining pseudo-first-order conditions. The results in Table II show that for both copper(III) complexes, k_{obs} varied linearly with $[Co^{II}(EDTA)^{2-}]$, as described by eqn. 1:

$$k_{obs} = k_2[Co^{II}(EDTA)^{2-}] \qquad (1)$$

The effect of H^+ concentration on the magnitude of the second-order rate constant, k_2, was investigated over the 3.22–4.51 pH range for the $[Cu^{III}(Pre)]^+$ reaction and 2.25–3.60 pH range for the $[Cu^{III}(Enio)]^+$ reaction at various temperatures. The results in Table III show that, at any given temperature, the magnitude of k_2 decreases with increasing pH for the $[Cu^{III}(Pre)]^+$ reaction. For the $[Cu^{III}(Enio)]^+$ reaction, however, an opposite behaviour was exhibited with k_2 increasing with increasing pH. This, most probably, reflects the relative reactivities of the protonated, $[Co^{II}(HEDTA)(H_2O)]^-$, and unprotonated, $[Co^{II}(EDTA)]^{2-}$, forms of the cobalt(II) complex towards the copper(III)–imine–oxime complexes. These results indicate that $[Cu^{III}(Pre)]^+$ reacts much more readily with $[Co^{II}(HEDTA)(H_2O)]^-$ than with $[Co^{II}(EDTA)]^{2-}$ whereas for $[Cu^{III}(Enio)]^+$ the reverse is true. This seems to agree with the fact that the $Cu^{III/II}$ electrode potential is pH-dependent and increases with decreasing pH for $[Cu^{II}(preH)]^+$ while it is pH-independent for the

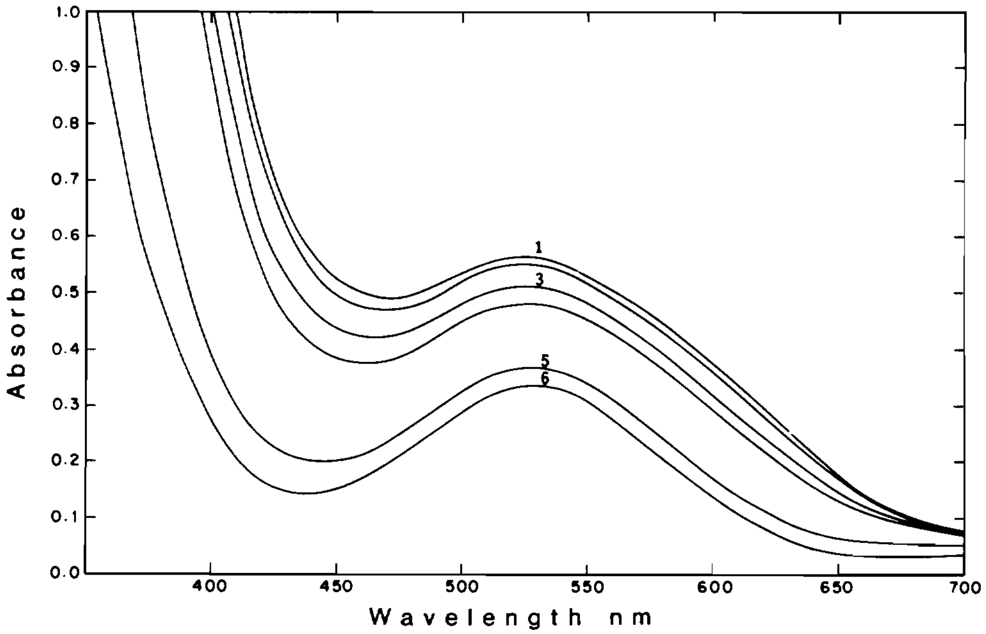


Fig. 1. Visible absorption spectrum of the $[Cu^{III}(Pre)]^+/[Co^{II}(EDTA)]^{2-}$ reaction showing the formation and decomposition of an intermediate. Curves 1–6 were measured after ~10 min, ~30 min, ~90 min, ~150 min, ~24 h and ~48 h respectively from the initiation of the reaction. $[Cu^{III}(Pre)]^+ = 1.87 \times 10^{-4}$ M. $[Co^{II}(edta)^{2-}] = 2.12 \times 10^{-4}$ M and pH = 4.0 (4.0 cm cell).

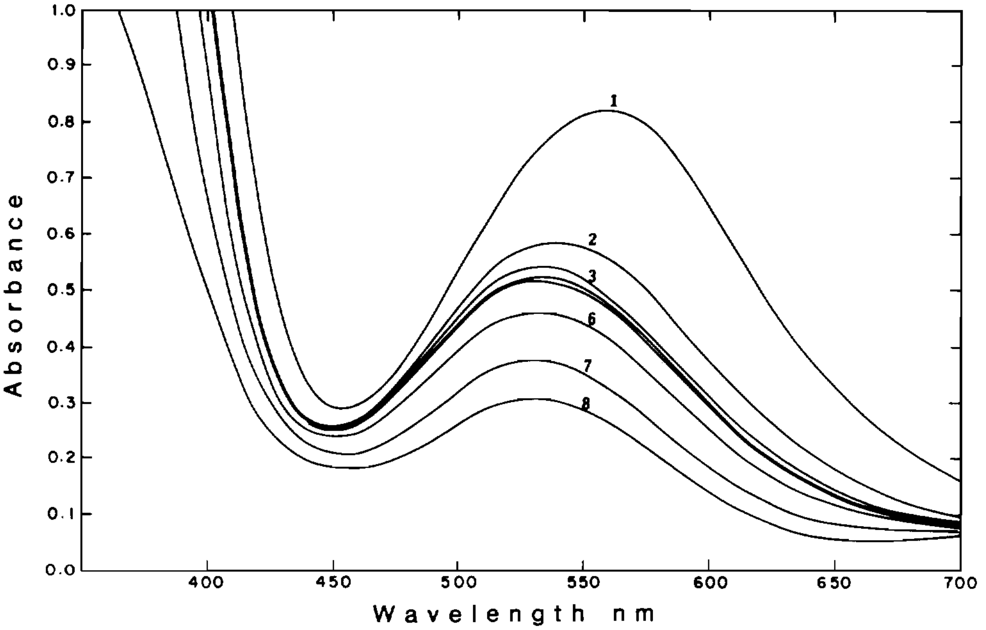


Fig. 2. Visible absorption spectrum of the $[Cu^{III}(Enio)]^+/[Co^{II}(EDTA)]^{2-}$ reaction showing the formation and decomposition of an intermediate. Curves 1, 2 and 3 were recorded after ~5 min, ~60 min and 120 min, respectively from initiation of the reaction. Curves 6–8 were recorded after 6, 24 and 48 h respectively. $[Cu(Enio)^+] = [Co(EDTA)^{2-}] = 2.0 \times 10^{-4}$ M and pH = 4.0 (4 cm cell).

$[Cu^{II}(Enio)]$ [1]. The presence of a proton, which might be brought in by $[Co^{II}(HEDTA)(H_2O)]^-$ to the reaction site, seems to enhance the rate of the reaction. The higher reactivity of $[Cu^{III}(Enio)]^+$ towards $[Co^{II}(EDTA)]^{2-}$, relative to its reaction with $[Co^{II}(HEDTA)(H_2O)]^-$, seems to reflect the difference in the magnitudes of the $Co^{III/II}$ redox potentials of the two forms of the cobalt(II)

TABLE I. First-order Dependence on copper(III) complexes concentrations.

$10^4[Cu^{III}(Pre)^+]$(M)	k_{obs} (s^{-1})[a]	$10^4[Cu^{III}(Enio)^+]$(M)	k_{obs} (s^{-1})[b]
0.5	7.99 ± 0.04	0.20	0.45 ± 0.04
1.0	7.99 ± 0.19	1.10	0.45 ± 0.03
2.0	7.22 ± 0.06	2.20	0.46 ± 0.02
3.0	7.53 ± 0.14		
4.0	7.74 ± 0.18		
5.0	7.48 ± 0.23		

[a] $[Co^{II}(EDTA)^{2-}]_T = 8.0 \times 10^{-3}$ M, pH = 3.46, $\mu = 0.50$ M and $T = 27.0$ °C. [b] $[Co^{II}(EDTA)^{2-}]_T = 3.0 \times 10^{-3}$ M, pH = 3.11, $\mu = 0.50$ M and $T = 25.0$ °C.

TABLE II. Variation of the Observed Pseudo-First-Order Rate Constant for the Oxidation of $[Co^{II}(EDTA)]^{2-}$ by $[Cu^{III}(Pre)]^+$ and $[Cu^{III}(Enio)]^+$ with the Cobalt(II) Complex Concentration.

$[Cu^{III}(Pre)]^+$		$[Cu^{III}(Enio)]^+$	
$10^3[Co^{II}(EDTA)^{2-}]_T$(M)	k_{obs} (s^{-1})[a]	$10^3[Co^{II}(EDTA)^{2-}]_T$(M)	k_{obs} (s^{-1})[b]
2.0	1.40 ± 0.09	3.0	0.89 ± 0.01
6.0	4.62 ± 0.06	6.0	1.59 ± 0.03
10.0	7.68 ± 0.34	8.8	2.85 ± 0.05
14.0	11.15 ± 0.16	10.5	3.02 ± 0.06
20.0	15.97 ± 0.26	20.0	5.88 ± 0.13
		30.0	8.33 ± 0.22

[a] $[Cu^{III}(Pre)^+] = 2.0 \times 10^{-4}$ M, pH = 3.95, $\mu = 0.56$ M and $T = 25.0$ °C. [b] $[Cu^{III}(Enio)^+] = 2.2 \times 10^{-4}$ M, pH = 3.22, $\mu = 0.55$ M and $T = 25$ °C.

TABLE III. Variation of the Observed Pseudo-First-Order Rate Constant for the Oxidation of $[Co^{II}(EDTA)]^{2-}$ by $[Cu^{III}(Pre)]^+$ with pH at Various Temperatures.[a]

T(°C)	pH	k_{obs} (s^{-1})[a]	$10^2 k_2$ (M^{-1} s^{-1})
25.0	3.22	5.35 ± 0.06	8.92 ± 0.10
	3.52	4.55 ± 0.13	7.58 ± 0.22
	3.59	4.38 ± 0.04	7.30 ± 0.07
	3.93	4.20 ± 0.13	7.00 ± 0.22
	4.04	3.99 ± 0.16	6.65 ± 0.27
	4.51	3.71 ± 0.11	6.18 ± 0.18
30.0	3.40	6.81 ± 0.06	11.35 ± 0.10
	3.61	6.25 ± 0.05	10.42 ± 0.08
	3.85	5.36 ± 0.03	8.93 ± 0.05
	4.12	4.91 ± 0.17	8.18 ± 0.28
	4.51	4.54 ± 0.13	7.57 ± 0.22
35.0	3.39	8.66 ± 0.22	14.43 ± 0.37
	3.63	7.56 ± 0.08	12.60 ± 0.13
	3.85	6.95 ± 0.13	11.58 ± 0.22
	4.12	6.52 ± 0.20	10.87 ± 0.33
	4.52	5.72 ± 0.01	9.53 ± 0.01
40.0	3.39	11.41 ± 0.14	19.03 ± 0.23
	3.63	9.40 ± 0.07	15.67 ± 0.12
	3.85	8.64 ± 0.12	14.40 ± 0.20
	4.12	7.74 ± 0.17	12.90 ± 0.28
	4.52	7.17 ± 0.15	11.95 ± 0.25

[a] $[Cu^{III}(Pre)^+] = 2.0 \times 10^{-4}$ M, $[Co^{II}(EDTA)^{2-}]_T = 6.0 \times 10^{-3}$ M, $\mu = 0.50$ M.

complex, the unprotonated form having the lower potential. This may be deduced from a consideration of the known potential of $[Co^{III}EDTA]^-/[Co^{II}EDTA]^{2-}$ and the equilibrium $[Co^{II}(HEDTA)(H_2O)]^- \rightleftharpoons [Co^{II}(EDTA)]^{2-} + H^+$. The higher potential for the protonated form of the cobalt(II) complex is in agreement with the finding that for quinquedentate ligands such as N(2-hydroxyethyl)ethylenediaminetriacetate, the potential is higher than for hexadentate EDTA [9].

The reaction sequence of eqns. (2)–(4) is proposed to account for the kinetics of the oxidation of $[Co^{II}(EDTA)]^{2-}$ by $[Cu^{III}(Pre)]^+$ and $[Cu^{III}(Enio)]^+$ (both Cu^{III} complexes are designated as $[Cu^{III}L]^+$)

$$[Co^{II}(EDTA)]^{2-} + H^+ \rightleftharpoons [Co^{II}(HEDTA)(H_2O)]^- \quad K_1 \qquad (2)$$

$$[Co^{II}(EDTA)]^{2-} + [Cu^{III}L]^+ \longrightarrow \text{products } k_2^0 \qquad (3)$$

$$[Co^{II}(HEDTA)(H_2O)]^- + [Cu^{III}L]^+ \longrightarrow \text{products } k_2^H \qquad (4)$$

An additional pathway may also operate in the $[Cu^{III}(Pre)]^+$ reaction which may account for the pH-dependence of the $Cu^{III/II}$ electrode potential. The Cu^{III} reactive species could be the protonated species $[Cu^{III}(PreH)]^{2+}$ having a small protonation constant K_2:

$$[Co^{II}(EDTA)]^{2-} + [Cu^{III}(PreH)]^{2+} \longrightarrow \text{products } k_3^H \quad (5)$$

The rate law of eqn. (6) derived from the reaction sequence 2–4 accounts for the kinetics of the fast step of the oxidation of the Co^{II}–EDTA complex by $[Cu^{III}(Enio)]^+$:

$$-d[Cu^{III}(Enio)^+]/dt = \frac{\{k_2^o + k_2^H K_1[H^+]\}[Co^{II}(EDTA)^{2-}]_T[Cu^{III}(Enio)^+]}{1 + K_1[H^+]} \quad (6)$$

The rate law for the fast step of the oxidation of Co^{II}–EDTA complex by $[Cu^{III}(Pre)]^+$ derived from the reaction sequence 2–5 is given by eqn. (7):

$$-d[Cu^{III}(Pre)^+]/dt = \frac{\{k_2^o + (k_2^H K_1 + k_3^H K_2)[H^+]\}[Co^{II}(EDTA)^{2-}]_T[Cu^{III}(Pre)^+]}{1 + K_1[H^+]} \quad (7)$$

The dependence of the second-order rate constant, k_2, on $[H^+]$ is given by eqn. (8),

$$k_2 = \frac{k_2^o + k'[H^+]}{1 + K_1[H^+]} \quad (8)$$

for both reactions; with $k' = k_2^H K_1$ and $k' = k_2^H K_1 + k_3^H K_2$ for the $[Cu^{III}(Enio)]^+$ and the $[Cu^{III}(Pre)]^+$ reactions respectively. Eqn. (8) could be rearranged to the linear form of eqn. (9) and hence a plot of $k_2(1 + K_1[H^+])$ vs. $[H^+]$ should be linear with an intercept k_2^o and a slope k':

$$k_2(1 + K_1[H^+]) = k_2^o + k'[H^+] \quad (9)$$

Plots of eqn. (9) for both $[Cu^{III}(Pre)]^+$ and $[Cu^{III}(Enio)]^+$ reactions at various temperatures are shown in Figs. 3 and 4 respectively. In these plots it is assumed that the magnitude of K_1 is unaffected by changes of temperature of the range used and the value of 10^3 M^{-1} was used in all calculations [10]. The values of k_2^o and k' obtained from the intercept and the slope respectively for both reactions at different temperatures are collected in Table IV. The enthalpies and entropies of activation $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ associated with the H^+-independent pathway for both reactions were calculated from the linear plots of $\ln(k_2^o/T)$ vs. $1/T$. $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ for the H^+-dependent pathway, for the two reactions, were obtained from the linear plots of $\ln(k'/T)$ vs. $1/T$. These activation parameters are collected in Table V. It is to be noted that these are composite values.

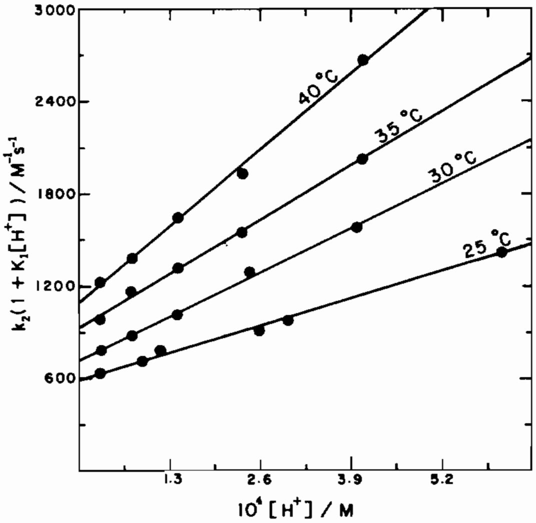


Fig. 3. Plots of $k_2(1 + K_1[H^+])$ vs. $[H^+]$ for the $[Cu^{III}(Pre)]^+/[Co^{II}(EDTA)]^{2-}$ reaction at different temperatures.

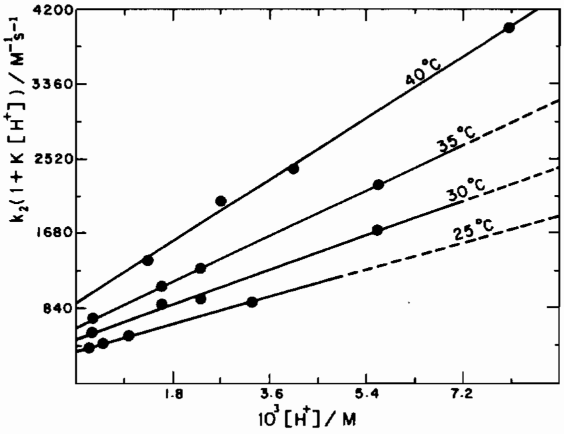


Fig. 4. Plots of $k_2(1 + K_1[H^+])$ vs. $[H^+]$ for the $[Cu^{III}(Enio)]^+/[Co^{II}(EDTA)]^{2-}$ reaction at different temperatures.

The formation of long-lived intermediates in the reactions of $[Cu^{III}(Pre)]^+$ and $[Cu^{III}(Enio)]^+$ with the Co^{II}–EDTA complex suggest that the reaction proceeds via an innersphere mechanism. The deprotonated oximato oxygens could act as bridging atoms. Coordination by oximato oxygens was reported even when these were hydrogen-bonded [11]. One oximato oxygen may replace a coordinated acetate arm in $[Co^{II}(EDTA)]^{2-}$ or the water molecule in $[Co^{II}(HEDTA)(H_2O)]^-$ prior to electron transfer. It may also be possible for both the oximato oxygens to coordinate to $[Co^{II}(EDTA)]^{2-}$ by displacing two acetate arms of EDTA or by substituting the water molecule and one acetate arm of EDTA in $[Co^{II}(HEDTA)(H_2O)]^-$. Structures (3) and (4) may represent the intermediates formed post electron transfer:

TABLE IV. Variation of the Observed Pseudo-First-Order Rate Constant for the Oxidation of $[Co^{II}(EDTA)]^{2-}$ by $[Cu^{III}(Enio)]^{+}$ with pH at Various Temperatures.[a]

T(°C)	pH	k_{obs} (s^{-1})	$10^2\ k_2$ ($M^{-1}\ s^{-1}$)
25.0	2.48	1.27 ± 0.01	2.12 ± 0.02
	3.00	1.62 ± 0.01	2.70 ± 0.02
	3.30	1.79 ± 0.04	2.98 ± 0.07
	3.60	1.89 ± 0.01	3.15 ± 0.02
30.0	2.25	1.30 ± 0.01	2.17 ± 0.02
	2.63	1.69 ± 0.04	2.82 ± 0.07
	2.79	2.04 ± 0.01	3.40 ± 0.02
	3.51	2.60 ± 0.08	4.33 ± 0.13
35.0	2.25	2.02 ± 0.05	3.37 ± 0.08
	2.63	2.27 ± 0.01	3.78 ± 0.02
	2.79	2.81 ± 0.04	4.68 ± 0.07
	3.51	3.38 ± 0.18	5.63 ± 0.30
40.0	2.08	2.30 ± 0.05	3.83 ± 0.08
	2.39	2.85 ± 0.02	4.75 ± 0.03
	2.57	3.32 ± 0.09	5.53 ± 0.15
	2.87	3.50 ± 0.05	5.83 ± 0.08

[a] $[Cu^{III}(Enio)^{+}] = 2.2 \times 10^{-4}$ M, $[Co^{II}(EDTA)^{2-}] = 6.0 \times 10^{-3}$ M, $\mu = 1.0$ M.

The results in Table VI show that for both reactions, at fixed reaction conditions, the magnitude of k_{obs} decreases with increasing ionic strength. Plots of log k_{obs} *vs.* $\sqrt{\mu}/(1 + \sqrt{\mu})$ for both reactions, were found to be linear with negative slopes. This is in agreement with the involvement of oppositely charged species in the rate determining step. The magnitudes of the slopes for the $[Cu^{III}(Enio)]^{+}$

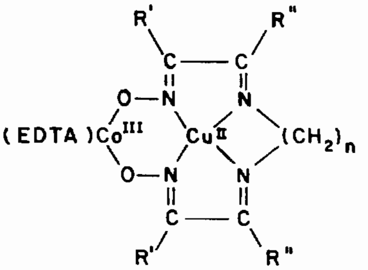
TABLE VI. Effect of Ionic Strength on the Rate of Oxidation of $[Co^{II}(EDTA)]^{2-}$ by $[Cu^{III}(Pre)]^{+}$ and $[Cu^{III}(Enio)]^{+}$.

$[Cu^{III}(Pre)]^{+a}$		$[Cu^{III}(Enio)]^{+b}$	
μ(M)	k_{obs} (s^{-1})	μ(M)	k_{obs} (s^{-1})
0.10	8.56 ± 0.09	0.17	3.30 ± 0.09
0.30	6.23 ± 0.05	0.47	2.64 ± 0.04
0.50	5.28 ± 0.04	0.67	2.35 ± 0.02
0.70	4.19 ± 0.04	0.97	2.04 ± 0.03
1.00	3.71 ± 0.04	1.37	1.75 ± 0.08

[a] $[Cu^{III}(Pre)^{+}] = 2.0 \times 10^{-4}$ M, $[Co^{II}(EDTA)^{2-}]_T = 6.0 \times 10^{-3}$ M, pH = 3.49 and $T = 25.0$ °C. [b] $[Cu^{III}(Enio)^{+}] = 2.2 \times 10^{-4}$ M $[Co^{II}(EDTA)^{2-}] = 6.0 \times 10^{-3}$ M, pH = 3.50 and $T = 25.0$ °C.

TABLE V. Values of k_2^0 and k' at Various Temperatures and the Activation Parameters for the Two Reactions.

T(°C)	$[Cu^{III}(Pre)]^{+}$		$[Cu^{III}(Enio)]^{+}$	
	$10^{-2}\ k_2^0$ ($M^{-1}\ s^{-1}$)	$10^{-6}\ k'$ ($M^{-2}\ s^{-1}$)	$10^{-2}\ k_2^0$ ($M^{-1}\ s^{-1}$)	$10^{-5}\ k'$ ($M^{-2}\ s^{-1}$)
25.0	5.92 ± 0.15	1.36 ± 0.05	3.61 ± 0.07	1.67 ± 0.04
30.0	7.15 ± 0.17	2.23 ± 0.08	4.98 ± 0.44	2.14 ± 0.14
35.0	9.31 ± 0.20	2.71 ± 0.09	6.27 ± 0.20	2.82 ± 0.07
40.0	10.97 ± 0.28	3.81 ± 0.13	8.99 ± 0.86	3.85 ± 0.18
$\Delta H_1^{\ddagger}$ (kJ mol^{-1})	30.2 ± 1.9		43.3 ± 2.8	
$\Delta S_1^{\ddagger}$ (J K^{-1} mol^{-1})	−90.6 ± 5.4		−50.7 ± 3.2	
$\Delta H_2^{\ddagger}$ (kJ mol^{-1})		48.1 ± 5.9		40.6 ± 1.9
$\Delta S_2^{\ddagger}$ (J K^{-1} mol^{-1})		+34.5 ± 2.9		−9.0 ± 0.3



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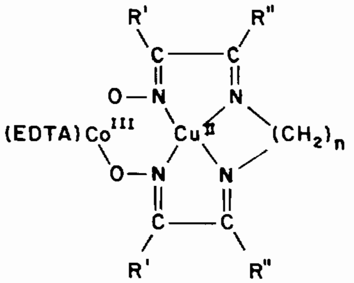

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R′ = CH_3(Pre) and $COCH_3$ for (Enio)
R″ = CH_3 for both (Pre) and (Enio)
n = 2 for (Enio) and n = 3 for (Pre)

and [Cu^{III}(Pre)]$^+$ reactions were found to be -1.10 ± 0.10 and -1.41 ± 0.10, respectively. These values seem to be consistent with the suggestion that [Co^{II}(EDTA)]$^{2-}$ and [Co^{II}(HEDTA)(H_2O)]$^-$ are the reactive cobalt(II) species.

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