

Figure 5. Possible structure of the trihydroxy-lead cryptate species formed at or prior to the rate-determining step of the hydroxide-assisted dissociation of lead(II) cryptates.

1. Since no appreciable concentration of $\text{Pb}(\text{Cryp})(\text{OH})_2$ was detected, and since the second stepwise constant for the reaction of $\text{Eu}(2.2.1)^{3+}$ with OH^- is $\sim 13\,000$ -fold smaller than the first stepwise constant,³ it is reasonable to assume that $K_{\text{PbC}(\text{OH})_2}[\text{OH}^-] < 1$. If this is the case, eq 8 may be reduced to give

$$k_{\text{obsd}} = k_1 K_{\text{PbC}(\text{OH})_2} [\text{OH}^-]^2 \quad (9)$$

which is consistent with the observed results for $[\text{OH}^-] \geq 0.005$ M. Although the $\text{Pb}(\text{Cryp})\text{OH}^+$ species is stable with respect to dissociation in the pH range 8.5–10.5, the complex readily dissociates in the presence of excess hydroxide ion, $\text{pH} \geq 11.5$. The addition of a second and third hydroxide ion to $\text{Pb}(\text{Cryp})\text{OH}^+$ lowers the overall charge of the complex, facilitating removal of the metal ion from the cryptate cavity. Yee et al. proposed a

similar argument to explain the enhanced rate of dissociation of lanthanide cryptates in the presence of OH^- and F^- .³ Since the major species of the final product mixture, $\text{Pb}(\text{OH})_3^-$, and the transition-state complex, $(\text{Pb}(\text{Cryp})(\text{OH})_3)^{\ddagger}$, both contain three hydroxide ions, it seems reasonable that the lead ion is partially removed from the cryptate in the transition-state complex. If the $\text{Pb}-\text{O}(\text{ether})$ bond(s) are broken in one bridge of the cryptate, the resulting intermediate would be similar to a metal-crown ether complex with the lead ion sitting on or in one face of the cryptand. Figure 5 shows one possible structure of such an intermediate. The bound hydroxides would compensate for the energy required to break the $\text{Pb}-\text{O}(\text{ether})$ bonds. Unlike the case of proton-assisted dissociation, no conformational change at a bridgehead nitrogen atom is required.^{1,2,4} The preceding considerations are consistent with the fact that the value of k_{OH} for $\text{Pb}(2.2.1)^{2+}$ is ~ 150 times greater than the corresponding value for $\text{Pb}(2.2.2)^{2+}$ even though $\text{Pb}(2.2.1)^{2+}$ is slightly more stable than $\text{Pb}(2.2.2)^{2+}$.²⁹ In the case of $\text{Pb}(2.2.1)^{2+}$ only one $\text{Pb}-\text{O}(\text{ether})$ bond must break to form a pseudo-crown type intermediate whereas two must break for $\text{Pb}(2.2.2)^{2+}$.

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Registry No. $\text{Pb}(2.2.2)^{2+}$, 61624-56-4; $\text{Pb}(2.2.1)^{2+}$, 98970-55-9; $\text{Pb}(2.2.2)\text{OH}^+$, 111437-94-6; OH^- , 14280-30-9.

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Formation and Reactions of an Organochromium(III)-Acetamido-Pentaamminecobalt(III) Complex

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The reaction of $(\text{NH}_3)_5\text{CoNHC}(\text{OH})\text{CH}_2\text{I}^{3+}$ with chromium(II) proceeds in a biphasic manner. The first stage yields $(\text{H}_3\text{N})_5\text{CoNHC}(\text{OH})\text{CH}_2\text{Cr}(\text{OH})_2^{5+}$ (II) as the major product, and the next stage produces $(\text{H}_2\text{O})_5\text{Cr}-\text{OC}(\text{NH}_2)\text{CH}_2\text{Cr}(\text{OH})_2^{5+}$ (I) as cobalt(III) is reduced to Co(II). For the first and second stages, respectively, $k_{\text{obsd}} = (1.16 \pm 0.05 \text{ M}^{-1} \text{ s}^{-1})[\text{Cr}^{2+}]$ and $((8.8 \pm 0.25) \times 10^{-3} \text{ s}^{-1})[\text{Cr}^{2+}][\text{H}^+]^{-1}$, both in 1.0 M $\text{LiClO}_4/\text{HClO}_4$ at 25 °C. The reaction of II with Hg^{2+} has been studied, and the reactivity of the dimer is compared to that of monomer analogues and the $\text{Co}-\text{NCCH}_2-\text{Cr}$ dimer. The acidolysis of II is unusual in that it yields two products, which are linkage isomers of II at Co and Cr, respectively. In each case the metal atoms move to the carboxamide oxygen in the products.

Introduction

Chromium(II) reacts with organic halides (RX) to form organochromium(III) species $(\text{RCr}(\text{OH})_2)_3^{2+}$ by what is believed to be a halide atom abstraction mechanism.² It also has been shown that $(\text{NH}_3)_5\text{CoNCCH}_2\text{I}^{3+}$ reacts with chromium(II) to produce $(\text{NH}_3)_5\text{Co}-\text{NCCH}_2-\text{Cr}(\text{OH})_2^{5+}$.³ It was found that the supposed radical intermediate $\{(\text{NH}_3)_5\text{CoNCCH}_2^{3+}\}$ did not undergo intramolecular electron transfer to give cobalt(II) but rather gave the $\text{Co}(\text{II})-\text{Cr}(\text{III})$ dimer exclusively.

Recently the reaction of chromium(II) and $\text{ICH}_2\text{CO}(\text{NH}_2)$ has been shown⁴ to yield a mixture of $(\text{H}_2\text{O})_5\text{CrOC}(\text{NH}_2)\text{CH}_3^{3+}$ and $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CO}(\text{NH}_2)^{2+}$. The latter species is a weak base for which the conjugate acid has a $\text{p}K_a$ of 1.15. The present study concerns the reaction of $(\text{NH}_3)_5\text{CoNHC}(\text{OH})\text{CH}_2\text{I}^{3+}$ ^{5,6} and

Table I. Kinetic Data for the Chromium(III) Reduction of $(\text{NH}_3)_5\text{CoNHC}(\text{O})\text{CH}_3^{2+}$ in Aqueous Acid^a

$10^2[\text{Cr}(\text{II})]$, M	$[\text{H}^+]$, M	$10^5 k_{\text{exptl}}$, s^{-1}		$10^5 k_{\text{exptl}}$, s^{-1} ($10^5 k_{\text{calcd}}$, s^{-1})
		346 nm	476 nm	
3.20	0.0904	2.84	2.74	2.85 (2.93)
1.60	0.122	1.18	1.12	1.10 (1.09)
3.20	0.122	2.35	2.21	2.19 (2.17)
3.20	0.188	1.53	1.43	1.54 (1.41)

^a $[\text{Co}(\text{III})] = 1.0 \times 10^{-3}$ M, ionic strength = 0.973 M ($\text{HClO}_4-\text{LiClO}_4$), 24.7 °C. ^b Values in parentheses assume $k_1 = 0$ and $k_2 = 8.28 \times 10^{-5} \text{ s}^{-1}$ in eq 2.

chromium(II). The products have been separated and quantified and the reactivity of the main product $(\text{NH}_3)_5\text{CoNH}(\text{OH})-\text{CCH}_2\text{Cr}(\text{OH})_2^{5+}$ has been investigated. The results provide comparisons to the analogous nitrile and free organic halide reactions.

The kinetics of the chromium(II) reduction of the acetamido complex of pentaamminecobalt(III) has also been studied. These

- (1) Permanent address: Department of Chemistry, University of Rajasthan, Jaipur, India.
- (2) Espenson, J. H. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 1.
- (3) Kupferschmidt, W. C.; Jordan, R. B. *J. Am. Chem. Soc.* **1984**, *106*, 991.
- (4) Kita, P.; Jordan, R. B. *Inorg. Chem.* **1986**, *25*, 4791.
- (5) The acetamido complex is a weak acid and recent work⁶ indicates that the site of protonation is on the carbonyl oxygen. This formulation has been adopted here for the iodoacetamido and other carboxamido complexes.

- (6) (a) Fairlie, D. P. Ph.D. Dissertation, University of New South Wales, 1983. (b) Buckingham, D. A.; Keene, F. R.; Sargeson, A. M. *J. Am. Chem. Soc.* **1973**, *95*, 5649.

Table II. Summary of Products from the Reaction of $(\text{H}_3\text{N})_5\text{CoNHC}(\text{OH})\text{CH}_2\text{I}^{3+}$ and Cr(II)

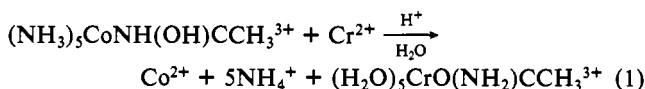
band	[eluent], ^a M	color	λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)	10^4 mol of tot. Co	10^4 mol of tot. Cr	species
1	0.3	green	474 (38.6), 650 (35.3)	0.27	0.97	Co^{2+} , $(\text{H}_2\text{O})_5\text{CrI}^{2+}$
2	0.4	blue-green	1.70	$\text{Cr}(\text{OH})_2^{3+}$
3	0.4	yellow	...	0.13	0.20	reactant
4	0.5	gray-pink	414 (36.4), 560 (21.2)	...	0.53	I
5	0.8	green	418 (25.3), 581 (17.0)	...	2.31	$\text{Cr}(\mu\text{-OH})_2\text{Cr}^{4+}$
6	1.0	red	414 (103), 470 (72)	0.51	0.81	II
7	1.0	red	...	1.55	1.41	II
8	2.5	green	retained on resin	...	1.95	Cr-polymer

^a Ionic strength made up from 0.10 M HClO_4 and various concentrations of NaClO_4 , eluting from Sephadex SP C-25 at 4 °C.

results provide useful information on the reduction properties of the cobalt(III) in the iodoacetamido complex and provide an interesting comparison to earlier work on the formamido complex.⁷

Results

Reduction of $(\text{NH}_3)_5\text{CoNH}(\text{OH})\text{CCH}_3^{3+}$ by Cr^{2+} . This reaction has been studied to give an indication of the probable reactivity of the iodoacetamido complex toward direct reduction of cobalt(III). The overall reaction is given by eq 1. The reaction is



presumed to proceed with ligand transfer based on results with the formamido system,⁷ but this feature has not been established because interest was primarily in the reaction kinetics for comparative purposes.

The reaction rate has been monitored at the two absorption maxima for the cobalt(III) complex, and the results are summarized in Table I. A least-squares fit of the data to the k_{obsd} expression defined by eq 2 gives $k_1 = (1 \pm 1.4) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$

$$-d[\text{Co(III)}]/dt = k_{\text{obsd}}[\text{Co(III)}] = (k_1 + k_2[\text{H}^+]^{-1})[\text{Cr(II)}][\text{Co(III)}] \quad (2)$$

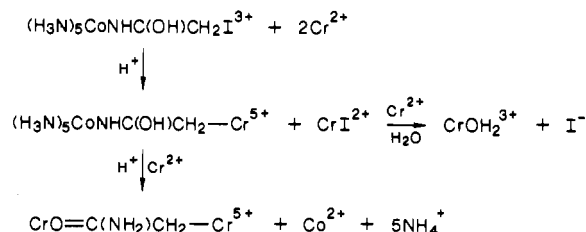
and $k_2 = (7.1 \pm 1.7) \times 10^{-5} \text{ s}^{-1}$.⁸ Clearly k_1 is not defined statistically, and the results can be described by assuming that $k_1 = 0$, in which case $k_2 = (8.3 \pm 0.4) \times 10^{-5} \text{ s}^{-1}$. The calculated results from the two fits are compared in Table I.

Reaction of $(\text{NH}_3)_5\text{CoNHC}(\text{O})\text{CH}_2\text{I}^{3+}$ and Chromium(II). Products. Spectrophotometric observations of this reaction show that there are at least two processes occurring with different rates. The more rapid stage causes an increase in absorbance throughout the visible region with the largest change between 400 and 470 nm. The slower stage gives an absorbance decrease at wavelengths below an isobestic point at ~ 550 nm, with a small increase between 550 and ~ 600 nm and a small decrease between 620 and 700 nm. In a solution containing 0.032 M Cr(II), 0.10 M HClO_4 , and 1×10^{-3} M cobalt(III), the absorbance reaches a maximum in ~ 60 s, and then the slower stage changes occur with a half-time of 3.2×10^2 s. As noted below, both stages show a first-order dependence on $[\text{Cr(II)}]$.

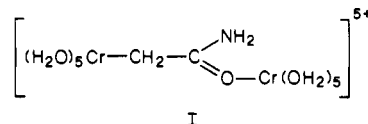
The products of the faster stage were separated by cation-exchange chromatography, and the results are summarized in Table II. The first colored fraction (band 1) is identified as $(\text{H}_2\text{O})_5\text{CrI}^{2+}$ from the electronic spectrum and elution characteristics. This band also contains some cobalt(II). Band 2 is blue-green and contains only chromium. The color and elution properties suggest that this species is $\text{Cr}(\text{OH})_2^{3+}$. The third band is pale yellow and contains both cobalt and chromium. The latter is assumed to be tailing from the preceding band. The cobalt constitutes about 5% of the total in the system, and could be unreacted starting material. Very slow elution was necessary to achieve even partial separation of bands 2 and 3. As a result the products were obtained in solutions too dilute to provide meaningful electronic spectra.

Band 4 is gray-pink, contains no cobalt, and must have a charge $>+3$ from the ion-exchange properties. The pink color and ab-

Scheme I



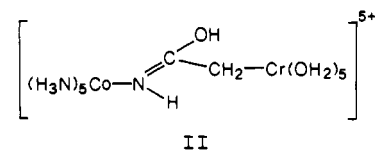
sorbance maximum in the 410–415 region are typical of organochromium species. This product reacts rapidly with Hg(II) to lose the pink color and the absorbance at 414 nm. The gray-pink product is assigned to I. Formation of I requires that



the cobalt(III) has been reduced to cobalt(II). The amount of cobalt(II) in band 1 (0.27×10^{-4} mol) is close to half of the amount of chromium in band 4 (0.53×10^{-4} mol), as expected if the two products are related.

Band 5 has the ion-exchange behavior and electronic spectrum of $(\text{H}_2\text{O})_4\text{Cr}(\mu\text{-OH})_2\text{Cr}(\text{OH})_2^{4+}$,⁹ which is the major product of oxidation of chromium(II) by dioxygen.

The major product appears in bands 6 and 7 and is assigned as II. The absorbance maxima at 414 and 470 nm are typical



of the Cr-C and Co-N chromophoric centers, respectively. The excess chromium in band 6 is thought to be due to tailing from band 5, but the Co:Cr ratio in band 7 of 1.1 is close to the expected 1.0.

The final band was not eluted from the column but was analyzed by batch treatment of the resin. This band contains only chromium and is believed to be a product of the oxidation of excess chromium(II) by dioxygen. The total excess chromium should correspond to that in band 8 plus band 5 plus $\sim 0.5 \times 10^{-4}$ mol in band 2 as described in the Experimental Section. This gives a total of 4.76×10^{-4} mol compared to the 5.0×10^{-4} mol expected for a 2:1 stoichiometry for iodide abstraction. The difference is accounted for by the 0.27×10^{-4} mol of chromium(II) that must be used to produce the cobalt(II) in band 1.

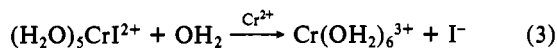
The qualitative spectrophotometric observations and products can be understood in terms of the reactions in Scheme I. The first stage of the reaction produces II, and this is the major cobalt product if the reaction is quenched when the absorbance reaches a maximum. The slower reaction produces I and cobalt(II), and some of these are observed in the products because the two stages are not completely separated in time. Aquation of $(\text{H}_2\text{O})_5\text{CrI}^{2+}$ also occurs during the slower stage.

(7) Balahura, R. J.; Jordan, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 1533.
(8) Error limits are uncertainties at the 95% confidence level.

(9) Ardon, M.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3197.

Kinetics. The more rapid stage of the reaction is first order in chromium(II) and independent of $[H^+]$ (0.10–1.00 M) with a specific rate constant of $1.16 \pm 0.05 \text{ M}^{-1} \text{ s}^{-1}$. This rate law does not show the $[H^+]^{-1}$ dependence found for reduction of $(\text{NH}_3)_5\text{CoNHC(O)CH}_3^{2+}$. This is consistent with the product analysis, which also indicates that the first reaction is iodine atom abstraction rather than cobalt(III) reduction.

The slower reaction appears to be first order in $[\text{Cr(II)}]$ and inverse first order in $[H^+]$. But the observed rate constants vary significantly with the observation wavelength. This may be attributed to decomposition of the two products from the rapid stage according to the independent reactions



The minor products described above are consistent with these possibilities. The aquation of the iodo complex is known¹⁰ to be catalyzed by chromium(II) with an inverse acid dependence and rate constants qualitatively consistent with those observed.

Reduction of II by Chromium(II). In order to study the kinetics of eq 4, species II was prepared and separated from other species essentially as described above, but on a preparative scale.

The reduction of II ($1 \times 10^{-3} \text{ M}$) was studied at 400 and 470 nm as a function of $[\text{Cr(II)}]$ (1.54×10^{-2} to $3.2 \times 10^{-2} \text{ M}$) and $[H^+]$ (8.3×10^{-1} to 0.203 M) in $1 \text{ M LiClO}_4/\text{HClO}_4$ at 25°C . The observed pseudo-first-order rate constant is given by eq 5.⁸

$$k_{\text{obsd}} = (8.76 \pm 0.25) \times 10^{-3} [\text{Cr(II)}][H^+]^{-1} \quad (5)$$

The reaction was shown to produce cobalt(II), but it was not possible to isolate the expected product I from the products of oxidation of excess chromium(II). Nonetheless, the facts that cobalt(II) is a product and that the rate law has the same form as that for reduction of the acetamido complex are good evidence that the observed reaction is described by eq 4.

Reaction of II with Hg(II). Organochromium(III) species are known to undergo electrophilic attack by Hg(II) to form organomercury species.² As expected, II reacts rapidly with Hg(II), and the reaction was studied at 415 nm by stopped-flow spectrophotometry with $[\text{II}] \sim 4 \times 10^{-4} \text{ M}$, $[\text{Hg(II)}]$ between 1.0×10^{-2} and $2.5 \times 10^{-2} \text{ M}$, and $[H^+]$ between 0.16 and 0.65 M. The observed pseudo-first-order rate constant is given by eq 6.^{8,11}

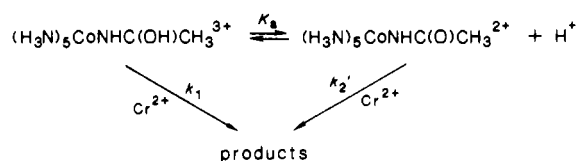
$$k_{\text{obsd}} = (4.6 \pm 0.5 + (1.0 \pm 0.16)/[H^+])[Hg(II)] \quad (6)$$

Acidolyses of II. It was initially anticipated that thermal decomposition of the dimer would cleave the Cr–C bond heterolytically to give $\text{Cr}(\text{OH})_6^{3+}$ and the cobalt(III)–acetamido complex. Homolytic cleavage was not expected for a system with an electron-withdrawing substituent on the C attached to Cr, and this was confirmed by the absence of cobalt(II) in the decomposition products. The latter would be formed by Cr(II) reduction after homolysis.

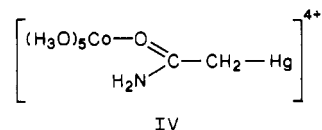
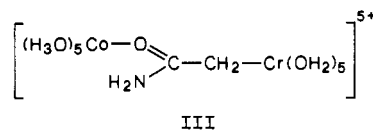
Preliminary experiments showed that the dimer decomposes in dilute acid ($\sim 0.1 \text{ M HClO}_4$) with a half-time of $\sim 4 \text{ h}$ at ambient temperature. However, the electronic spectrum of the product did not correspond to that of a mixture of $\text{Cr}(\text{OH})_6^{3+}$ and $(\text{NH}_3)_5\text{CoNHC(O)CH}_3^{3+}$. Instead the absorbance in the 410 nm region was much too high, and the peak around 470 nm had shifted to above 500 nm. Product analysis (Experimental Section) revealed pink and greenish yellow products.

For the pink product, the color and absorbance maximum at 414 nm are indicative of a Cr–C bond. This was confirmed by noting that this species reacts rapidly with Hg(II) to give a product with maxima at 338 and 496 nm with absorption coefficients of 70.8 and $62.0 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The shift from 470 nm in the original dimer to 496 nm in the Hg(II) product is typical of

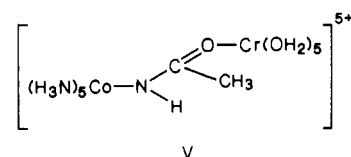
Scheme II



N- to O-linkage isomerism at cobalt(III). Therefore the decomposition product is assigned to III, which reacts with Hg(II) to give IV.



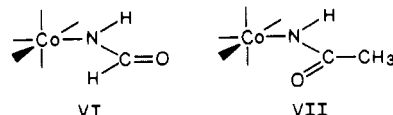
The electronic spectrum of the greenish yellow decomposition product is consistent with the formulation shown in V.



The product distribution, based on chromate analysis, is 60% III and 40% V. The kinetics of the decomposition was studied at various acidities (0.025–0.40 M) in $1 \text{ M LiClO}_4/\text{HClO}_4$ at 25°C . The observed rate constant was independent of wavelength (between 420 and 650 nm) and acidity and gave an average value of $(5.83 \pm 0.32) \times 10^{-5} \text{ s}^{-1}$. The product ratio then can be used to calculate a rate constant for linkage isomerization at Co(III) of $2.3 \times 10^{-5} \text{ s}^{-1}$ and at Cr(III) of $3.5 \times 10^{-5} \text{ s}^{-1}$.

Discussion

The rate law for reduction of the acetamido complex is consistent with the reaction sequence in Scheme II, which gives $k_{\text{obsd}} = (k_1[H^+] + k_2'K_a)[\text{Cr}^{2+}]/(K_a + [H^+])$ and reduces to the form of eq 2 since $[H^+] \gg K_a$. As already noted, k_1 is not defined by the data but $k_2 = k_2'K_a$ from Scheme II. The known value of K_a^{6b} can be used to calculate $k_2' = 0.08 \text{ M}^{-1} \text{ s}^{-1}$. This value is ~ 20 times smaller than that for the analogous formamido complex. Barrett et al.¹² have noted a similar reactivity difference for the chromium(II) reduction of the acetato and formato complexes ($k = 0.35$ and $7.0 \text{ M}^{-1} \text{ s}^{-1}$ respectively at 25°C , $I = 1.0 \text{ M}$). It has been suggested that this reactivity difference is due to a conformation preference that causes the C=O to be exposed in the formato complex but tucked in next to the cis NH_3 ligands in the acetato complex due to the relative steric bulk of $\text{CH}_3 > \text{O} > \text{H}$. The same effect can operate for the carboxamido complexes to give the preferred conformers as VI and VII.



From the standpoint of the results on the iodoacetamido complex, the acetamido rate law indicates that cobalt(III) reduction should proceed with a dominant inverse dependence on $[H^+]$.

The initial reaction in the $\text{Cr(II)} + (\text{NH}_3)_5\text{CoNHC(OH)CH}_3^{3+}$ system does not show any dependence on $[H^+]$. This observation, along with the products, shows that cobalt(III) is not being reduced and the reaction is due to iodine atom abstraction.

(10) (a) Pennington, D. E.; Haim, A. *J. Am. Chem. Soc.* **1966**, *88*, 3450; *Inorg. Chem.* **1967**, *6*, 2138. (b) Adin, A.; Doyle, J.; Sykes, A. G. *J. Chem. Soc. A* **1967**, 1504.
(11) The data analysis included six to eight kinetic runs under each set of concentration conditions.

(12) Barrett, M. B.; Swinehart, J. H.; Taube, H. *Inorg. Chem.* **1971**, *10*, 1983.
(13) Kupferschmidt, W. C.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 3469.

Table III. Summary of Kinetic Results for Reactions of Cobalt(III)-Alkylchromium(III) Dimers and Analogous Monomers

reaction	$k_{\text{obsd}},^a \text{ M}^{-1} \text{ s}^{-1}$
$\text{Cr}^{2+} + (\text{H}_3\text{N})_5\text{CoNHC}(\text{OH})\text{CH}_2-\text{Cr}^{5+}$	$8.8 \times 10^{-3}[\text{H}^+]^{-1}$
$\text{Cr}^{2+} + (\text{H}_3\text{N})_5\text{CoNHC}(\text{OH})\text{CH}_3^{3+}$	$8.3 \times 10^{-3}[\text{H}^+]^{-1}$
$\text{Cr}^{2+} + (\text{H}_3\text{N})_5\text{CoNCCH}_2-\text{Cr}^{5+}$	$2.4 \times 10^{-3}{}^b$
$\text{Cr}^{2+} + (\text{H}_3\text{N})_5\text{CoNCCH}_3^{3+}$	$9.4 \times 10^{-3}{}^c$
$\text{Hg}^{2+} + (\text{H}_3\text{N})_5\text{CoNHC}(\text{OH})\text{CH}_2-\text{Cr}^{5+}$	$4.6 + 1.0[\text{H}^+]^{-1}$
$\text{Hg}^{2+} + \text{H}_2\text{NC}(\text{O})\text{CH}_2-\text{Cr}^{2+}$	$2.5 \times 10^3{}^d$
$\text{Hg}^{2+} + (\text{H}_3\text{N})_5\text{CoNCCH}_2-\text{Cr}^{5+}$	$3.5 \times 10^{-2} + 5.8 \times 10^{-4}[\text{H}^+]^b$
$\text{Hg}^{2+} + \text{NCCH}_2-\text{Cr}^{2+}$	8.7^b

^a Values in 1 M HClO₄-LiClO₄ at 25 °C unless otherwise indicated. ^b Reference 3. ^c Kupferschmidt, W. C.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 3469. In 0.5 M HClO₄-LiClO₄. ^d Reference 4: in 1 M HClO₄-NaClO₄.

The rate constant for iodine atom abstraction from the cobalt(III)-iodoacetamido complex ($1.16 \text{ M}^{-1} \text{ s}^{-1}$) is about twice that for free iodoacetamide ($0.56 \text{ M}^{-1} \text{ s}^{-1}$).⁴ A similar but larger reactivity difference has been observed in the iodoacetone nitrile systems (45.2 versus $9.2 \text{ M}^{-1} \text{ s}^{-1}$). The lesser effect of complexing on iodoacetamide may be due, at least in part, to the different tautomeric forms of the free and complexed ligand.⁵

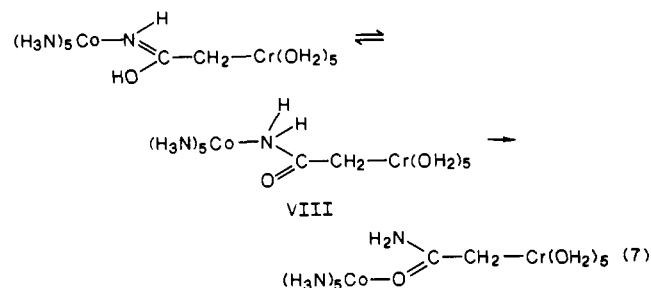
The reactivity of the cobalt-alkylchromium dimer (II) toward Cr(II) and Hg(II) is compared to that of other systems in Table III. One noteworthy feature of these results is that the acetamide dimer reacts with Cr(II) 100 times more rapidly than the cobalt(III) acetamido monomer, while in the acetonitrile system the dimer is ~ 4 times less reactive than the monomer. Both the acetamide monomer and dimer reactions with Cr(II) show an $[\text{H}^+]^{-1}$ dependence, which can be explained by a scheme analogous to Scheme II. Then the rate constants in Table III are equal to k_2/K_a (Scheme II). The larger value for the dimer could be ascribed to a larger K_a for the dimer compared to the monomer, and if this is the only factor then $K_a \gtrsim 0.1 \text{ M}$ for the dimer. However, then it would not longer be true that $[\text{H}^+] \gg K_a$ as required for Scheme II to explain the experimental rate law. It also seems unlikely that the alkylchromium substituent would greatly increase the K_a of the dimer since $(\text{H}_2\text{O})_5\text{Cr}-\text{CH}_2\text{C}(\text{O})\text{NH}_2^{2+}$ actually undergoes protonation in the 0.05–0.20 M $[\text{H}^+]$ range.⁴

The acid-independent rate constant for reaction of Hg(II) with the dimers is smaller than that of the monomer in both the carboxamide and nitrile systems. This may be attributed to the charge, steric, and/or electron-withdrawing effects of the $(\text{N}-\text{H}_3)_5\text{Co}$ substituent making the dimer less reactive to electrophilic attack. The lower electron-withdrawing power of the carboxamide substituent may account for its greater reactivity compared to the nitrile. Similar arguments have been used in connection with electrophilic susceptibility in these systems.²

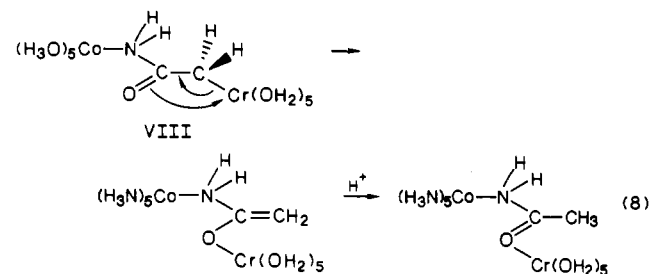
The $[\text{H}^+]^{-1}$ term in the Hg(II) rate law for the carboxamide dimer could be attributed to the reaction of the conjugate base of the carboxamide. A similar kinetic term appears for the nitrile dimer where there is no obvious ionizable proton on the bridging ligand. It was suggested originally that this term arose from ionization of an H₂O ligand on chromium(III), and that remains a possibility with the carboxamido complex also. The fact that the numerical values of the acid-independent and acid-dependent rate constants differ by a factor of 60 for the nitrile and 4.6 for the carboxamide may indicate that a different site of ionization is involved with the carboxamide (i.e. the bridging ligand).

The acidolysis of II is unusual in that it produces neither $\text{Cr}(\text{OH})_6^{3+}$ or $(\text{H}_3\text{N})_5\text{CoOH}_2^{3+}$. Rather, the two products appear to arise from independent linkage isomerism at the two metal centers. This type of N- to O-isomerism at $(\text{H}_3\text{N})_5\text{Co}^{3+}$ has been observed by Dixon et al.¹⁴ for the dimethylurea complex and by Fairlie^{6a} for the acetamide complex. The reaction is faster with dimethylurea and it was suggested that this could be due to

preferred protonation at the coordinated -NH. Fairlie has noted that the protonated conformer analogous to VII also would be more likely to show linkage isomerism because of the proximity of the Co and carbonyl oxygen. Therefore the mechanism of eq 7 would be consistent with the current observations on the linkage isomerism at cobalt(III).



Isomerism at the alkyl-chromium center has been observed during the acidolysis of $(\text{H}_2\text{O})_5\text{CrCH}_2\text{C}(\text{O})\text{NH}_2^{2+}$. In acidic solution, the latter is protonated and the linkage isomerism and other hydrolysis products suggest N-protonation so that $(\text{H}_2\text{O})_5\text{CrCH}_2(\text{O})\text{C}(\text{NH}_3)^{3+}$ and VIII (eq 7) formally are analogous in the degree of substitution on the carboxamide nitrogen. Nonetheless, apparently exclusive movement of chromium to the carbonyl oxygen in VIII is surprising in view of the proximity of the $(\text{H}_3\text{N})_5\text{Co}^{3+}$ to this site. The essentially tetrahedral geometry at the α -carbon does allow the chromium to be close to the carbonyl oxygen, and the isomerization could occur as shown in eq 8.



Experimental Section

Materials. (Iodoacetone nitrile)pentaamminecobalt(III) perchlorate (IX) was prepared as described previously.³ The iodoacetamido complex was prepared by alkaline hydrolysis of IX. A 0.2-g sample of IX was dissolved in 10.5 mL of $3.8 \times 10^{-2} \text{ M}$ NaOH, the solution was immediately filtered, and the product was precipitated by addition of sodium perchlorate. The mixture was cooled in ice, and then the product was collected by filtration and washed with ethanol (yield 78%). The complex was recrystallized from warm water (pH ~ 9.2) by adding sodium perchlorate and cooling and collecting as before.

The electronic spectrum of the iodoacetamido complex in 0.01 M NaOH has maxima at 485 and 346 nm with molar absorptivity coefficients of 77.8 and $98.8 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. In 0.1 M HClO₄, the same parameters are 480 and 336 nm and 65.9 and $86.8 \text{ M}^{-1} \text{ cm}^{-1}$, respectively.

In some experiments the iodoacetamido complex was prepared from IX by using a 10% excess of NaOH, and then the solution was used directly without isolation of the solid. In the various studies reported here both sources were used without any significant difference in results.

The preparation and handling of standard reagents have been described previously.^{3,13}

Instrumentation. The electronic spectra for species characterization were recorded on a Cary 219 spectrophotometer. The absorbance-time data for kinetic measurements were collected on a Hewlett-Packard 8451 diode array spectrophotometer and analyzed by nonlinear least-squares methods to obtain the observed rate constants. The stopped-flow studies were done on a modified Aminco-Morrow system described previously.¹³

Products of Cr(II) Reduction. The reaction products after the faster stage were determined from the reaction of $2.3 \times 10^{-3} \text{ M}$ $(\text{NH}_3)_5\text{CoNHC}(\text{O})\text{CH}_2\text{I}^{3+}$ with $9.6 \times 10^{-3} \text{ M}$ chromium(II) in 0.40 M perchloric acid in a 100-mL sample. A large excess of chromium(II) was avoided in order to minimize complications caused by minor products from the reaction of dioxygen with excess chromium(II). Under these conditions the absorbance of the solution reaches a maximum in 10 min, and at that time the solution was exposed to air, diluted by an equal

(14) Dixon, N. E.; Fairlie, D. P.; Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 4038.

volume of ice-cold water, and charged onto a column of Sephadex SP-C25 at 4 °C. The products were eluted by using 0.10 M HClO₄ with increasing concentrations of NaClO₄. The total cobalt and chromium concentrations were determined in each fraction, and the electronic spectrum was recorded whenever possible. The observations are summarized in Table II.

The total chromium in bands 1 through 3 is 2.87×10^{-4} mol. This amount should equal the 2.3×10^{-4} mol required for iodide abstraction. The excess Cr(OH₂)₆³⁺ is believed to come as a minor product of air oxidation of chromium(II). For the expected overall stoichiometry, $2 \times 2.3 \times 10^{-4}$ mol of chromium(II) should be consumed leaving an excess of 5.0×10^{-4} mol. Previous experience indicates that about 10% of the latter will appear as Cr(OH₂)₆³⁺ after air oxidation. Therefore, the total chromium in bands 1 through 3 can be corrected to give $2.87 \times 10^{-4} - 0.5 \times 10^{-4} = 2.4 \times 10^{-4}$ mol of chromium consumed by the first reaction, in good agreement with the 2.3×10^{-4} mol expected.

Products of Acidolysis of II. Ion-exchange separation of the reaction products on Sephadex SP-C25 at 5 °C revealed two products. The first

to elute with 0.1 M H⁺ + 0.7 M NaClO₄ was pink and has absorbance maxima at 414 and 510 nm with absorption coefficients of 82.7 and 63.9 M⁻¹ cm⁻¹, respectively (based on Cr analysis). The second product was eluted with 0.1 M HClO₄ and 1.1 M NaClO₄ and was greenish yellow. The absorbance maxima are at 340, 470, and 600 nm with absorption coefficients of 66.9, 70.4, and 34.4 M⁻¹ cm⁻¹, respectively.

Acknowledgment. We acknowledge the financial support for this research from the Natural Sciences and Engineering Research Council of Canada. P.S. wishes to thank the University of Rajasthan for a leave of absence.

Registry No. I, 111410-16-3; II, 111410-17-4; III, 111410-18-5; IV, 111410-19-6; V, 111410-20-9; VII, 42947-06-8; IX, 88157-86-2; [(H₃N)₅CoNH₂C(O)CH₂I](ClO₄)₃, 111410-15-2; (H₂O)₂CrI²⁺, 18955-06-1; Cr(H₂O)₆³⁺, 14873-01-9; (H₂O)₄Cr(μ-OH)₂Cr(OH₂)₄⁴⁺, 23852-05-3; (H₃N)₅CoNH(OH)CCH₃³⁺, 51538-47-7; Cr²⁺, 22541-79-3; Hg²⁺, 14302-87-5.

Contribution from Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

Kinetics and Mechanism of Reduction of Pentaamminecobalt(III) Complexes, [CoX(NH₃)₅]²⁺ (X = F, Cl, Br, N₃), by [N'-(2-Hydroxyethyl)ethylenediamine-N,N,N'-triacetato]aquavanadium(III)

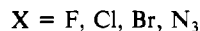
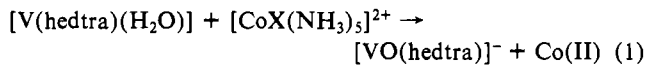
Hiroshi Ogino,* Makoto Shimura, Noriko Yamamoto, and Nobuyuki Okubo

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[N'-(2-Hydroxyethyl)ethylenediamine-N,N,N'-triacetato]aquavanadium(III), [V(hedtra)(H₂O)], was found to reduce [CoX(NH₃)₅]²⁺ (X = F, Cl, Br, N₃) in acidic HEDTRA solutions to give [VO(hedtra)]⁻ and [Co(hedtra)(H₂O)]⁻. The reactions obeyed the pseudo-zeroth-order rate law in the presence of excess [V(hedtra)(H₂O)], while the reactions were first order in the presence of excess [CoX(NH₃)₅]²⁺. The kinetic measurements have suggested that the rate of the reaction is controlled by the conversion of [V(hedtra)(H₂O)] to a species ([V(hedtra)]) that is either the deaquated species or an isomer of the parent [V(hedtra)(H₂O)] and that only [V(hedtra)] is reactive toward the electron transfer to the [CoX(NH₃)₅]²⁺ complexes (X = F, Cl, Br, N₃). The averaged rate constant of the conversion of [V(hedtra)(H₂O)] to [V(hedtra)], determined by the [CoX(NH₃)₅]²⁺ complexes, was $(3.5 \pm 1.3) \times 10^{-4}$ s⁻¹ at I = 0.10 (NaCl) and 40.0 °C. For the reaction of [CoF(NH₃)₅]²⁺, the reduction by [V(hedtra)(H₂O)] ($(2.4 \pm 0.4) \times 10^{-2}$ M⁻¹ s⁻¹) gives a minor contribution to the electron transfer in addition to the reduction by [V(hedtra)]. The effect of the halide ligands in the [CoX(NH₃)₅]²⁺ complexes (X = F, Cl, Br) on the rates of reduction by [V(hedtra)(H₂O)] indicates that these reactions form a system showing the so-called "inverse order" for the electron transfer. When excess [CoX(NH₃)₅]²⁺ is allowed to react with [V(hedtra)(H₂O)] in an acidic HEDTRA solution, the electron-transfer reaction between [CoX(NH₃)₅]²⁺ and [Co(hedtra)(H₂O)]⁻ also occurs in addition to the reaction of [V(hedtra)(H₂O)] with [CoX(NH₃)₅]²⁺. The relative rates of the reactions of [CoX(NH₃)₅]²⁺ with [Co(hedtra)(H₂O)]⁻ conform to the "normal order".

Introduction

In the course of our continuing efforts to investigate the reactions of transition-metal-polyamino polycarboxylate complexes,¹ we have found that the vanadium(III)-HEDTRA complex [V(hedtra)(H₂O)]² reduces pentaamminecobalt(III) complexes in acidic HEDTRA buffer solutions (eq 1), whereas the reduction



of cobalt(III) complexes with V³⁺ is immeasurably slow.³ The kinetics of reaction 1 showed an anomaly: Reaction 1 obeyed the zeroth-order rate law when [V(III)]₀ ≫ [Co(III)]₀. Since the zeroth-order reaction has been rarely encountered,⁴⁻¹¹ kinetic

studies of reaction 1 were carried out. We also developed the rate equations for analyzing the pseudo-zeroth-order reactions, which have not been discussed in detail previously.⁴

Experimental Section

Materials. [V(hedtra)(H₂O)]·2H₂O. H₃hedtra (3.1 g, 0.011 mol) in 25 mL of water was neutralized with Na₂CO₃ (1.6 g, 0.015 mol). Anhydrous VCl₃ (1.6 g, 0.010 mol) was added to the solution under nitrogen atmosphere. After the solution was stirred for a few minutes, brown [V(hedtra)(H₂O)]·2H₂O crystallized. The crystals were collected and washed with cold water and acetone. Yield: 3.2 g (85%). Anal. Calcd for C₁₀H₂₁N₂O₁₀V: C, 31.59; H, 5.57; N, 7.37. Found: C, 31.54; H, 5.83; N, 7.35.

K[VO(hedtra)]·0.25H₂O. H₃hedtra (2.8 g, 0.010 mol) in 10 mL of water was neutralized with BaCO₃ (2.0 g, 0.010 mol). A solution of VOSO₄·nH₂O (2.9 g, 0.01 mol) in 10 mL of water was added dropwise with stirring to the solution at 80 °C. To this mixture was added 0.79 g of K₂CO₃ (5.0 mmol). After the solution was kept for 30 min at 80 °C, the BaSO₄ precipitated was removed by filtration. The filtrate was concentrated to small volume by a rotary evaporator. When ethanol was

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- Abbreviations: edta⁴⁻, ethylenediamine-N,N,N',N'-tetraacetate; hedtra³⁻, N'-(2-hydroxyethyl)ethylenediamine-N,N,N'-triacetate.
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