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Kinetics of the Electron-transfer Reactions of Tetranuclear Isomeric Species of Cobalt(III)–Ammine Complexes with Hexaaquochromium(II) and Hexaaquovanadium(II) Ions

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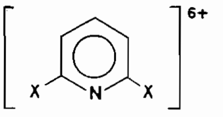
Abstract

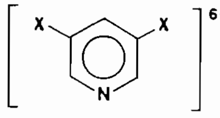
The electron-transfer reaction kinetics of the $Cr(OH_2)_6^{2+}$ and $V(OH_2)_6^{2+}$ complexes with tetranuclear isomeric species of cobalt(III)–ammine complexes containing pyridine 2,6-, 3,5-, 2,4- and 2,5-dicarboxylate bridging ligands (**I**–**IV**) have been studied in solution with various hydrogen ion concentrations. Inner-sphere mechanism with attack of Cr(II) at a deprotonated remote pyridine nitrogen atom and subsequent electron transfer through the organic ligands are assigned for complexes **II**, **III** and **IV**. Due to steric hindrance by carboxylate groups, an outer-sphere mechanism is observed for complex **I**. The electron-transfer rates for complexes **III** and **IV** are 20–50 times faster than that in complex **II**, and are discussed in terms of the lowering of the energy barrier caused by a significant π orbital interaction of oxidant and reductant through a heterocyclic bridge ligand. Outer-sphere mechanism for reduction of **I** is assigned on the basis of a k_{Cr}/k_V ratio of 0.026. Reduction of complex **II** by V(II) is independent of $[H^+]$ and proceeds by the outer sphere.

Introduction

The reduction mechanism of binuclear amminocobalt(III) complexes by $Cr(OH_2)_6^{2+}$ and $V(OH_2)_6^{2+}$ through organic structural moieties has been extensively investigated by Wieghardt, Sykes and coworkers [1–5]. An inner-sphere mechanism is found when both an 'electron mediator' structural bridge and a second functional group are attached to a cobalt(III) center. A 'two step' reduction mechanism is found to operate in such a system, because of the reduced π-electron density caused by the presence of an electronegative nitrogen atom in the ring [4]. Otherwise, an outer-sphere mechanism will be dominant in the absence of such an electron mediator bridge.



I



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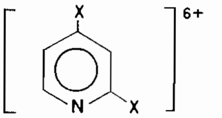

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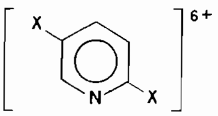
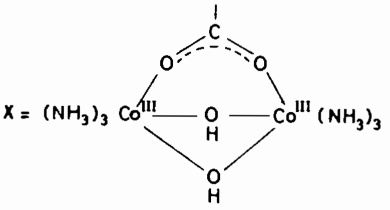


IV



The present paper deals with the electron-transfer reaction kinetics of tetranuclear isomeric species of general structure **I**–**IV** with $Cr(OH_2)_6^{2+}$ and $V(OH_2)_6^{2+}$ complexes. An attempt to elucidate the reaction mechanism will be made on the basis of the kinetics results determined in solution with various hydrogen ion concentrations.

Experimental

Chemicals

The preparation of cobalt(III) complexes was derived from synthetic methods described by Linhardt and Siebert [6]. The stability of all complexes in solution was checked spectrophotometrically; no spectral changes were detected for at least 24 h at 25 °C.

$[Co_2(NH_3)_6(OH)_3](ClO_4)_3 \cdot 2H_2O$ was prepared by a dropwise addition of 600 ml 1 M ammonium hydroxide into a well stirred cold solution of [Co-

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TABLE 1. Elemental analyses of complexes **I**–**IV**

Complex	Found (%)					Calculated (%)				
	C	H	N	Co	ClO_4	C	H	N	Co	ClO_4
I·$3H_2O$	6.34	3.70	13.6		45.8	6.4	3.75	13.4		46.0
II·$4H_2O$	5.83	3.60	12.62	16.34	48.28	5.83	3.80	12.67	16.80	47.00
III·$2H_2O$	5.98	3.44	12.95	16.76	49.51	6.0	3.55	12.91	16.68	49.47
IV	6.13	3.21	13.28	17.2		6.46	3.56	12.97	18.2	

$(NH_3)_3H_2OCl_2]Cl$ (100 g dissolved in 100 ml of water) over a 2 h period, resulting in a deep red solution. A precipitate obtained by adding perchlorate solution, was collected by filtration, washed with ethanol followed by anhydrous diethyl ether.

The complexes **I**–**IV** were prepared by the addition of 0.5 g of heterocyclic ligands (2,6-pyridine carboxylic acid, 3,5-pyridine carboxylic acid, 2,4-pyridine carboxylic acid and 2,5-pyridine carboxylic acid) in a 50 ml acidic solution made by 0.5 M $HClO_4$ of $[Co_2(NH_3)_6(OH)_3](ClO_4)_3 \cdot 2H_2O$. After the addition was completed, the mixture was kept at 60 °C with continuous stirring for 20 min. Then the reaction mixture was allowed to cool (5 °C) and $NaClO_4$ was added to precipitate the tetranuclear cobalt(III) complexes. The precipitate was collected by filtration, washed with ethanol and anhydrous diethyl ether, and air-dried for several minutes. Elemental analyses of all new complexes are given in Table 1.

Solutions of $V(OH_2)_6^{2+}$ and $Cr(OH_2)_6^{2+}$ were prepared under argon atmosphere by electrolytic reduction of vanadium(IV) and chromium(III) perchlorate, in perchloric acid media. The concentrations of $V(OH_2)_6^{2+}$ and $Cr(OH_2)_6^{2+}$ were determined spectrophotometrically at 850 nm ($\epsilon = 3.22\ M^{-1}\ cm^{-1}$) for vanadium(II) and 715 nm ($\epsilon = 4.82\ M^{-1}\ cm^{-1}$) for chromium(II).

Kinetic Measurements

The kinetic experiments were carried out by using a conventional UV–Vis spectrophotometer Shimadzu model UV-190, which is equipped with thermostated cell compartments. The temperature was kept at 25.0 ± 0.1 °C. All solutions for kinetics measurements were prepared using syringe-septa methods under an atmosphere of vanadium-scrubbed argon.

All reactions conform to linear plots to at least four half-lives, and the pseudo-first-order rate constants were obtained from the slopes of the linear fits of $\log(A_\infty - A_t)$ *versus* time plots using a least-squares program.

Results

Determination of Dissociation Constants

The basic pyridine nitrogen of complexes **I**–**IV** can be protonated in acidic media. The apparent pK_a values for these compounds were spectrophotometrically determined at constant ionic strength ($I = 0.25$ M $LiClO_4$) [7, 8]. The absorbance at 277 (**I** and **IV**), 288 (**II**) and 286 (**III**) nm, as a function of pH was used to calculate the dissociation constants shown in Table 2.

TABLE 2. Acid dissociation constants of complexes **I**–**IV** at ionic strength 0.25 M ($LiClO_4$) and 25 °C

Complex	pK_a
I	<0
II	1.60 ± 0.01
III	1.57 ± 0.01
IV	1.48 ± 0.01

Reduction of μ-Pyridine-2,6-dicarboxylate Co(III) (I) by Cr(II)

The stoichiometry of reduction of complex **I** through Cr(II) was checked by measuring the tetranuclear cobalt(III) complex consumed at its visible absorbance peak ($\lambda_{max} = 524$ nm, $\epsilon = 215$ l mol^{-1} cm^{-1}) under the conditions of a ten-fold excess of reductant over the tetranuclear cobalt(III) oxidant. The stoichiometry was found to be 4:1, eqn. (1)

$$4Cr^{2+} + Co_4^{3+} \longrightarrow 4Cr^{3+} + 4Co^{2+} \qquad (1)$$

The observed first-order rate constants are independent of the hydrogen concentration in the range 0.05–0.3 M. Thus the following rate law is obtained (eqn. (2))

$$-d[Co(III)]/dt = k_{Cr}[Co(III)][Cr^{2+}] \qquad (2)$$

with yielded rate constants at 25 °C displayed in Table 3.

Reduction of μ-Pyridine-3,5-dicarboxylate Co(III) (II) by Cr(II)

Four moles of Cr(II) are consumed per mole of complex **II**. The observed second-order rate constants k_{Cr} are dependent on hydrogen ion concentration in the range 0.3–0.03 M (Table 4). This may be expressed by eqn. (3)

$$k_{Cr} = k_a[H^+] + k_bK_a/(K_a + [H^+]) \qquad (3)$$

TABLE 3. Pseudo-first-order rate constants, k_{obs} (s^{-1}) for reduction of complex I by Cr^{2+} at 25 °C[a]

$[H^+]$ (M)	$10^2 \times [Cr^{2+}]$ (M)	$10^4 \times k_{obs}$ (s^{-1})	k_{Cr} ($M^{-1} s^{-1}$)
0.3	0.176	8.6	
0.3	0.097	4.9	
0.3	0.050	2.8	
0.3	0.019	1.2	
0.15	0.019	1.2	
0.10	0.019	1.3	
0.05	0.019	1.4	
0.007	0.019	1.4	5×10^{-3}

[a]Ionic strength $I = 1.0$ M ($LiClO_4$), [Co(III)] = 5×10^{-4} M.

TABLE 4. Second-order rate constants, k_{Cr} (M^{-1} s^{-1}) for reduction of complexes II–IV by Cr^{2+} at 25 °C[a]

Complex	$[H^+]$ (M)	$10^2 \times [Cr^{2+}]$ (M)	$10^2 \times k_{Cr}$ ($M^{-1} s^{-1}$)
II	0.3	9.7	0.722
	0.3	4.9	0.747
	0.3	1.8	0.840
	0.1	1.8	1.07
	0.05	1.8	1.37
	0.03	1.9	1.80
III	0.3	9.71	24.9
	0.3	4.87	23.6
	0.3	1.88	23.8
	0.1	1.88	67.0
	0.05	1.91	128.0
IV	0.3	1.96	12
	0.3	9.85	11
	0.3	4.90	11
	0.10	1.92	23
	0.20	1.83	15
	0.07	1.88	27
	0.05	1.93	35

[a]Ionic strength $I = 1.0$ M ($LiClO_4$), [Co(III)] = 5×10^{-4} M.

where k_a = rate constant in the protonated form for **II**, k_b = rate constant in the deprotonated form of **II** and K_a = dissociation constant of the protonation equilibrium. A plot of k_{Cr} (K_a + $[H^+]$) against $[H^+]$ should give straight lines with intercepts $K_a k_b$ and slope k_a. As illustrated in Fig. 1, the linear behavior is best achieved for $K_a = 0.025$ mol dm^{-3}. A mechanism consistent with the above rate law (eqn. (3)) is given by eqns. (4)–(6), where steps (5) and (6) are rate determining

$$Co_4(III)LH^{7+} \overset{K_a}{\rightleftharpoons} Co_4(III)L^{6+} + H^+ \qquad (4)$$

$$Co_4(III)LH^{7+} + Cr^{2+} \xrightarrow{k_a} Products \qquad (5)$$

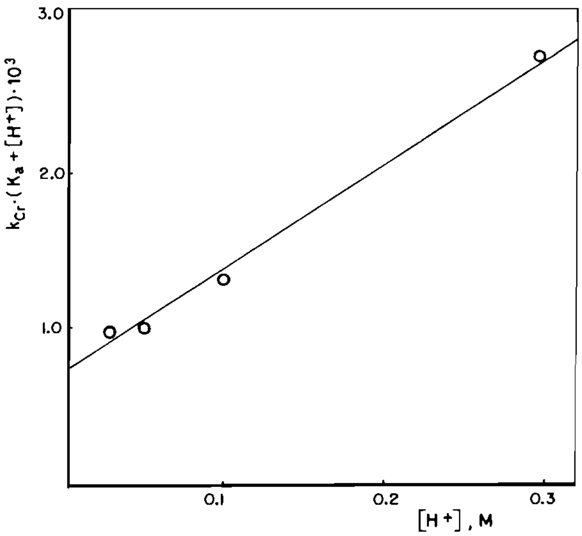

Fig. 1. Dependence of $k_{Cr}(K_a + [H^+])$ on $[H^+]$ for the reduction of complex **II** by chromium(II) with $K_a = 3.5 \times 10^{-2}$ at 25 °C.

$$Co_4(III)L^{6+} + Cr^{2+} \xrightarrow{k_b} Products \qquad (6)$$

Reduction of μ-Pyridine-2,4-dicarboxylate Co(III) (III) and μ-pyridine-2,5-dicarboxylate Co(III) (IV) by Cr(II)

The stoichiometry for the reduction of complexes **III** and **IV** by Cr(II) was derived from detailed analyses of absorbance changes during the observed single-stage processes and was found to be 4:1. A dramatic hydrogen ion concentration dependence was found as expected. The reaction rate fit the experimental rate law expressed by eqn. (3) which reduces to eqn. (7) for $K_a \ll [H^+]$.

$$k_{Cr} = k_a + k_b K_a / [H^+] \qquad (7)$$

The kinetic data are summarized in Table 4 and the linear dependence of electron-transfer rate constant *versus* the reciprocal of hydrogen ion concentration is shown in Fig. 2.

Reduction of Complexes I and II by V(II)

The stoichiometry of reduction of complexes **I** and **II** by V(II) was found to be 4:1 and the experimental rate law is found to be (eqn. (8))

$$-d[Co(III)]/dt = k_V [Co(III)] [V(II)] \qquad (8)$$

The observed first-order rate constants are completely independent of hydrogen ion concentration in the range 0.3–0.03 M for complex **I** and 0.7–0.07 M for complex **II**. The kinetic data are summarized in Table 5.

With respect to the reduction kinetics of cobalt complexes by vanadium(II) the systematic study was

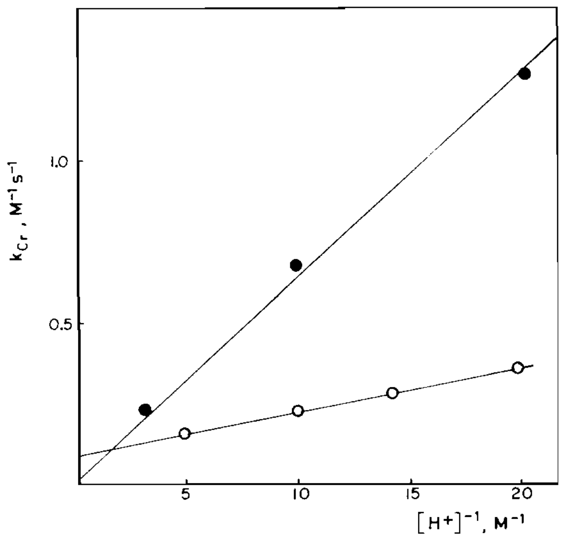

Fig. 2. Dependence of the reaction rate on $[H^+]$ for the reduction of complex III (●) and complex IV (○) by chromium(II) at 25 °C.

TABLE 5. Second-order rate constants, k_V (M^{-1} s^{-1}) for reduction of complexes I and II by vanadium(II) at 25 °C[a]

Complex	$[H^+]$ (M)	$10^2 \times [V^{2+}]$ (M)	k_V (M^{-1} s^{-1})
I	0.3	7.76	0.197
	0.3	4.10	0.197
	0.3	2.10	0.190
	0.3	0.96	0.18
	0.03	0.96	0.18
II	0.3	7.00	0.17
	0.3	4.30	0.17
	0.3	2.84	0.17
	0.3	2.00	0.16
	0.3	0.80	0.16
	0.7	1.80	0.16
	0.1	1.80	0.16
	0.07	1.80	0.18

[a] Ionic strength $I = 1.0$ M ($LiClO_4$), $[Co(III)] = 2.5 \times 10^{-4}$ M.

restricted to complexes I and II due to a possible occurrence of auto-catalysis involving complexes III and IV and their formed reaction products.

Discussion

Both the experimental rate law and the lack of proton dependence on the electron-transfer rates between Cr(II) or V(II) and the tetranuclear complexes of μ-pyridine-2,6-dicarboxylate (I) are fully in agreement with an outer-sphere mechanism. At this point it is useful to compare the experimental rate constant ratios of Cr(II) and V(II) with the values found in other studies. Spiecker and Wieghardt [3] have studied the reduction of binuclear complexes containing μ-carboxylate-3-pyridine-di-μ-hydroxo-bis triammine Co(III) and have found a forty-fold increase in the rate constant for vanadium(II) reduction in comparison to Cr(II) reduction. So, the experimental ratio $k_{Cr(II)}/k_{V(II)} = 0.026$ is certainly compatible with an outer-sphere mechanism [9].

In fact, an attack on the heterocyclic nitrogen by reductants (Cr(II) or V(II)) is excluded due to the presence of bulky carboxylate groups on 2,6 positions of the pyridine ring.

Cr(II) reduces the μ-pyridine-3,5-dicarboxylate (II) complexes by an inner-sphere mechanism in its deprotonated form and by an outer-sphere mechanism in its protonated form. From eqn. (3), one can calculate the rate constants for the protonated ($k_a = 6.9 \times 10^{-3}$ M^{-1} s^{-1}) and the deprotonated ($k_b = 1.34 \times 10^{-2}$ M^{-1} s^{-1}) form. It has been suggested [10] that a remote attack on nitrogen and a further intramolecular electron transfer for complex II is the predominant mechanism in its nonprotonated form. The V(II) ion shows the complete opposite behavior in the electron-transfer reaction. The reduction of II is completely hydrogen ion independent in the 0.3–0.03 M range, suggesting an outer-sphere electron-transfer mechanism. The ratio $k_{Cr(II)}/k_{V(II)} = 0.040$ may be regarded as complementary evidence for the mechanism proposed for the reduction of II in its protonated form by V(II) and Cr(II) ions.

The values of protonated k_a and deprotonated k_b forms of complexes III and IV are displayed in Table 6 and were estimated from eqn. (7). These data suggest that complex IV reacts by an outer-sphere mechanism in its protonated form and an inner-sphere mechanism in its deprotonated form. However, the inner-sphere mechanism is predominant in this case. The Cr(II) ion reacts with complexes III by an inner-sphere mechanism (see Table 6). Our data suggests three pieces of evidence in support of this conclusion: (i) the experimental rate law (eqn. (7) lies within the range of characteristic substitution rate constants for the substitution of various ligands into the co-ordination sphere of cobalt(III); (b) the strong hydrogen ion dependence is suggestive of a reduction of the first cobalt(III) center by a remote attack of the Cr(II) ion on the unprotonated pyridine nitrogen; (c) the rates of reduction of complexes III and IV are quite similar*. A pentanuclear Co(II)–

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*An inner-sphere mechanism by a remote attack at the heterocyclic pyridine nitrogen atoms was proposed by Spiecker and Wieghardt [3] for the reduction of μ-carboxylate-2-pyridine-di-μ-hydroxo-bis-triammine Co(III) and μ-carboxylate-4-pyridine-di-μ-hydroxo-bis-triammine Co(III).

TABLE 6. Summary of kinetic parameters of the reduction of complexes **II**, **III** and **IV** by chromium(II) at 25 °C and $I = 1.0$ M ($LiClO_4$)

Complex	k_a ($M^{-1} s^{-1}$)[a]	Mechanism[c]	k_b ($M^{-1} s^{-1}$)[b]	Mechanism[c]	k_b/k_a
II	6.9×10^{-3}	o.s.	1.34×10^{-2}	i.s.	1.9
III	3.9×10^{-2}		1.44	i.s.	37.0
IV	7.7×10^{-2}	o.s.	0.393	i.s.	5.0

[a] The reactants are in protonated forms. [b] The reactants are in deprotonated forms. [c] o.s. = outer sphere; i.s. = inner sphere.

Cr(III) intermediate may be envisaged to form $Cr(OH_2)_6^{3+}$ due to the labile nature of the Cr–N bond. The reduction of the first Co(III) center represents the determining step of these redox reactions, in agreement with data published on the literature for binuclear cobalt(III) systems [3]. The electronic configuration change accompanying the electron-transfer processes are $t_{2g}^6 \rightarrow t_{2g}^6 e_g^1$ for Co(III)/Co(II) and $t_{2g}^3 \rightarrow t_{2g}^2$ for V(II)/V(III) and $t_{2g}^3 e_g^1 \rightarrow t_{2g}^3$ for Cr(II)/Cr(III). Part of the energetics of these processes may be considerably satisfied exothermally by the favorable free energy of the system. It is interesting to point out that the Co(III)/Co(II) redox potential for the complex series containing ammonia as a non-bridging ligand and having the μ-pyridine-dicarboxylate structural moiety is constant [11]. However, the electron-transfer rates for complexes **III** and **IV** are 20–50 times faster relative to complexes **I** and **II**. The experimental results suggest that the energy barrier for the reactions of complexes **III** and **IV** is likely to be considerably lower than those of complexes **I** and **II**, due to a significant π orbital interaction between oxidants and reductants through a heterocyclic bridging ligand. This may be considered as additional evidence for an inner-sphere mechanism for reduction of these cobalt complexes.

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