it increases through $[Co(cdta)]^-$ (5.8 ppm) to $[Co(l\text{-sdta})]^-$ (6.9 ppm). In terms of the size of the backbone substituents, it is easy to rationalize that $[Co(l\text{-sdta})]^-$ would have the largest chemical shift separation between R-ring and G-ring methylene carbons. Table III lists the ^{13}C NMR chemical shifts and their assignments for $[Co(xdta)]^-$ and $[Co(l\text{-sdta})]^-$ together with those for model complexes $[Co(edta)]^-$ and $[Co(cdta)]^-$.

Registry No. Ag[Co(xdta)], 69596-90-3; K[Co(*l*-sdta)], 69596-91-4; *l*-stilbenediamine *d*-tartrate, 29841-69-8; *l*-stilbenediamine *d*-tartrate, 69576-66-5; *d,l*-stilbenediamine, 16635-95-3; *d,l*-stilbenediamine dihydrobromide, 69576-64-3; *d,l*-*N*-acetyl-*N'*-benzoylstilbenediamine, 69576-65-4; *d,l*-isoamarine, 33722-46-2; dimethyl aminodiacetate, 6096-81-7; iminodiacetonitrile, 628-87-5.

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Stoichiometric, Kinetic, and Mechanistic Investigations of the Reactions of O-Bonded (Ethylenediamine-*N,N,N',N'*-tetraacetato)pentaamminecobalt(III) Complex and Its Related Complexes with Hexaaquachromium(II) Ions

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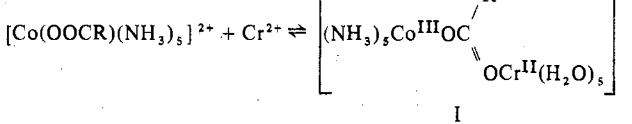
The products of the reactions of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$, $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$, $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$, and $[Co(edta)]^-$ with $[Cr(H_2O)_6]^{2+}$ in acid solutions were separated with the aid of SP-Sephadex column chromatography and identified from the chromatographic behavior, visible absorption spectra, and chemical analyses of chromium and/or cobalt ions. Three chromium(III) complexes were newly characterized as the reaction products: $[(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+}$, $[(NH_3)_5Co(H_nedta)Cr(H_2O)_5]^{(n+2)+}$, and $[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$. From the determination of the quantitative product distribution, stoichiometry of the reactions was established. Then, kinetic measurements were made for these reactions. On the basis of these results, the mechanisms of the reactions are discussed.

Introduction

Many studies on the electron-transfer reactions of cobalt(III) complexes with hexaaquachromium(II) ions (Cr^{2+}) have been carried out. Through the characterization of the chromium(III) complexes produced in these reactions, attempts to infer the structures of the precursor and/or activated complexes have also been made. These studies provide not only the information on the mechanisms of the electron-transfer reactions but also, sometimes, an elegant way for the preparation of novel chromium(III) complexes.

In the chromium(II) reductions of (carboxylato)pentaamminecobalt(III) complexes ($[Co(OOCR)(NH_3)_5]^{2+}$), Cr^{2+} is believed to attack the carbonyl oxygen to form a precursor complex I.[1]



$$[Co(OOCR)(NH_3)_5]^{2+} + Cr^{2+} \rightleftharpoons \left[(NH_3)_5Co^{III}OC{\overset{\displaystyle R}{\diagup}}{\underset{\displaystyle OCr^{II}(H_2O)_5}{\diagdown}} \right]^{4+}$$

I

$$\rightarrow Co^{2+} + [Cr(OOCR)(H_2O)_5]^{2+} + 5NH_4^+ \quad (1)$$

The rate constants of reaction 1 lie in the range of 10^{-3}–10 $M^{-1}\ s^{-1}$.[2] However, if the $RCOO^-$ ligand contains such an appropriate functional group that the ligand can serve to chelate Cr^{2+}, it is known that the electron-transfer reaction is accelerated.[3]

It was found, in this work, that the reactions of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$, $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$, $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$, and $[Co(edta)]^-$ with Cr^{2+} ions in acid solutions gave various chromium(III) products.[4]

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Attempts to elucidate the mechanisms of the reactions are made through the characterizations of the products, the determination of the stoichiometry, and the kinetic measurements.

Experimental Section

A. Materials. The complexes $[Co(H_2edta)(NH_3)_5]ClO_4 \cdot 6H_2O$,[5] $[(NH_3)_5Co\{edtaCr(H_2O)\}](ClO_4)_2$,[5] $[(NH_3)_5Co\{edtaCo(H_2O)\}](ClO_4)_2$,[5] and $Na[Co(edta)] \cdot 4H_2O$[6] were prepared as reported in the literature. All solutions were prepared with redistilled water. A stock solution of hexaaquachromium(III) perchlorate was prepared by the reduction of chromium trioxide in perchloric acid with hydrogen peroxide. Chromium(II) perchlorate solutions were prepared by the electrolytic reduction of the hexaaquachromium(III) perchlorate under an atmosphere of nitrogen and found always to contain several percentages of hexaaquachromium(III) ions. The concentrations of the hydrogen ions in chromium(III) and chromium(II) solutions were determined by the method reported in the literature.[7,8] Lithium perchlorate trihydrate was prepared by the neutralization of lithium bicarbonate with perchloric acid and was recrystallized twice from redistilled water.

B. Product Analyses. The reaction vessel was a quartz spectrophotometer cell of 1-cm optical path length which was sealed with a serum cap. The reaction was initiated by mixing the solutions of a complex and Cr^{2+} under nitrogen atmosphere and was monitored with a Union-Giken SM-401 spectrophotometer until the spectral changes were not observed. Then, air was introduced into the system to oxidize excess Cr^{2+}, if present. The products of all the reactions were separated by the use of an SP-Sephadex C-25 column (1.8 × 10 cm). The solution containing the products was poured into the column. Cationic species were adsorbed on the column in several bands. The species with different charges could be separated very easily by the elution with appropriate eluents. Usually, 2+ charged species were eluted with a 0.1 M $NaClO_4$ solution or a 0.1 M $HClO_4$–0.1 M $NaClO_4$ solution, while 3+ and 4+ charged species were eluted with a 0.1 M $HClO_4$–0.4 M $NaClO_4$ solution and a 0.1 M $HClO_4$–0.9 M $NaClO_4$ solution, respectively. When 2+ charged chromium(III) product was formed together with Co^{2+}, Co^{2+} ions were separated from the other products by the following procedure. The adsorbed species were eluted with a 0.1 M $NaClO_4$ solution until the band containing 2+ charged species was separated completely from the species with higher charges than 2+. Then, the resin containing the latter species was removed from the column and the column was rinsed with a 0.01 M EDTA–0.025 M sodium acetate–acetic acid solution of pH 4.7. By this treatment, only Co^{2+} ions could be eluted out very easily in the form of $[Co(edta)]^{2-}$. After the column was washed with water, the species that remained in the column was eluted with an appropriate eluent.

The chromium content was determined spectrophotometrically in the form of CrO_4^{2-} after oxidation with an alkaline hydrogen peroxide solution. The cobalt(II) content was determined by Kitson's method.[9] The cobalt(III) complexes were reduced to cobalt(II) with zinc amalgam and then subjected to the determination of the cobalt(II) by the Kitson's method.

C. Kinetic Measurements. Kinetic studies were made for the reactions of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$, $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$, and $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$ with Cr^{2+}. As the rates of the former two systems were found to be very large, the stopped-flow technique was employed by the use of a Hitachi RSP-2 rapid scanning spectrophotometer and Union-Giken RA-401 stopped-flow spectrophotometer. Wavelengths used for the measurements were 547 nm for the reaction of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ and 538 and 486 nm for that of $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$. The measurements for the reaction of $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$ were carried out by a conventional syringe method. The change of the absorbance with time was followed at 510 nm with the Union-Giken SM-401 spectrophotometer.

The temperature was controlled at 25.0 ± 0.1 °C and the ionic strength (I) was adjusted to 1.0 or 0.2 M with lithium perchlorate.

Results

A. Stoichiometry of the Reactions and Characterization of New Chromium(III) Products. Reaction of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ with Cr^{2+}. The products of the title reaction were examined under the condition where the concentrations of Cr^{2+} exceeded those of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$. The reaction was completed within the time of mixing. When the solution containing the reaction products was poured on the Sephadex column, a reddish violet species which was identified as $[Cr(edta)(H_2O)]^-$ passed through the column.[10] Cationic species were adsorbed on the column in two bands: the lower pink and the upper green. The pink and green species were Co^{2+} and $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$ ($Cr(OH)_2Cr^{4+}$), respectively. The results of the product analyses are summarized in Table I.

Table I. Products of the Reaction of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ with Cr^{2+} at 25.0 °C and I = 1.0 M ($LiClO_4$)

initial concn of reactants			concn of products		
$[Cr^{2+}]_0$, 10^{-3} M	$[Co(III)]_0$, 10^{-3} M	$[H^+]$, M	$[[Cr(edta)(H_2O)]^-]$, 10^{-3} M	$[Co^{2+}]$, 10^{-3} M	$[Cr(OH)_2Cr^{4+}]$, 10^{-3} M
8.7	3.25	*a*	3.50	3.11	2.4
10.9	0.74	*a*	0.70	0.74	5.1
20.3	1.97	0.401	2.02	1.95	9.2
24.0	5.58	0.134	5.41	5.70	9.3
30.5	3.01	0.908	2.60	2.98	13.9
52.8	1.97	0.401	1.79	1.88	24.6
63.8	1.97	0.401	1.87	1.95	31.0

[a] pH 2.32 (glycine buffer).

The data given in Table I indicate that the equimolar amounts of Co^{2+} and $[Cr(edta)(H_2O)]^-$ are produced by the reaction and each concentration is almost equal to the initial concentration of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$. Therefore, the stoichiometry of the reaction can be expressed as

$$[Co(H_nedta)(NH_3)_5]^{(n-1)+} + Cr^{2+} + (5-n)H^+ \rightarrow [Cr(edta)(H_2O)]^- + Co^{2+} + 5NH_4^+ \quad (2)$$

The data given in Table I also indicate that the following relation holds:

$$[Cr(OH)_2Cr^{4+}] = \tfrac{1}{2}([Cr^{2+}]_0 - [Co(III)]_0) \quad (3)$$

where brackets represent the concentration and the subscript 0 means the initial state. This result suggests that the $Cr(OH)_2Cr^{4+}$ ions were formed by the air oxidation of Cr^{2+} ions[12,13] which had remained after the completion of the title reaction.

Reaction of $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$ with Cr^{2+}. The reaction was found to proceed at a measurable rate. The products were examined under the condition where the concentrations of Cr^{2+} exceeded those of $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$. A reddish violet species which had no affinity to the resin was found to be $[Cr(edta)(H_2O)]^-$. Cationic species were adsorbed on the column in four bands: reddish violet, pink, bluish violet, and green from the bottom to the top of the column. The pink, bluish violet, and green species were identified as Co^{2+}, $[Cr^{III}(H_2O)_6]^{3+}$ (Cr^{3+}), and $Cr(OH)_2Cr^{4+}$, respectively.

The reddish violet species was found to have a 2+ charge from the elution behavior[14] and moved slightly faster than Co^{2+} ions. The separation of these two species was achieved by washing the column with a 0.01 M EDTA–0.025 M sodium acetate–acetic acid solution. After Co^{2+} ions were removed from the column, the reddish violet species was eluted with a 0.1 M $HClO_4$–0.2 M $NaClO_4$ solution. This species did not contain cobalt ions but contained chromium ions. The electronic spectrum of this species (Table II) was quite similar to the sum of the spectra of $[Cr(edta)(H_2O)]^-$ and $[Cr(OOCCH_3)(H_2O)_5]^{2+}$.[15] From these results, the reddish violet species was assigned to $[(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+}$. This formulation was supported also by the kinetic results described below.

Table II. Electronic Absorption Spectra of the Complexes Newly Characterized in This Work and of Their Related Complexes

complex	medium	abs max, nm (molar abs coeff, M^{-1} cm^{-1})	ref
$[(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+}$ (reddish violet)	0.1 M$HClO_4$–0.1 M $NaClO_4$	554 (164), 388 (129)	this work
$[(NH_3)_5Co(H_2edta)Cr(H_2O)_5]^{4+}$ (reddish brown)	0.1 M $HClO_4$–0.9 M $NaClO_4$	508 (71), 342 (83)	this work
violet Cr(III) species[a]	1 M $NaClO_4$	547 (134), 387 (98)	this work
$[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$ (bluish violet)	0.1 M $HClO_4$	578 (22), 412 (23)	this work
$[Cr(H_2edta)(H_2O)_4]^+$ (high-acid product)		572 (27.5), 409 (25.0)	18
$[Cr(H_nedta)(H_2O)_3]^{(n-1)+}$ (n = 1 or 0, low-acid product)		568 (35.4), 407 (29.7)	18
$[Cr(OOCCH_3)(H_2O)_5]^{2+}$	0.02 M $HClO_4$	570 (24.4), 410 (22.2)	15
$[Co(OOCCH_3)(NH_3)_5]^{2+}$	H_2O	503 (77.9), 353 (68.4)	5
$[Cr(edta)(H_2O)]^-$	H_2O	545 (199), 392 (112)	5

[a] One of the products of the reaction between $[Co(edta)]^-$ and Cr^{2+}. See the text for the details of this species.

The results of the product analyses are summarized in Table III. The data shown in Table III reveal that a small amount of $[Cr(edta)(H_2O)]^-$ is produced by the reaction. Furthermore, the following relation holds:

$$[[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}]_0 = [[(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+}] + [[Cr(edta)(H_2O)]^-] = [Co^{2+}] \tag{4}$$

From these results, it was concluded that the stoichiometry of the reaction can be expressed as eq 5. The formation of

$$[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+} + Cr^{2+} + 5H^+ \rightarrow [(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+} + Co^{2+} + 5NH_4^+ \tag{5}$$

the small amount of the $[Cr(edta)(H_2O)]^-$ may be interpreted by the occurrence of the Cr^{2+}-catalyzed aquation of $[(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+}$ (eq 6). The $Cr(OH)_2Cr^{4+}$ ion

$$[(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+} + Cr^{2+} \rightarrow Cr^{2+} + [Cr(edta)(H_2O)]^- + Cr^{3+} \tag{6}$$

was again considered to be derived from excess Cr^{2+} ions, because the data shown in Table III satisfy eq 3.

Reaction of $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$ with Cr^{2+}. The reaction was completed practically within the time of mixing. The product survey revealed that only cationic species were formed, and no formation of $[Cr(edta)(H_2O)]^-$ was observed.

When the reaction condition was $[[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}]_0 > [Cr^{2+}]_0$, the column showed three bands: reddish violet, pink, and reddish brown from the bottom to the top of the column. The reddish violet and pink species were identified as the starting material, $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$, and Co^{2+}, respectively. The separation of these two species was made very easily by the use of EDTA–acetate buffer solution. The reddish brown species showed such a flow rate on a Sephadex column that the ion must be the 4+ charged species[14] and consisted of equimolar amounts of cobalt(III) and chromium(III). The electronic spectrum of this species whose numerical data are given in Table II is quite similar to the sum of the spectra of $[Co(OOCCH_3)(NH_3)_5]^{2+}$ and $[Cr(OOCCH_3)(H_2O)_5]^{2+}$. From these results, this species was formulated as $[(NH_3)_5Co(H_2edta)Cr(H_2O)_5]^{4+}$, where the EDTA is coordinated to the $[Co(NH_3)_5]^{3+}$ and $[Cr(H_2O)_5]^{3+}$ moieties through two acetate arms. The result of the product analyses obtained under the condition $[[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}]_0 > [Cr^{2+}]_0$ is given in the first row of Table IV. The data revealed that the concentration of the $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$ which reacted with Cr^{2+} was equal to $[[(NH_3)_5Co(H_2edta)Cr(H_2O)_5]^{4+}]$. This indicates that the stoichiometry of the reaction is expressed as eq 7.

$$[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+} + Cr^{2+} + 2H^+ \rightarrow [(NH_3)_5Co(H_2edta)Cr(H_2O)_5]^{4+} + Co^{2+} \tag{7}$$

When the reaction condition was $[[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}]_0 \ll [Cr^{2+}]_0$, the column showed three bands: reddish violet, pink, and green from the bottom to the top of the column. These species were identified as $[(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+}$, Co^{2+}, and $Cr(OH)_2Cr^{4+}$, respectively. The results of the product analyses are given in the second and third

Table III. Products of the Reaction of $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$ with Cr^{2+} at 25.0 °C and I = 0.20 M ($LiClO_4$)

initial concn of reactants				concn of products			
$[Cr^{2+}]_0$, 10^{-3} M	$[[Co\{YCr\}]^{2+}]_0$,[a] 10^{-3} M	$[H^+]$, M	reacn time,[b] h	$[[CrY]^-]$,[c] 10^{-3} M	$[[Cr\{YCr\}]^{2+}]$,[d] 10^{-3} M	$[Co^{2+}]$, 10^{-3} M	$[Cr(OH)_2Cr^{4+}]$, 10^{-3} M
6.9	1.17	0.017	4	0.15	0.98	1.17	2.9
51.1	2.56	0.064	1	0.44	2.22	2.63	24.2
31.7	1.30	0.101	1	0.19	0.98	1.28	14.7
31.1	1.38	0.101	1	0.14	1.03	1.28	14.4

[a] $[[Co\{YCr\}]^{2+}]_0 = [[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}]_0$. [b] The reaction was completed within the time indicated. [c] $[[CrY]^-] = [[Cr(edta)(H_2O)]^-]$. [d] $[[Cr\{YCr\}]^{2+}] = [[(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+}]$.

Table IV. Products of the Reaction of $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$ with Cr^{2+} at 25.0 °C and I = 0.20 M ($LiClO_4$)

initial concn of reactants			concn of products					
$[Cr^{2+}]_0$, 10^{-3} M	$[[Co\{YCo\}]^{2+}]_0$,[a] 10^{-3} M	$[H^+]$, M	$[[Cr\{YCr\}]^{2+}]$,[b] 10^{-3} M	$[Co^{2+}]$, 10^{-3} M	$[[Co\{YCo\}]^{2+}]$,[c] 10^{-3} M	$[[Co(Y)Cr]^{4+}]$,[d] 10^{-3} M		$[Cr(OH)_2Cr^{4+}]$, 10^{-3} M
						[Co]	[Cr]	
2.58	3.11	0.125	0	2.58	0.53	2.24	2.58	0
22.7	1.26	0.119	1.01	2.29	0	0	0	10.3
18.4	1.50	0.134	1.61	2.79	0	0	0	7.57

[a] $[[Co\{YCo\}]^{2+}]_0 = [[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}]_0$. [b] $[[Cr\{YCr\}]^{2+}] = [[(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+}]$. [c] $[[Co\{YCo\}]^{2+}] = [[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}]$. [d] $[[Co(Y)Cr^{4+}] = [[(NH_3)_5Co(H_2edta)Cr(H_2O)_5]^{4+}]$.

Table V. Products of the Reaction of $[Co(edta)]^-$ with Cr^{2+} at 25.0 °C and $I = 1.0$ M ($LiClO_4$)

initial concn of reactants				concn of products					
$[Cr^{2+}]_0$, 10^{-3} M	$[[CoY^-]_0]$,[a] 10^{-3} M	$[H^+]$, M	reaction time, min	$[[CoY^-]]$,[b] 10^{-3} M	$[[CrY^-]]$,[c] 10^{-3} M	[violet],[d] 10^{-3} M	$[Co^{2+}]$, 10^{-3} M	$[[Cr(H_nY)^{(n-1)+}]]$,[e] 10^{-3} M	$[Cr(OH)_2Cr^{4+}]$, 10^{-3} M
7.09[f]	10.28	0.010	1[g]	3.12	0	0.94	7.09	5.86	0
6.66[f]	10.05	0.100	1[g]	3.38	0	0.26	6.66	6.11	0
6.70[f]	9.95	0.100	1[g]	3.25	0	0.27	6.70	6.14	0
7.00[f]	9.80	0.200	1[g]	2.80	0	0	7.00	6.86	0
7.00[f]	8.50	0.300	1[g]	1.30	0	0	7.00	6.83	0
6.73[f]	9.50	0.500	1[g]	2.74	0	0	6.73	6.71	0
23.9	2.81	0.134	20	0	2.60	0	2.72	0	10.6
24.4	3.76	0.134	~0.1[h]	0	1.59	0	3.97	1.84	10.5

[a] $[[CoY^-]]_0 = [[Co(edta)]^-]_0$. [b] $[[CoY^-]] = [[Co(edta)]^-]$. [c] $[[CrY^-]] = [[Cr(edta)(H_2O)]^-]$. [d] [violet] = [violet Cr(III) species]. See the text for the details of this species. [e] $[[Cr(H_nY)]^{(n-1)+}] = [[Cr(H_nedta)(H_2O)_5]^{(n-1)+}]$. [f] The initial concentration of Cr^{2+} is assumed to be equal to the concentration of Co^{2+} produced by the reaction. [g] The reaction was completed practically within the time indicated. [h] The reaction was quenched by the introduction of air into the system.

rows of Table IV. Under this experimental condition, the relation of eq 8 holds. These results indicate that, after

$$[[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}]_0 = [[(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+}] \quad (8)$$

reaction 7 is completed, reaction 9 takes place. The formation

$$[(NH_3)_5Co(H_2edta)Cr(H_2O)_5]^{4+} + Cr^{2+} + 3H^+ \rightarrow [(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+} + Co^{2+} + 5NH_4^+ \quad (9)$$

of $Cr(OH)_2Cr^{4+}$ may be understood as the oxidation of excess Cr^{2+} by air, because the data given in Table IV indicate that the relation of eq 10 is fulfilled.

$$[Cr(OH)_2Cr^{4+}] = \tfrac{1}{2}[Cr^{2+}]_0 - [[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}]_0 \quad (10)$$

Reaction of $[Co(edta)]^-$ with Cr^{2+}. When the reaction condition was $[[Co(edta)]^-]_0 > [Cr^{2+}]_0$, the reaction was completed practically within the time of mixing. A reddish violet species which passed through the column was identified as the excess starting material $[Co(edta)]^-$. When the reaction was attempted at $[H^+] \geq 0.2$ M (Table V), two bands were observed on the column: pink and bluish violet. The former species was Co^{2+} ions. When these species were eluted with a 0.005 M $HClO_4$–0.045 M $NaClO_4$ solution, the bluish violet species moved faster than the Co^{2+} ions. When a 0.1 M $HClO_4$ solution was used as the eluent, the Co^{2+} ions moved faster than the bluish violet species. Under this condition, the bluish violet species behaved as 2+ charged species on the column. This chromatographic behavior is quite similar to that of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$.[5] Chemical analyses revealed that the bluish violet species does not contain cobalt but contains chromium ions. The wavelengths and molar absorption coefficients of the absorption maxima of the species are quite similar to those of $[Cr(OOCCH_3)(H_2O)_5]^{2+}$ (Table II). From these results, this species was assigned to $[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$, where the EDTA is coordinated to the $[Cr(H_2O)_5]^{3+}$ moiety through an acetate arm. Therefore, the reaction may be expressed as eq 11.

$$[Co(edta)]^- + Cr^{2+} + nH^+ \rightarrow [Cr(H_nedta)(H_2O)_5]^{(n-1)+} + Co^{2+} \quad (11)$$

When the reaction condition was $[H^+] = 0.1$ or 0.01 M and $[[Co(edta)]^-]_0 > [Cr^{2+}]_0$, an additional violet band was observed on the column as the lowest band. The violet species was separated from the Co^{2+} and $[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$ by the following procedure. The column was washed with 0.1 M $HClO_4$ solution until the $[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$ was separated completely from the bands of Co^{2+} and violet species. After the resin containing $[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$ was removed from the column, the column was washed with 0.050 M $NaClO_4$ solution. By this treatment, the violet species was separated completely from the Co^{2+} and could be eluted out. This chromatographic behavior may indicate that the violet species is a univalent cation under the above condition. This species was found to be a chromium(III) complex by chemical analyses (the species will be referred below as the violet Cr(III) species). The results of the product analyses are shown in Table V. The data indicate that the following relation holds:

$$[Cr^{2+}]_0 = [[Cr(H_nedta)(H_2O)_5]^{(n-1)+}] + [\text{violet Cr(III) species}] \quad (12)$$

The data also suggest that the formation of the violet Cr(III) species becomes appreciable with the decrease in $[H^+]$.

When the reaction condition was $[[Co(edta)]^-]_0 < [Cr^{2+}]_0$, the spectrophotometric monitoring showed that there were two stages in the title reaction. The first stage of the reaction was completed within the time of mixing, while the second stage of the reaction proceeded at a measurable rate and was completed practically within 20 min under the present experimental condition. The solution that finally resulted contained $[Cr(edta)(H_2O)]^-$, Co^{2+}, and $Cr(OH)_2Cr^{4+}$ but did not contain $[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$ and the violet Cr(III) species. If the reaction was quenched shortly after the initiation of the reaction, the products were $[Cr(edta)(H_2O)]^-$, Co^{2+}, $[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$, and $Cr(OH)_2Cr^{4+}$ (see Table V). These results suggest that the first stage of the reaction is reaction 11 and is followed by the slower reaction

$$[Cr(H_nedta)(H_2O)_5]^{(n-1)+} + Cr^{2+} \rightarrow Cr^{2+} + [Cr(edta)(H_2O)]^- + nH^+ \quad (13)$$

B. Kinetic Results. Reaction of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ with Cr^{2+}. On the assumption that the reaction 2 proceeds by the second-order rate law given in eq 14, kinetic mea-

$$\frac{d[Cr(III)]}{dt} = -\frac{d[Co(III)]}{dt} = k_{Co}[Co(III)][Cr^{2+}] \quad (14)$$

surements were made at various concentrations of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$, Cr^{2+}, and hydrogen ions. The observed second-order rate constants, k_{Co}, were independent of the initial concentrations of both the cobalt(III) complex and Cr^{2+} but were considerably dependent on the hydrogen ion concentrations. If the acid–base equilibria of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ are taken into consideration, the reaction in question can be expressed as the following four parallel reactions (eq 15–18). Then, eq 19 can be derived for the

$$[Co(edta)(NH_3)_5]^- + Cr^{2+} \xrightarrow{k_0} \text{products} \quad (15)$$

$$[Co(Hedta)(NH_3)_5] + Cr^{2+} \xrightarrow{k_1} \text{products} \quad (16)$$

$$[Co(H_2edta)(NH_3)_5]^+ + Cr^{2+} \xrightarrow{k_2} \text{products} \quad (17)$$

$$[Co(H_3edta)(NH_3)_5]^{2+} + Cr^{2+} \xrightarrow{k_3} \text{products} \quad (18)$$

$$k_{Co} = \frac{k_0K_1K_2K_3 + k_1K_2K_3[H^+] + k_2K_3[H^+]^2 + k_3[H^+]^3}{\alpha(H)} \quad (19)$$

second-order rate constant, where $\alpha(H) = K_1K_2K_3 + K_2K_3\cdot[H^+] + K_3[H^+]^2 + [H^+]^3$ and $K_n = [[Co(H_{n-1}edta)(NH_3)_5]^{(n-2)+}][H^+]/[[Co(H_nedta)(NH_3)_5]^{(n-1)+}]$. The acid dissociation constants, K_n (n = 1, 2, and 3), have been determined at 25.0 °C and I = 0.1 M (NaCl).[5] The plots of the values of $k_{Co}\alpha(H)$ vs. $[H^+]$ gave a linear relation as is shown in Figure 1. The intercept of the straight line was found to be practically zero. This means that reaction 16 is the dominant path of the reaction of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ with Cr^{2+} under the experimental condition. From the value of the slope, the rate constant k_1 was determined and is given in Table VI.

Reaction of $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$ with Cr^{2+}. The kinetics of the title reaction was studied under the pseudo-first-order condition; concentrations of Cr^{2+} greatly exceeded those of $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$. When the spectra over the range 340–600 nm were recorded during the reaction, three well-defined isosbestic points were observed at 392, 433, and 572 nm. The spectral changes are consistent with the occurrence of reaction 5. However, the isosbestic points began to collapse at almost the completion of reaction 5, presumably due to the occurrence of reaction 6. The plots of log $(A_t - A_\infty)$ vs. time gave a linear relation for at least 3 half-lives, where A_t and A_∞ represent absorbances at time t and infinity, respectively. The pseudo-first-order rate constant, k_{obsd}, was determined from the slope of this straight line. The values of k_{obsd} were found to be independent of the concentration of the hydrogen ions over the range 0.064–0.12 M. The second-order rate constants, k_{CoCr}, were calculated by dividing k_{obsd} by $[Cr^{2+}]_0$ and were found to be independent of the initial concentrations of both Cr^{2+} and $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$. Therefore, the rate law of the title reaction can be expressed as

$$-d[[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}]/dt = k_{CoCr}[[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}][Cr^{2+}] \quad (20)$$

The k_{CoCr} value determined is given in Table VI.

Reaction of $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$ with Cr^{2+}. Kinetic measurements were made under the condition that the initial concentration of Cr^{2+} exceeded that of $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$. Figure 2 shows one example of the change of absorbance at 538 nm against time and indicates that there are two well-resolved stages for the title reaction. The initial decrease in the absorbance was found to be due to the occurrence of reaction 7 and the subsequent increase in the absorbance to be due to that of reaction 9. The plots of log $|A_t - A_\infty|$ vs. time for the first stage gave a linear relation, where A_t and A_∞ denote the absorbances at time t and the time of completion of the first-stage reaction, respectively. The pseudo-first-order rate constant, k_{obsd}^A, was determined from the slope of this straight line. Then, the second-order rate constant of reaction 7, k_A, was calculated by dividing k_{obsd}^A by $[Cr^{2+}]_0$. Similarly, the pseudo-first-order rate constant of the second stage reaction, k_{obsd}^B, was determined from the plots of log $|A_t - A_\infty'|$ vs. time, where A_∞' represents the absorbance at the time of the completion of the second-stage reaction. The second-order rate constant of reaction 9, k_B, was calculated by dividing k_{obsd}^B by $\{[Cr^{2+}]_0 - [[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}]_0\}$. The first-stage reaction was also followed at 486 nm where the molar absorption coefficient of $[(NH_3)_5Co(H_2edta)Cr(H_2O)_5]^{4+}$ is identical with that of $[(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+}$. The values of k_A and k_B thus obtained were independent of the hydrogen ion concentrations over the range 0.060–0.13 M and are given in Table VI.

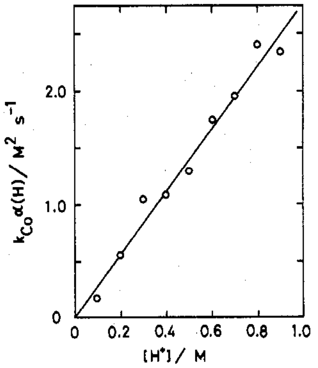
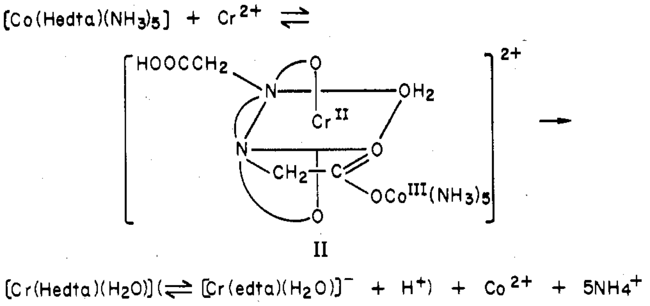


Figure 1. Plot of the value of $k_{Co}\alpha(H)$ vs. $[H^+]$ for the $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$–$Cr^{2+}$ system.

Discussion

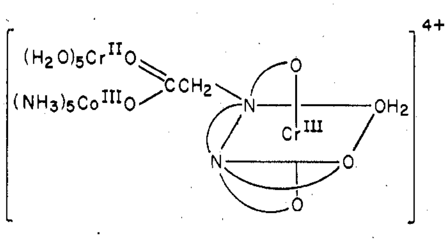
The predominant path for the reaction of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ with Cr^{2+} is reaction 16, and the rate constant of this path is 4.5 × 10^7 M^{-1} s^{-1}. This value is much larger than those expected for usual reactions of $[Co(OOCR)(NH_3)_5]^{2+}$ with Cr^{2+} and suggests the chelation of $[Co(Hedta)(NH_3)_5]$ to Cr^{2+}. The chromium(III) product was $[Cr(edta)(H_2O)]^-$. Therefore, the reaction would proceed via the formation of the precusor complex II.



(21)

Cannon and Gardiner[16] reported kinetic studies of $[Co(H_nnta)(NH_3)_5]^{n+}$ with Cr^{2+}. The reported second-order rate constant of $[Co(nta)(NH_3)_5]$ with Cr^{2+} is 1.5 × 10^{10} M^{-1} s^{-1} (at 25.0 °C and I = 1.0 M) which is again remarkably large. Therefore, it is evident that the $[Co(nta)(NH_3)_5]$ serves to chelate chromium(II) ion in the precursor complex.

The rate constant obtained for the reaction of $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$ with Cr^{2+} suggests the formation of the precursor complex III, because the value is very similar to those obtained for reaction 1 (compare 0.026 M^{-1} s^{-1} with, for example, 0.08 M^{-1} s^{-1} for the reaction of $[Co(OOC(CH_2)_2CH_3)(NH_3)_5]^{2+}$ with Cr^{2+} [17]).



III

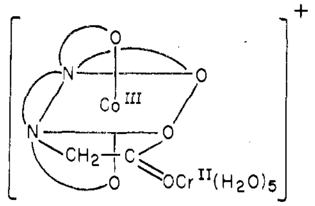
Wood and Higginson[18] investigated the reaction of $[Co(edta)]^-$ with Cr^{2+} and reported that the chromium(III) product in a solution containing 0.2 M or higher hydrogen ion was a univalent cation (high-acid product) and the chromi-

Table VI. The Rate Constants of the Reactions of Several Cobalt(III)-EDTA Complexes with Cr^{2+}

reaction	rate const, M^{-1} s^{-1}
$[Co(Hedta)(NH_3)_5] + Cr^{2+} \xrightarrow{k_1} Co^{2+} + [Cr(edta)(H_2O)]^- + 5NH_4^+$	$(4.5 \pm 0.2) \times 10^7$ [a]
$[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+} + Cr^{2+} \xrightarrow{k_{CoCr}} [(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+} + Co^{2+} + 5NH_4^+$	$(2.62 \pm 0.14) \times 10^{-2}$ [b]
$[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+} + Cr^{2+} \xrightarrow{k_A} [(NH_3)_5Co(H_2edta)Cr(H_2O)_5]^{4+} + Co^{2+}$	$(2.55 \pm 0.15) \times 10^{-3}$ [b]
$[(NH_3)_5Co(H_2edta)Cr(H_2O)_5]^{4+} + Cr^{2+} \xrightarrow{k_B} [(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+} + Co^{2+} + 5NH_4^+$	36.1 ± 5.0 [b]
$[Co(edta)]^- + Cr^{2+} \rightarrow$ products	1.6×10^5 [c]

[a] At 25.0 °C and $I = 1.0$ M ($LiClO_4$). [b] At 25.0 °C and $I = 0.2$ M ($LiClO_4$). [c] From P. B. Wood and W. C. E. Higginson, *J. Chem. Soc. A*, 1645 (1966); at 20 °C and $I = 1.0$ M ($NaClO_4$).

um(III) product at lower acidity was a noncharged species or univalent anion (low-acid product). Wood and Higginson assigned the high-acid product to $[Cr(H_2edta)(H_2O)_4]^+$ in which H_2edta is coordinated to the chromium(III) ion through two carboxylate groups and the low-acid product to $[Cr(H_nedta)(H_2O)_3]^{(n-1)+}$ (n = 1 or 0) in which H_nedta is coordinated to the chromium(III) ion through three carboxylate groups. The spectral data of these species reported by Wood and Higginson are also given in Table II. The numerical values of the high-acid product are very similar to those of the chromium(III) product which was assigned to $[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$ in this work. This observation suggests that both chromium(III) products are the same species, though the assigned charges on the complexes are different. The authors prefer the $[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$ formulation for the following reasons. (i) The chromatographic behavior of the products is quite similar to that of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$. (ii) Molecular models reveal that Cr^{2+} cannot coordinate the two carbonyl oxygens in $[Co(edta)]^-$ simultaneously. If the formation of $[Cr(H_2edta)(H_2O)_4]^+$ or $[Cr(H_nedta)(H_2O)_3]^{(n-1)+}$ is true, the second carboxylate group must be transferred to chromium ion after the reduction of the cobalt(III) complex was complete. This may be very unlikely. Therefore, the structure of the precursor complex in reaction 11 would be IV.



IV

The employment of the improved separation technique—the use of SP-Sephadex resin—allowed detection of the violet Cr(III) species which has probably not been reported. The positions of the d-d absorption maxima of this species shift to shorter wavelength than those of $[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$ and suggest that the violet Cr(III) species has a $CrNO_5$ moiety (compare the absorption maxima given in Table II, 547 and 387 nm, with, for example, 547 and 397 nm for $[Cr(NH_3)(H_2O)_5]^{3+}$ [19] and 544 and 393 nm for $[Cr(ida)(H_2O)_3]^+$ [20]). The molar absorption coefficients of the violet Cr(III) species are much larger than those of $[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$ and suggest that the Cr(III) ion in the violet species is wrapped partly with EDTA. However, further characterization for the species was not made. The spectral data of the violet Cr(III) species are quite different from those of the low-acid product reported by Wood and Higginson. A possible explanation for the discrepancy would be that the low-acid product is a mixture of the $[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$ and the violet Cr(III) species.

Reaction 11 is followed by reaction 13. As $[Cr(edta)(H_2O)]^-$ was produced in the latter reaction, the structure of the precursor complex in reaction 13 may be similar to that of the precursor complex II given in eq 21, though $[Cr(H_2O)_5]^{3+}$ must replace $[Co(NH_3)_5]^{3+}$.

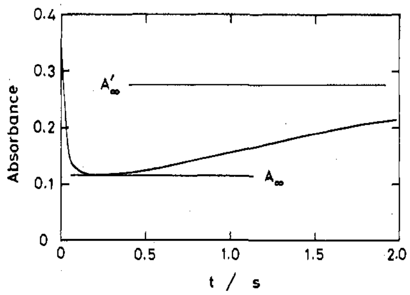
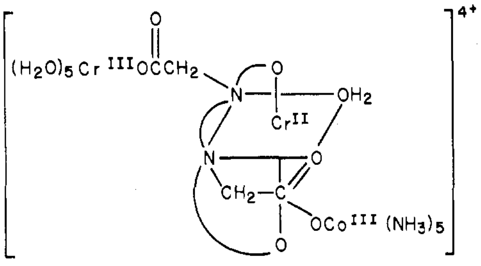
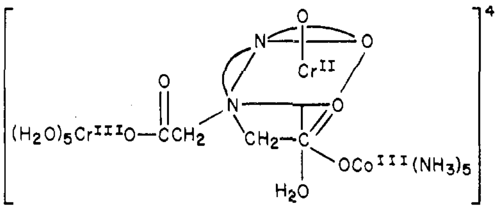


Figure 2. Change of the absorbance with the time for the reaction of $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$ with Cr^{2+}. $[Cr^{2+}]_0 = 1.85 \times 10^{-2}$ M, $[[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}]_0 = 1.50 \times 10^{-3}$ M, and $[H^+]$ = 0.098 M at 25.0 °C and I = 0.20 M ($LiClO_4$). The measurement was made at 538 nm.

When $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$ is reduced by Cr^{2+}, the $\{edtaCo(H_2O)\}$ moiety would be reduced by Cr^{2+} prior to the reduction of the $[Co(NH_3)_5]^{3+}$ moiety, because it is known that the rate constant of the reaction of $[Co(edta)]^-$ with Cr^{2+} is very large (Table IV).[18] In fact, the reaction occurs to give $[(NH_3)_5Co(H_2edta)Cr(H_2O)_5]^{4+}$ as is shown in eq 7. The $[(NH_3)_5Co(H_2edta)Cr(H_2O)_5]^{4+}$ thus formed reacts with Cr^{2+} to produce $[(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+}$ as is shown in eq 9. This may indicate that the chelated precursor complex V or V′ is formed before the electron transfer takes place. Therefore, it would be reasonable that the rate constant of reaction 9 is much larger than that expected for the usual reaction of $[Co(OOCR)(NH_3)_5]^{2+}$ with Cr^{2+}.



V



V′

The reactions studied in this work are summarized in Scheme I. It is apparent that all the reactions proceed through

Scheme I

$$\begin{tikzcd}
{[Co(H_nedta)(NH_3)_5]^{(n-1)+}} \arrow[rrd] & & \\
{[Co(edta)]^-} \arrow[r] & {[Cr(H_nedta)(H_2O)_5]^{(n-1)+}} \arrow[r] & {[Cr(edta)(H_2O)]^-} \\
{[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}} \arrow[rr] & & {[(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+}} \arrow[u] \\
{[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}} \arrow[rr] & & {[(NH_3)_5Co(H_nedta)Cr(H_2O)_5]^{(n+2)+}} \arrow[u]
\end{tikzcd}$$

inner-sphere mechanisms. Although various chromium(III)–EDTA complexes are produced by the reactions, it should be noted that these products are ultimately converted to $[Cr(edta)(H_2O)]^-$.

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Registry No. $[Co(edta)(NH_3)_5]^-$, 69576-62-1; $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$, 61813-16-9; $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$, 61813-10-3; $[Co(edta)]^-$, 15136-66-0; $Cr(H_2O)_6{}^{2+}$, 20574-26-9; $[(H_2O)_5Cr\{edtaCr(H_2O)\}]^{2+}$, 69531-92-6; $[(NH_3)_5Co(H_2edta)Cr(H_2O)_5]^{4+}$, 69596-66-3; $[Cr(edta)(H_2O)_5]^-$, 69531-93-7.

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(4) Abbreviations used in this paper: EDTA, ethylenediamine-*N,N,N′,N′*-tetraacetic acid; NTA, nitrilotriacetic acid; IDA, iminodiacetic acid. In $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$, the EDTA is coordinated to the $[Co(NH_3)_5]^{3+}$ moiety through an acetate arm.[5] In $[(NH_3)_5Co\{edtaM(H_2O)\}]^{2+}$ (M = Co(III) or Cr(III)), the EDTA acts as a quinquedentate ligand for M and a unidentate ligand for the $[Co(NH_3)_5]^{3+}$ moiety.[5]

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Structural and Mechanistic Studies of Coordination Compounds. 23. Evidence for Dissociative Substitution Reactions of Some *trans*-Acido(isothiocyanato)(1,4,8,11-tetraazacyclotetradecane)iron(III) Complexes, *trans*-$[Fe(cyclam)(NCS)X]^+$, X^- = NCS^-, CH_2ClCOO^-, $CHCl_2COO^-$, Cl^-, and Br^-

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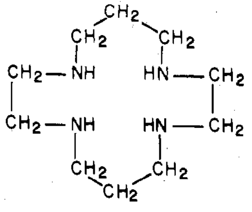
Mass-law retardation has been observed for the ligand substitution reactions of some low-spin *trans*-$[Fe(cyclam)(NCS)X]^+$ complexes by thiocyanate (cyclam = 1,4,8,11-tetraazacyclotetradecane; X^- = CH_2ClCOO^-, $CHCl_2COO^-$, Cl^-, Br^-) and *trans*-$[Fe(cyclam)(NCS)_2]^+$ by a series of nucleophiles in aqueous acidic solution. These rate constants (k_{-x}) are strongly dependent on the nature of the leaving ligands but are independent of the nature and concentration of the entering groups. A plot of log k_{-x} against –log Q_x, where Q_x represents the corresponding aquation equilibrium constant, is linear over 5 logarithmic units with a slope of 1.00 ± 0.05. These results are fully consistent with a dissociative mechanism for the substitution reactions of these low-spin iron(III)–amine complexes.

Introduction

As part of our program to extend the studies of ligand-substitution kinetics and mechanisms of octahedral amine complexes to systems other than those of the extensively explored cobalt(III)[1–6] and chromium(III) systems,[6–10] we report here the reactions of some low-spin iron(III) complexes of the type *trans*-$[Fe(cyclam)(NCS)X]^{n+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane; X = NCS^-, Cl^-, Br^-, CH_2ClCOO^-, $CHCl_2COO^-$, H_2O).



cyclam

To date, there has been little systematic study on kinetics and mechanisms of ligand substitution reactions of octahedral iron(III)–amine complexes.[11] Swaddle[12] proposed that all trivalent transition-metal complexes, with the exception of cobalt(III) complexes which are well documented to react by a dissociative mechanism, underwent ligand substitution reactions by an associative mechanism. Recently, evidence has accumulated to support a dissociative mechanism for the acid hydrolysis of some amine complexes of chromium(III)[10] and ruthenium(III).[13] This paper presents some kinetic evidence to support a dissociative mechanism for the ligand substitution reactions of some low-spin iron(III)–amine complexes.

Experimental Section

Materials. The complexes *trans*-$[Fe(cyclam)X_2]ClO_4$ (X^- = NCS^- and Cl^-) were prepared by published methods.[14] Sodium salts of CH_2ClCOO^- $CHCl_2COO^-$, and $H_2PO_4^-$ were prepared by neutralizing the corresponding acids with sodium hydroxide. Concentrations of ionic CH_2ClCOO^-, $CHCl_2COO^-$, and $H_2PO_4^-$ were calculated from the known acid dissociation constants of these acids[15] (pK_a = 2.86, 1.29, and 2.12, respectively).

Kinetics. The substitution reactions of *trans*-$[Fe(cyclam)(NCS)_2]^+$ by various nucleophiles were followed spectrophotometrically in situ by using a Unicam SP8000 recording spectrophotometer fitted with

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