Inorg. Chem. **1980**, *19*, 255–259 **255**

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Stoichiometric, Kinetic, and Mechanistic Investigations of the Reactions of (Oxygen-bonded aminopolycarboxylato)pentaamminecobalt(III) Complexes with Hexaaquachromium(II) Ions

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Received March 27, 1979

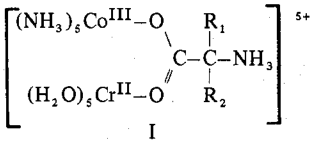
A product survey of the reactions of (O-bonded aminopolycarboxylato)pentaamminecobalt(III) complexes, $[Co(H_nY)(NH_3)_5]^{(n+1)+}$, with hexaaquachromium(II) ions (Cr^{2+}) in acid solutions was carried out, where Y^{2-} denotes ida^{2-} (iminodiacetate) and $edda^{2-}$ (ethylenediamine-*N*,*N'*-diacetate). The predominant chromium(III) product of the reaction of $[Co(H_nedda)(NH_3)_5]^{(n+1)+}$ with Cr^{2+} was found to be $[Cr(H_nedda)(H_2O)_5]^{(n+1)+}$, where $H_nedda^{(2-n)-}$ acts as the unidentate ligand. The chromium(III) products of the reaction of $[Co(H_nida)(NH_3)_5]^{(n+1)+}$ with Cr^{2+} were both $[CrH_nida)(H_2O)_5]^{(n+1)+}$ and $[Cr(ida)(H_2O)_3]^+$, where the $H_nida^{(2-n)-}$ in the former product acts as the unidentate ligand and the ida^{2-} in the latter product acts as the terdentate ligand, respectively. Kinetic measurements were made for these reactions in acid solutions at 25.5 °C and an ionic strength of 1.0 M. The rate law for the reaction of $[Co(H_nida)(NH_3)_5]^{(n+1)+}$ was $-d[Co(III)]/dt = \{(k_0K_1K_2 + k_1K_1[H^+] + k_2[H^+]^2)/(K_1K_2 + K_1[H^+] + [H^+]^2)\}[Co(III)][Cr^{2+}]$, where K_1 and K_2 denote the acid dissociation constants of $[Co(H_2ida)(NH_3)_5]^{3+}$. The values of k_0, k_1, and k_2 were $(9.2 \pm 0.5) \times 10^6$, $(4.3 \pm 2.0) \times 10^{-2}$, and $(5.0 \pm 0.7) \times 10^{-2}$ M^{-1} s^{-1}, respectively. $[Cr(ida)(H_2O)_3]^+$ was found to be formed exclusively by the k_0 path. The rate law for the reaction of $[Co(H_nedda)(NH_3)_5]^{(n+1)+}$ was $-d[Co(III)]/dt = k[Co(III)][Cr^{2+}]$, where the value of k was $(4.1 \pm 0.6) \times 10^{-2}$ M^{-1} s^{-1}. The mechanisms of these reactions are discussed.

Introduction

In previous papers,[1,2] it was shown that the reactions of a number of (O-bonded amino acid)pentaamminecobalt(III) complexes ($[Co(amH)(NH_3)_5]^{3+}$), with hexaaquachromium(II) ions (Cr^{2+}) in acid solutions ($[H^+]$ = 0.1–0.5 M) proceed through an inner-sphere mechanism and give (O-bonded amino acid)pentaaquachromium(III) complexes ($[Cr(amH)(H_2O)_5]^{3+}$).[3]

$$[Co(amH)(NH_3)_5]^{3+} + Cr^{2+} \xrightarrow{H^+} Co^{2+} + 5NH_4^+ + [Cr(amH)(H_2O)_5]^{3+} \quad (1)$$

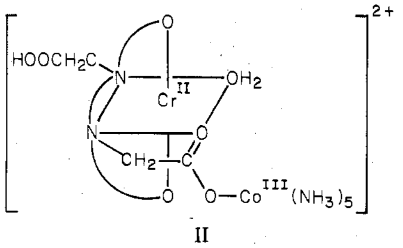
No formation of the chromium(III) complexes containing amino acidato chelate ($[Cr(am)(H_2O)_4]^+$) was observed. These results indicate that the precursor complex I is formed



I

prior to the electron-transfer process. On the other hand, the chromium(III) product of the reaction of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ with Cr^{2+} in acid solutions ($[H^+]$ = 0.1–0.9 M) is not $[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$ but $[Cr(edta)(H_2O)]^-$, so that the reaction was found to be expressed as eq 2 and the precursor complex was inferred to have the structure II.[4,20] If a proper choice of the aminopolycarboxylate ligand, $H_nY^{(m-n)-}$, is made in the reaction of $[Co(H_nY)(NH_3)_5]^{(3-m+n)+}$ with Cr^{2+}, it would be expected that both the chromium(III) complex containing O-bonded $H_nY^{(m-n)-}$, $[Cr(H_nY)(H_2O)_5]^{(3-m+n)+}$, and the chromium(III) complex containing the chelated Y^{m-}, $[CrY(H_2O)_{6-p}]^{(3-m)+}$, are formed simultaneously. Discovery of such a system may be useful to study the structural aspect of the precursor complexes formed in the electron-transfer reactions. From this point of view, the present work was undertaken; the reactions of $[Co(H_nida)(NH_3)_5]^{(n+1)+}$ and $[Co(H_nedda)(NH_3)_5]^{(n+1)+}$ with Cr^{2+} are investigated through the characterization of the products and kinetic measurements. On the basis of these results, structural assignments of the precursor complexes are attempted.

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



II

Experimental Section

Reagents. The complexes $[Co(Hida)(NH_3)_5](ClO_4)_2{\cdot}1.5H_2O$ and $[Co(H_2edda)(NH_3)_5](ClO_4)_3{\cdot}3H_2O$ were prepared by heating the solutions containing $[Co(H_2O)(NH_3)_5](ClO_4)_3$ and the aminopolycarboxylates as reported previously.[5,6] These complexes were purified by the use of an SP-Sephadex C-25 column (Na^+ form). The IDA complex adsorbed on the column moved much faster than the $[Co(H_2O)(NH_3)_5]^{3+}$ ions upon eluting with a 0.2 M $NaClO_4$ solution at pH 3. The EDDA complex adsorbed on the column moved slower than the $[Co(H_2O)(NH_3)_5]^{3+}$ ions upon eluting with a 0.4 M $NaClO_4$ solution at pH 3. Binuclear cobalt(III) complexes of IDA and EDDA were also obtained. From the elution behavior, elemental analyses, and visible and infrared absorption spectra, these were characterized as $[(NH_3)_5Co(Hida)Co(NH_3)_5](ClO_4)_5{\cdot}2H_2O$ and $[(NH_3)_5Co(H_2edda)Co(NH_3)_5](ClO_4)_6{\cdot}2.5H_2O$, where $Hida^-$ or H_2edda is coordinated to the two $[Co(NH_3)_5]^{3+}$ moieties through two acetate arms. The analytical data for the complexes prepared in this work are given in Table I.[7] The numerical data for the electronic spectra of the complexes are summarized in Table II.[7]

All the solutions used for the measurements were prepared from redistilled water. The lithium perchlorate and the solutions of hexaaquachromium(III) perchlorate were prepared as reported previously.[4] Chromium(II) perchlorate solutions were prepared by the electrolytic reduction of the hexaaquachromium(III) perchlorate under an atmosphere of nitrogen and always found to contain several percent of hexaaquachromium(III) ions (Cr^{3+}).

Product Analyses. Experiments were carried out under the conditions where the concentrations of Cr^{2+} exceeded those of $[Co(H_nida)(NH_3)_5]^{(n+1)+}$ or $[Co(H_nedda)(NH_3)_5]^{(n+1)+}$. After the reaction

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[1] Holwerda, H.; Deutsch, E.; Taube, H. *Inorg. Chem.* **1972**, *11*, 1965.
[2] Ogino, H.; Tsukahara, K.; Tanaka, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2743.
[3] Abbreviations used in this paper are as follows: amH = amino acid; $H_nY^{(m-n)-}$ = aminopolycarboxylate; EDTA = ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid; EDDA = ethylenediamine-*N*,*N'*-diacetic acid; IDA = iminodiacetic acid; NTA = nitrilotriacetic acid.
[4] Ogino, H.; Tsukahara, K.; Tanaka, N. *Inorg. Chem.* **1979**, *18*, 1271.
[5] Cannon, R. D.; Gardiner, J. *Inorg. Chem.* **1974**, *13*, 390.
[6] Ogino, H.; Tsukahara, K.; Tanaka, N. *Inorg. Chem.* **1977**, *16*, 1215.
[7] Supplementary material.

0020-1669/80/1319-0255$01.00/0

Table III. Numerical Data for the Electronic Spectra of the Chromium(III) Products and Related Complexes

complex	medium	λ_{max}/nm[a] (ϵ/M^{-1} cm^{-1})[b]
$[Cr(ida)(H_2O)_3]^+$ (reddish violet species)	0.1 M $HClO_4$	544 ± 1 (60.2 ± 1.5), 393 ± 1 (49.1 ± 1.5)
$[Cr(ida)(H_2O)_3]^+$ [c]		544 (60), 393 (50)
$[Cr(H_nida)(H_2O)_5]^{(n+1)+}$ (bluish violet species)	0.1 M $HClO_4$-0.3 M $NaClO_4$	574 ± 4 (21 ± 2), 410 ± 2 (23 ± 2)
$[Cr(H_nedda)(H_2O)_5]^{(n+1)+}$ (bluish violet species)	0.1 M $HClO_4$-0.6 M $NaClO_4$	573 ± 3 (21 ± 2), 412 ± 3 (21 ± 2)
$[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$ [d]	0.1 M $HClO_4$	578 (22), 412 (23)
$[Cr(OOCCH_3)(H_2O)_5]^{2+}$ [e]	0.02 M $HClO_4$	570 (24.4), 410 (22.2)

[a] Absorption maximum. [b] The molar absorption coefficient. [c] Reference 11. [d] Reference 4. [e] Reference 13.

had been quenched by the introduction of air into the system, the solution was poured into an SP-Sephadex C-25 column (1.8 × 10 cm). Cationic species adsorbed on the Sephadex column could be separated by elution with $HClO_4$–$NaClO_4$ solutions in a manner similar to those reported previously.[4,6,8]

The chromium content in each eluate was determined spectrophotometrically as CrO_4^{2-} after oxidation with an alkaline hydrogen peroxide solution. The cobalt content was determined by Kitson's method.[9]

Kinetic Measurements. All measurements were made under a nitrogen atmosphere. The reaction was initiated by injecting the solution of Cr^{2+} into the solution containing the required amounts of a complex, perchloric acid, and lithium perchlorate. The change in absorbance with time was followed with a Union-Giken SM-401 spectrophotometer. Wavelengths used for the measurements were 480 nm for the reaction of $[Co(H_nida)(NH_3)_5]^{(n+1)+}$ and 502 nm for the reaction of $[Co(H_nedda)(NH_3)_5]^{(n+1)+}$. The temperature was controlled at 25.5 ± 0.1 °C and the ionic strength (I) was adjusted to 1.0 M with lithium perchlorate.

Acid Dissociation Constants. For determining acid dissociation constants of the cobalt(III) complexes, pH titrations were made with a Toa HM-20B digital pH meter, as described previously.[10] The pK_1 and pK_2 values at 25 °C and I = 0.1 M (NaCl) were 1.36 and 8.22 for $[Co(H_2ida)(NH_3)_5]^{3+}$ and 5.55 and 8.94 for $[Co(H_2edda)(NH_3)_5]^{3+}$.

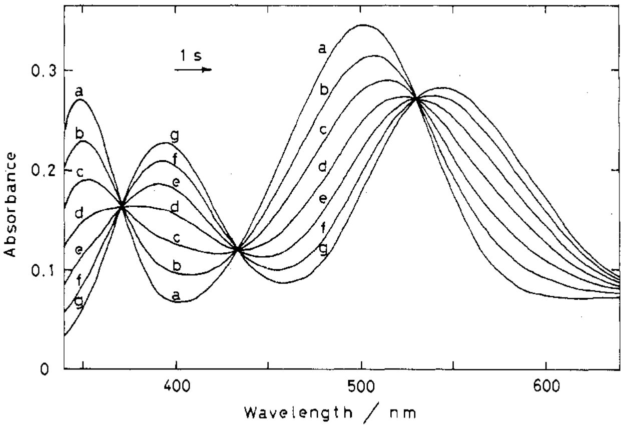

Figure 1. Spectral changes during the reaction of $[Co(H_nida)(NH_3)_5]^{(n+1)+}$ with Cr^{2+} at $[Cr^{2+}]_0 = 1.38 \times 10^{-2}$ M, $[Co(III)]_0 = 5.08 \times 10^{-3}$ M, and $[H^+]$ = 0.121 M: a, 25 s; b, 2 min; c, 4 min; d, 7 min; e, 11 min; f, 18 min; g, 45 min after the reaction. The times given are for the start of scan at 340 nm.

Results and Discussion

Net Reaction of $[Co(H_nY)(NH_3)_5]^{(n+1)+}$ with Cr^{2+} and Characterization of Chromium(III) Products. The spectral changes observed during the reaction of $[Co(H_nida)(NH_3)_5]^{(n+1)+}$ with Cr^{2+} gave three isosbestic points within the range of 340–650 nm. Figure 1 shows one example of such spectral changes. After the reaction was completed, the solution was poured on a Sephadex column. The column showed five bands: reddish violet, pink, bluish violet, bluish violet, and green from the bottom to the top of the column. The pink, upper bluish violet, and green species were identified as Co^{2+}, Cr^{3+}, and $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$, respectively. The last is considered to be formed by the air oxidation of Cr^{2+} ions which had remained after the completion of the reaction.[4] The reddish violet species could be easily eluted with a 0.1 M $HClO_4$ solution; hence this species was concluded to have unipositive charge.[11] The electronic spectrum of this species whose numerical data are given in Table III agreed with that of $[Cr(ida)(H_2O)_3]^+$.[12] The lower bluish violet species moved faster than the Cr^{3+} (upper bluish violet species) upon elution with a 0.1 M $HClO_4$–0.3 M $NaClO_4$ solution. This indicates that the lower bluish violet species has 2+ and/or 3+ charge(s). The electronic spectrum of this species is quite similar to that of $[Cr(H_nedta)(H_2O)_5]^{(n-1)+}$ [4] and $[Cr(OOCCH_3)(H_2O)_5]^{2+}$ [13] (Table III). From these results, this species was assigned to $[Cr(H_nida)(H_2O)_5]^{(n+1)+}$, where $H_nida^{(2-n)-}$ is coordinated to the $[Cr(H_2O)_5]^{3+}$ moiety through an acetate arm. The chromatographic behavior can be interpreted by the following equilibrium:

$$[Cr(H_2ida)(H_2O)_5]^{3+} \rightleftharpoons [Cr(Hida)(H_2O)_5]^{2+} + H^+ \tag{3}$$

The separation of $[Cr(H_nida)(H_2O)_5]^{(n+1)+}$ and Cr^{3+} on the column was incomplete. Therefore, the direct determination of the respective concentrations of $[Cr(H_nida)(H_2O)_5]^{(n+1)+}$ and Cr^{3+} could not be made, but the value of $\{[[Cr(H_nida)(H_2O)_5]^{(n+1)+}] + [Cr^{3+}]\}$ could be determined. The concentration of $[Cr(H_nida)(H_2O)_5]^{(n+1)+}$ was calculated by the equation $[[Cr(H_nida)(H_2O)_5]^{(n+1)+}] = [Co^{2+}] - [[Cr(ida)(H_2O)_3]^+]$. Then, the difference between $\{[[Cr(H_nida)(H_2O)_5]^{(n+1)+}] + [Cr^{3+}]\}$ and $[[Cr(H_nida)(H_2O)_5]^{(n+1)+}]$ was taken as the value of $[Cr^{3+}]$. From the amount of the Cr^{3+} thus estimated, this species was considered to be the Cr^{3+} contained in the original chromium(II) solution (see Experimental Section).[14] The results of the product analyses are summarized in Table IV. No chelation of $[Cr(H_nida)(H_2O)_5]^{(n+1)+}$ was observed at 0.1 M $HClO_4$ in the absence of Cr^{2+}. Also, no chromium(II)-catalyzed conversion of $[Cr(H_nida)(H_2O)_5]^{(n+1)+}$ to $[Cr(ida)(H_2O)_3]^+$ was observed, even after prolonged contact (several hours) of $[Cr(H_nida)(H_2O)_5]^{(n+1)+}$ with Cr^{2+} under the present experimental conditions. It is known that the aquation of $[Cr(ida)(H_2O)_3]^+$ is quite slow.[15] These results indicate that the reaction of $[Co(H_nida)(NH_3)_5]^{(n+1)+}$ with Cr^{2+} proceeds through the following two parallel paths:

$$[Co(H_nida)(NH_3)_5]^{(n+1)+} + Cr^{2+} + (5-n)H^+ \rightarrow Co^{2+} + 5NH_4^+ + [Cr(ida)(H_2O)_3]^+ \tag{4}$$

$$[Co(H_nida)(NH_3)_5]^{(n+1)+} + Cr^{2+} + 5H^+ \rightarrow Co^{2+} + 5NH_4^+ + [Cr(H_nida)(H_2O)_5]^{(n+1)+} \tag{5}$$

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(8) Ogino, H.; Tsukahara, K.; Tanaka, N. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 308.

(9) Kitson, R. E. *Anal. Chem.* **1950**, *22*, 664.

(10) Ogino, H.; Watanabe, T.; Tanaka, N. *Inorg. Chem.* **1975**, *14*, 2093.

(11) Ogino, H.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1836.

(12) Weyh, J. A.; Hamm, R. E. *Inorg. Chem.* **1968**, *7*, 2431.

(13) Deutsch, E.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1532.

(14) The possibility cannot be ruled out that a part of Cr^{3+} comes from the Cr^{2+}-catalyzed aquation of $[Cr(H_nida)(H_2O)_5]^{(n+1)+}$.

(15) Weyh, J. A.; Hamm, R. E. *Inorg. Chem.* **1969**, *8*, 2298.

Table IV. Product Analyses of the Reaction of $[Co(H_n ida)(NH_3)_5]^{(n+1)+}$ with Cr^{2+} at 25.5 °C and $I = 1.0$ M ($LiClO_4$)

initial concn of reactants			concn of products					
$10^2 \times [Cr^{2+}]_0$,[a] M	$10^3 \times [Co(III)]_0$,[b] M	$[H^+]$, M	$10^3 \times [Co^{2+}]$, M	$10^3 \times [Cr(ida)^+]$,[c] M	$10^3 \times [Cr(H_n ida)^{(n+1)+}]$, M[d,e]	$10^3 \times \{[Cr(H_n ida)^{(n+1)+}] + [Cr^{3+}]\}$, M	$10^3 \times [Cr^{3+}]$,[f] M	$10^3 \times [Cr(OH)_2Cr^{4+}]$,[g] M
1.36	2.09	0.090	2.07	1.65	0.42	1.52	1.10	5.75
1.38	5.08	0.121	5.00	3.46	1.54	2.25	0.71	4.38
1.36	6.35	0.150	6.37	3.78	2.50	2.92	0.42	3.63
1.33	6.01	0.196	5.97	2.89	3.08	3.44	0.36	3.68
1.44	4.29	0.276	4.28	1.37	2.91	3.80	0.89	5.05
1.31	5.03	0.523	5.05	0.66	4.39	6.56	2.17	4.01
1.47	5.69	0.938	5.65	0.31	5.34	6.12	0.78	4.52

[a] The value was calculated as $[Co^{2+}] + 2[Cr(OH)_2Cr^{4+}]$. [b] $[Co(III)]_0 = [[Co(H_n ida)(NH_3)_5]^{(n+1)+}]_0$. [c] $[Cr(ida)^+] = [[Cr(ida)(H_2O)_3]^+]$. [d] $[Cr(H_n ida)^{(n+1)+}] = [[Cr(H_n ida)(H_2O)_5]^{(n+1)+}]$. [e] The concentration of this species was calculated as $[Co^{2+}] - [Cr(ida)^+]$. [f] The value of $[Cr^{3+}]$ was calculated as $\{[Cr(H_n ida)^{(n+1)+}] + [Cr^{3+}]\} - [Cr(H_n ida)^{(n+1)+}]$. [g] $[Cr(OH)_2Cr^{4+}] = [[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}]$.

Table IV shows that, with the increase of the hydrogen ion concentration, the amount of the chromium(III) product containing the chelated IDA, $[Cr(ida)(H_2O)_3]^+$, decreases and that of the chromium(III) product containing O-bonded IDA, $[Cr(H_n ida)(H_2O)_5]^{(n+1)+}$, increases.

When the solution containing the products of the reaction of $[Co(H_n edda)(NH_3)_5]^{(n+1)+}$ with Cr^{2+} was poured in the column, four bands were observed by visual inspection: pink, bluish violet, bluish violet, and green from the bottom to the top of the column. The pink, lower bluish violet, and green species were identified as Co^{2+}, Cr^{3+}, and $Cr(OH)_2Cr^{4+}$, respectively. The major part of the Cr^{3+} was again considered to be the Cr^{3+} contained in the original chromium(II) solution and the $Cr(OH)_2Cr^{4+}$, to be formed by the air oxidation of Cr^{2+} ions. The upper bluish violet species was eluted with a 0.1 M $HClO_4$–0.6 M $NaClO_4$ solution and found to have a 3+ charge. The electronic spectrum of this species is quite similar to that of $[Cr(H_n ida)(H_2O)_5]^{(n+1)+}$, $[Cr(H_n edta)(H_2O)_5]^{(n-1)+}$, and $[Cr(OOCCH_3)(H_2O)_5]^{2+}$ (Table III). From these results, this species was assigned to $[Cr(H_2edda)(H_2O)_5]^{3+}$. The effluent was collected until the Co^{2+} band almost reached the bottom of the column by eluting with a 0.1 M $HClO_4$–0.1 M $NaClO_4$ solution. When this effluent was treated with an alkaline hydrogen peroxide solution, a small amount of CrO_4^{2-} was detected. Since the species in question moved faster than Co^{2+}, the species has unipositive charge. Although further characterization of this species was not attempted because of the limited amount, it may be reasonable to consider that the species is $[Cr(edda)(H_2O)_2]^+$ where $edda^{2-}$ acts as the quadridentate ligand. The results of the product analyses are summarized in Table V.[7] The concentrations of $[Cr(H_2edda)(H_2O)_5]^{3+}$ were determined spectrophotometrically as CrO_4^{2-} after the oxidation of $[Cr(H_2edda)(H_2O)_5]^{3+}$ eluted from the Sephadex column. However, the values were always found to be smaller than those calculated by the relation $[[Cr(H_2edda)(H_2O)_5]^{3+}] = [Co^{2+}] - [[Cr(edda)(H_2O)_2]^+]$ (Table V[7]). This suggests strongly the occurrence of the Cr^{2+}-catalyzed aquation of $[Cr(H_2edda)(H_2O)_5]^{3+}$. The data given in Table V[7] indicate that the major path in the reaction of $[Co(H_n edda)(NH_3)_5]^{(n+1)+}$ with Cr^{2+} is

$$[Co(H_n edda)(NH_3)_5]^{(n+1)+} + Cr^{2+} + 5H^+ \rightarrow Co^{2+} + 5NH_4^+ + [Cr(H_n edda)(H_2O)_5]^{(n+1)+} \quad (6)$$

Determination of the Rate Constants of the Reactions of $Co(H_n ida)(NH_3)_5]^{(n+1)+}$ and $[Co(H_n edda)(NH_3)_5]^{(n+1)+}$ with Cr^{2+}. The kinetics of the title reactions were studied in various concentrations of Cr^{2+} (1.3×10^{-2}–2.5×10^{-2} M), cobalt(III) (2.1×10^{-3}–6.4×10^{-3} M), and hydrogen ions (0.090–0.94 M). On the assumption that the reaction proceeds by the second-order rate law

$$-d[Co(III)]/dt = k[Co(III)][Cr^{2+}] \quad (7)$$

the following equation was derived:

$$\ln \frac{([Cr^{2+}]_0 - [Co(III)]_0)A_0 + [Co(III)]_0 A_t - [Cr^{2+}]_0 A_\infty}{A_t - A_\infty} = ([Cr^{2+}]_0 - [Co(III)]_0)kt + \ln [Cr^{2+}]_0 \quad (8)$$

where $[\ ]_0$ represents the initial concentration of the given species and A_0, A_t, and A_∞ denote the absorbances at time zero, t, and infinity, respectively. The plots of the left-hand side of eq 8 vs. t for each system gave a linear relation for at least 3 half-lives. The second-order rate constant, k, was calculated from the slope of this straight line.

In the reaction of $[Co(H_n ida)(NH_3)_5]^{(n+1)+}$ with Cr^{2+}, the values of k were considerably dependent on the hydrogen ion concentrations. For simplicity, the acid dependency of the rate data was analyzed as the simultaneous occurrence of reactions 9, 10, and 11, though other interpretations also are known to

$$[Co(ida)(NH_3)_5]^+ + Cr^{2+} \xrightarrow{k_0} \text{products} \quad (9)$$

$$[Co(Hida)(NH_3)_5]^{2+} + Cr^{2+} \xrightarrow{k_1} \text{products} \quad (10)$$

$$[Co(H_2ida)(NH_3)_5]^{3+} + Cr^{2+} \xrightarrow{k_2} \text{products} \quad (11)$$

be possible.[16-19] Then, eq 12 can be derived for the second-order rate constant:

$$k = \frac{k_0K_1K_2 + k_1K_1[H^+] + k_2[H^+]^2}{\alpha(H)} \quad (12)$$

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(16) Haim, A. *Acc. Chem. Res.* **1975**, *8*, 264.

(17) Cannon, R. D.; Gardiner, J. *J. Chem. Soc., Dalton Trans.* **1976**, 622.

(18) Martin, A. H.; Liang, A.; Gould, E. S. *Inorg. Chem.* **1976**, *15*, 1925 and the references cited therein.

(19) Kennard, G. J.; Deutsch, E. *Inorg. Chem.* **1978**, *17*, 2225.

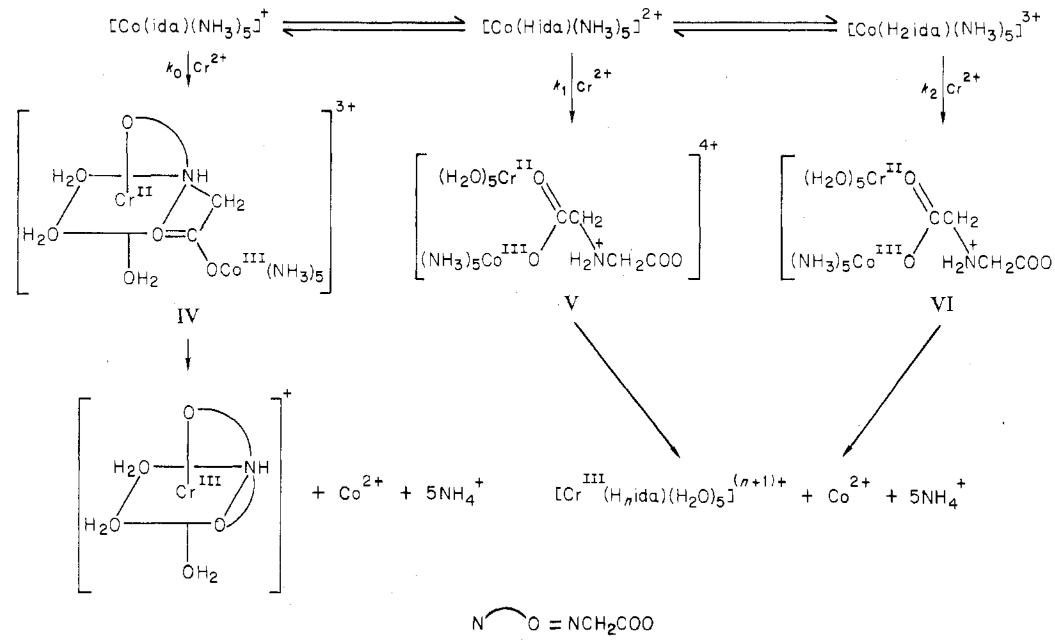
(20) A referee commented on this point: "Inferring the existence of a chelated precursor from observation of a chelated product is very dangerous. The rings could well close after electron transfer; the authors are well aware (see ref 10) of the special lability of chromium(III) aminocarboxylate complexes." Recent investigations[10,21-23] disclosed that the substitution reactions of some chromium(III)–aminopolycarboxylate complexes are very rapid. In the systems studied in this work, however, we have not found the reactions which signaled the rapid ring closure of the partially chelated chromium(III) products formed immediately after the electron-transfer reactions. The thermal and chromium(II)-catalyzed ring closing reactions of $[Cr(H_n edta)(H_2O)_5]^{(n-1)+}$ also have been found to be slow.[4] Furthermore, it is known that the conversion of quadridentate chromium(III)–EDTA(aqua) complex to quinquedentate complex is not so rapid in highly acidic solution.[21]

(21) Thorneley, R. N. F.; Sykes, A. G.; Gans, P. *J. Chem. Soc. A* **1971**, 1494.

(22) Sulfab, Y.; Taylor, R. S.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 2388.

(23) Ogino, H.; Shimura, M.; Tanaka, N. *Inorg. Chem.* **1979**, *18*, 2497.

Scheme I



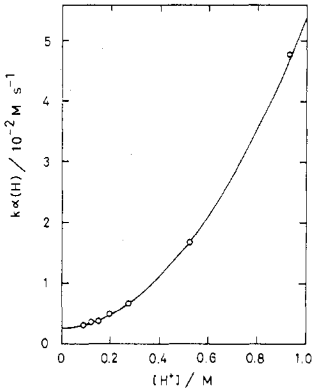


Figure 2. Plots of $k\alpha(\mathrm{H})$ vs. $[\mathrm{H}^+]$ for the reaction of $[\mathrm{Co(H}_n\mathrm{ida)(NH_3)_5}]^{(n+1)+}$ with Cr^{2+} at 25.5 °C and I = 1.0 M ($\mathrm{LiClO_4}$).

Table VI. The Individual Rate Constants of the Reactions of (Aminopolycarboxylato)pentaamminecobalt(III) Complexes with Cr^{2+}

complex	rate constant, $M^{-1}\ s^{-1}$	ref
$[\mathrm{Co(Hedta)(NH_3)_5}]^{a}$	$(4.5 \pm 0.2) \times 10^{7}$	4
$[\mathrm{Co(nta)(NH_3)_5}]^{b}$	1.5×10^{10}	17
$[\mathrm{Co(ida)(NH_3)_5}]^{+\ c,d}$	$(9.2 \pm 0.5) \times 10^{6}$	this work
$[\mathrm{Co(Hida)(NH_3)_5}]^{2+\ c,e}$	$(4.3 \pm 2.0) \times 10^{-2}$	this work
$[\mathrm{Co(H_2ida)(NH_3)_5}]^{3+\ c,f}$	$(5.0 \pm 0.7) \times 10^{-2}$	this work
$[\mathrm{Co(H_2edda)(NH_3)_5}]^{3+\ c}$	$(4.1 \pm 0.6) \times 10^{-2}$	this work
$[\mathrm{Co(OOCCH_2NH_3)(NH_3)_5}]^{3+\ a,b}$	6.4×10^{-2}	1, 2

[a] At 25.0 °C and I = 1.0 M ($\mathrm{LiClO_4}$). [b] At 25.0 °C and I = 1.0 M ($\mathrm{NaClO_4}$). [c] 25.5 °C and I = 1.0 M ($\mathrm{LiClO_4}$). [d] k_0 path (reaction 9). [e] k_1 path (reaction 10). [f] k_2 path (reaction 11).

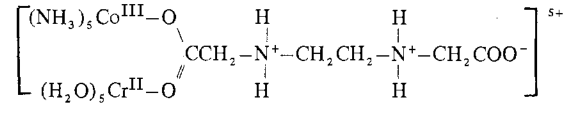
where $\alpha(\mathrm{H}) = K_1K_2 + K_1[\mathrm{H}^+] + [\mathrm{H}^+]^2$. The plots of the values of $k\alpha(\mathrm{H})$ vs. $[\mathrm{H}^+]$ gave a quadratic curve as shown in Figure 2. In order to determine the values of k_0, k_1, and k_2, we employed the least-squares method for the quadratic curve $y = \alpha + \beta[\mathrm{H}^+] + \gamma[\mathrm{H}^+]^2$, where y corresponds to the most probable values of $k\alpha(\mathrm{H})$. According to the principle, the following three simultaneous equations were solved to minimize $[rr] = \sum(y - y_{\mathrm{obsd}})^2$: $\partial[rr]/\partial\alpha = 0$, $\partial[rr]/\partial\beta = 0$, and $\partial[rr]/\partial\gamma = 0$. The values thus determined are given in Table VI.

In the reaction of $[\mathrm{Co(H}_n\mathrm{edda)(NH_3)_5}]^{(n+1)+}$ with Cr^{2+}, the values of the observed second-order rate constants, k, were independent of the hydrogen ion concentrations ($[\mathrm{H}^+]$ = 0.121–0.926 M). When the magnitude of the acid dissociation constants of $[\mathrm{Co(H}_n\mathrm{edda)(NH_3)_5}]^{(n+1)+}$ and the present experimental conditions are considered, the dominant path of the reaction can be expressed as eq 13. The second-order rate

$$[\mathrm{Co(H_2edda)(NH_3)_5}]^{3+} + \mathrm{Cr}^{2+} \xrightarrow{k} \mathrm{Co}^{2+} + 5\mathrm{NH_4}^+ + [\mathrm{Cr(H_2edda)(H_2O)_5}]^{3+} \quad (13)$$

constant is given in Table VI along with the data of the other related reactions.

Structures of the Precursor Complexes. The predominant chromium(III) product of the reaction of $[\mathrm{Cr(H}_n\mathrm{edda)(NH_3)_5}]^{(n+1)+}$ with Cr^{2+} was $[\mathrm{Cr(H_2edda)(H_2O)_5}]^{3+}$ (Table V[7]). Furthermore, the value of the rate constant is very similar to that of pentaammine(glycine)cobalt(III), $[\mathrm{Co(OOCCH_2NH_3)(NH_3)_5}]^{3+}$, with Cr^{2+}.[1,2] These facts suggest that the major part of the reaction (>96%) proceeds through the precursor complex III.



III

The reaction of $[\mathrm{Co(H}_n\mathrm{ida)(NH_3)_5}]^{(n+1)+}$ with Cr^{2+} proceeds through the three parallel reactions (reactions 9, 10, and 11) to produce $[\mathrm{Cr(ida)(H_2O)_3}]^+$ and $[\mathrm{Cr(H}_n\mathrm{ida)(H_2O)_5}]^{(n+1)+}$. The values of k_1 and k_2 are very similar to the rate constants of the reactions of $[\mathrm{Co(H_2edda)(NH_3)_5}]^{3+}$ and $[\mathrm{Co(OOCCH_2NH_3)(NH_3)_5}]^{3+}$ with Cr^{2+}. Therefore, in reactions 10 and 11, Cr^{2+} is considered to attack the carbonyl oxygen in the (carboxylato)pentaamminecobalt(III) moiety to form the precursor complex V or VI given in Scheme I. The completion of these reactions may lead to the formation of $[\mathrm{Cr(H}_n\mathrm{ida)(H_2O)_5}]^{(n+1)+}$. On the other hand, the value of k_0 is 2×10^8 times larger than those of k_1 and k_2. If a ligand bound to the cobalt(III) complex 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.[4,18] The significant rate enhancement observed in the k_0 path suggests that the chelation occurs between Cr^{2+} and the ida^{2-} bound to the $[\mathrm{Co(NH_3)_5}]^{3+}$ moiety. The ratio of the reaction

Table VII. Comparison between the Ratio of the Reaction Rate via k_0 Path to the Overall Reaction Rate and the Product Ratio of $[[\mathrm{Cr(ida)(H_2O)_3}]^+]$ to $\{[[\mathrm{Cr(ida)(H_2O)_3}]^+] + [[\mathrm{Cr(H}_n\mathrm{ida)(H_2O)_5}]^{(n+1)+}]\}$ in the Reaction of $[\mathrm{Co(H}_n\mathrm{ida)(NH_3)_5}]^{(n+1)+}$ with Cr^{2+} at 25.5 °C and $I = 1.0$ M ($\mathrm{LiClO_4}$)

$[\mathrm{H}^+]$, M	rate ratio[a]	product ratio[b]
0.090	0.810	0.797
0.121	0.718	0.692
0.150	0.635	0.608
0.196	0.516	0.484
0.276	0.361	0.320
0.523	0.143	0.131
0.938	0.051	0.055

[a] $k_0K_1K_2/(k_0K_1K_2 + k_1K_1[\mathrm{H}^+] + k_2[\mathrm{H}^+]^2)$. [b] $[[\mathrm{Cr(ida)(H_2O)_3}]^+]/\{[[\mathrm{Cr(ida)(H_2O)_3}]^+] + [[\mathrm{Cr(ida)(H_2O)_5}]^{(n+1)+}]\}$.

rate of the k_0 path to the overall reaction rate ($k_0K_1K_2/k\alpha(\mathrm{H}) = k_0K_1K_2/(k_0K_1K_2 + k_1H_1[\mathrm{H}^+] + [\mathrm{H}^+]^2)$) was found to agree well with the ratio of the yield of $[\mathrm{Cr(ida)(H_2O)_3}]^+$ to that of the total chromium(III) products containing IDA ($[[\mathrm{Cr(ida)(H_2O)_3}]^+]/([[\mathrm{Cr(ida)(H_2O)_3}]^+] + [[\mathrm{Cr(H}_n\mathrm{ida)(H_2O)_5}]^{(n+1)+}])$) as shown in Table VII. Therefore, it is concluded that $[\mathrm{Cr(ida)(H_2O)_3}]^+$ is formed exclusively by the k_0 path. The proposed paths for the reaction of $[\mathrm{Co(H}_n\mathrm{ida)(NH_3)_5}]^{(n+1)+}$ with Cr^{2+} are summarized in Scheme I.

Acknowledgment. The authors wish to thank the Ministry of Education for Scientific Research Grant-in-Aid No. 147043.

Registry No. $[\mathrm{Co(Hida)(NH_3)_5}](\mathrm{ClO_4})_2$, 72016-80-9; $[\mathrm{Co(H_2edda)(NH_3)_5}](\mathrm{ClO_4})_3$, 72016-83-2; $\mathrm{Cr(H_2O)_6}^{2+}$, 20574-26-9; $\{\mathrm{Cr(H_2ida)(H_2O)_5}]^{3+}$, 72016-84-3; $\{\mathrm{Cr(H_2edda)(H_2O)_5}]^{3+}$, 72016-85-4; $[\mathrm{Co(ida)(NH_3)_5}]^+$, 72016-78-5; $[\mathrm{Co(H_2ida)(NH_3)_5}]^{3+}$, 72016-86-5; $[\mathrm{Cr(ida)(H_2O)_3}]^+$, 72059-09-7; $[\mathrm{Cr(edda)(H_2O)_2}]^+$, 32151-23-8; $[\mathrm{(NH_3)_5Co(Hida)Co(NH_3)_5}](\mathrm{ClO_4})_5$, 72016-89-8; $[\mathrm{(NH_3)_5Co(H_2edda)Co(NH_3)_5}](\mathrm{ClO_4})_6$, 72016-92-3.

Supplementary Material Available: Table I listing analytical data, Table II listing numerical data for the electronic spectra, and Table V listing product analyses of the reaction of $[\mathrm{Co(H}_n\mathrm{edda)(NH_3)_5}]^{(n+1)+}$ with Cr^{2+} (3 pages). Ordering information is given on any current masthead page.

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Preparation and Properties of $\mathrm{FeO(O_2C_2H_4)_{1/2}}$

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Received April 24, 1979

An organic derivative of the layer compound FeOCl was obtained by the reaction of an intercalated compound $\mathrm{FeOCl(4\text{-}NH_2py)_{1/4}}$ and ethylene glycol $\mathrm{C_2H_4(OH)_2}$ at 110 °C for 6 days. The reaction product was a brown crystal of flake shape. Its basal spacing was 14.5 Å when the product was still in ethylene glycol, but it shrank to 10.98 Å by washing with acetone. The chemical composition of the final product was $\mathrm{FeO(O_2C_2H_4)_{1/2}}$. Mössbauer isomer shift and quadrupole splitting were respectively 0.38 mm/s and 0.59 mm/s at room temperature. Thermal analysis and the infrared spectrum suggested a substitution of ethylene glycolate anions $\mathrm{O_2C_2H_4}^{2-}$ for chloride ions in the FeOCl layer. A possible layer structure derived from FeOCl is proposed.

Introduction

Some layer compounds intercalate many kinds of organic molecules and metal ions. Intercalation compounds are divided into three classes according to their bonding characteristics between host layer and guest molecules. One is the sorption-type complex in which organic molecules are loosely bonded to host layers by hydrogen bonds, ion–dipole interactions, charge-transfer bonds, and so on.[1-3] Transition-metal dichalcogenides are typical of charge-transfer type complexes. Some clay–organic complexes are representative of the other class of intercalation compounds.[4,5] In these complexes organic cations are bonded to host aluminosilicate layers by electrostatic interaction. The last type of complex is organic derivatives of layered inorganic compounds. Organic molecules in the derivatives are directly bonded to the host layers by covalent bonds or by replacing the outermost atoms of the layers with organics. Few examples of this kind of complex have been reported.[6,7] We have reported the synthesis of $\mathrm{FeOOCH_3}$ with a layer structure derived from the substitution of $\mathrm{OCH_3}^-$ ions for chloride ions in FeOCl.[8]

The oxychloride FeOCl has layers formed by the sharing of O–O and O–Cl edges of *cis*-$\mathrm{FeCl_2O_4}$ octahedra. Its layers pack together so that the Cl^- ions on the outsides of adjacent layers are closely packed. In FeOCl, there are layers similar to those in γ-FeOOH with Cl^- ions instead of OH^- ions. The chloride ions can really be substituted by $\mathrm{NH_2}^-$, $\mathrm{OCH_3}^-$, and so on without the reconstruction of the other part of the layers. This unaltered part of the layer is hereafter called the FeO double layer since it can be assumed to be a double sheet formed with Fe and O.

One of the interesting approaches is the preparation of another type of organic derivative of FeOCl, in which organic molecules such as diols bridge two adjacent FeO double layers. This paper deals with the reaction of $\mathrm{FeOCl(4\text{-}NH_2py)_{1/4}}$ with ethylene glycol, hereafter denoted as EG, and the structural characterization of the product.

Experimental Section

Preparation. Reddish violet and thin, bladelike FeOCl crystals were prepared by heating the mixture of α-$\mathrm{Fe_2O_3}$ and $\mathrm{FeCl_3}$ in a sealed Pyrex tube at 370 °C for 2 days. FeOCl was reacted with 4-aminopyridine, hereafter called 4-AP, in acetone solution at 110 °C

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(1) Gamble, F. R.; Osieki, J. H.; Disalvo, F. J. *J. Chem. Phys.* **1971**, *55*, 3525.
(2) Subba Rao, G. V.; Shafer, M. W.; Kawarazaki, S.; Toxen, A. M. *J. Solid State Chem.* **1974**, *9*, 323.
(3) Kanamaru, F.; Yamanaka, S.; Koizumi, M.; Nagai, S. *Chem. Lett.* **1973**, 373.
(4) MacEwan, D. M. C. *Trans. Faraday Soc.* **1948**, *44*, 349.
(5) Grim, R. E. "Clay Mineralogy"; McGraw-Hill: New York, 1968; Chapter 10.
(6) Yamanaka, S. *Inorg. Chem.* **1976**, *15*, 2811.
(7) Hagenmuller, P.; Portier, J.; Barbe, B.; Bouclier, P. *Z. Anorg. Allg. Chem.* **1967**, *355*, 209.
(8) Kikkawa, S.; Kanamaru, F.; Koizumi, M. *Inorg. Chem.* **1976**, *15*, 2195.

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