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Chromium(II) Reduction of 2-, 3-, and 4-Carboxamidopyridinopentaamminecobalt(III)

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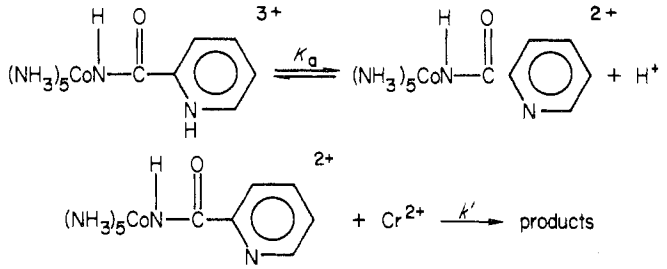
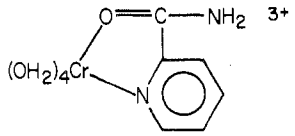
Received October 9, 1973 AIC307420

The kinetics of the reaction of $Cr(OH_2)_6^{2+}$ with 2-, 3-, and 4-carboxamidopyridinopentaamminecobalt(III), I, II, and III, have been studied spectrophotometrically in acidic solution. For all systems an inner-sphere pathway for the reduction has been demonstrated. For the 3- and 4-substituted complexes, the reduction is described by the rate law $-d \ln [Co(III)]/dt = k[Cr^{2+}]$, and $k = 0.017$ and $0.078\ M^{-1}\ sec^{-1}$ at 25° and $\mu = 1.0\ M$ ($LiClO_4$) with $\Delta H^{\ddagger} = 10.3 \pm 2$ and 8.6 ± 2 kcal mol^{-1} and $\Delta S^{\ddagger} = -32 \pm 8$ and -35 ± 8 eu, respectively. For the latter complexes the initial product of the reduction is the chromium(III)-amide compound, resulting from attack of Cr^{2+} at the adjacent carbonyl oxygen. The 2-carboxamidopyridine complex is reduced according to the rate law $-d \ln [Co(III)]/dt = k[Cr^{2+}]/[H^+]$. The following mechanism is consistent with the rate law



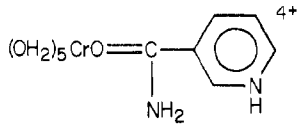
At 25° and $\mu = 1.0\ M$ ($LiClO_4$), $K_a = 1.55 \times 10^{-3}\ M$ and $k' = 1.31 \times 10^5\ M^{-1}\ sec^{-1}$ with $\Delta H^{\ddagger} = 1.3 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -31 \pm 2$ eu. The product of this reaction is formulated as the chelate



The results are discussed with respect to those obtained for reduction of the $(NH_3)_5Co^{3+}$ complexes of nicotinamide and isonicotinamide which involve coordination through the pyridine nitrogen.

Introduction

The reduction of nicotinamido- and isonicotinamidopentaamminecobalt(III) by chromium(II)[1] proceeds by remote attack of the reductant at the amide carbonyl producing



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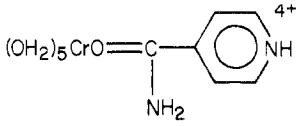
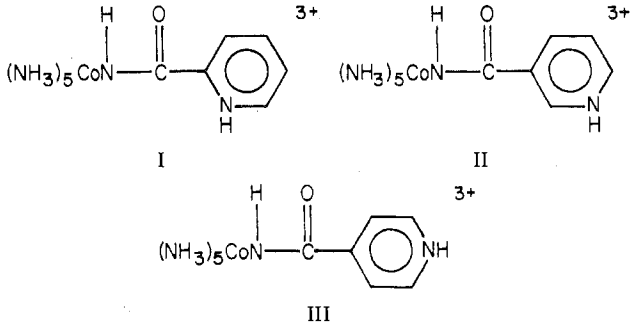


The kinetic parameters for reduction of the isonicotinamide complex as well as the rate constants for reduction of the products strongly suggest a radical ion mechanism.[1] The reduction of the nicotinamide complex on the other hand is consistent with a resonance-transfer process.

The present study is concerned with the reduction of complexes I–III by chromium(II). These complexes are isomers of the pyridine-bonded amides except that protonation occurs at the pyridine nitrogen instead of the coordinated nitrogen. It was of interest to determine if similar mechanisms operate in the reduction of these latter complexes as compared to the isonicotinamide and nicotinamide complexes.



Experimental Section

Complexes. The complexes were prepared by the general synthetic scheme outlined below starting with 2-, 3-, and 4-cyanopyridine rather than the corresponding amides (TEP = triethyl phosphate; py = pyridine). The nitrile complexes are easily hydrolyzed to the corresponding amides. Without rigorous exclusion of traces of water the triethyl phosphate preparation yields a mixture of nitrile and amide complexes. These may be separated by cation-exchange chromatography. The detailed procedures are described elsewhere.[2]

$$(NH_3)_5CoN_3^{2+} + NO^+ \xrightarrow{TEP} (NH_3)_5CoTEP^{3+} + N_2 + N_2O \quad (1)$$

$$(NH_3)_5CoTEP^{3+} + pyC{\equiv}N \rightarrow (NH_3)_5CoN{\equiv}Cpy^{3+} \quad (2)$$

$$(NH_3)_5CoN{\equiv}Cpy^{3+} + OH^- \xrightarrow{H_2O} (NH_3)_5CoN{=}C(HO)py^{2+} \quad (3)$$

Reagents. Standard solutions of lithium perchlorate and perchloric acid were prepared as described previously.[3] Chromium(II)

(1) F. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, 90, 1162 (1968). It should be pointed out that 29% of the reduction of the nicotinamide complex proceeds *via* an outer-sphere path.

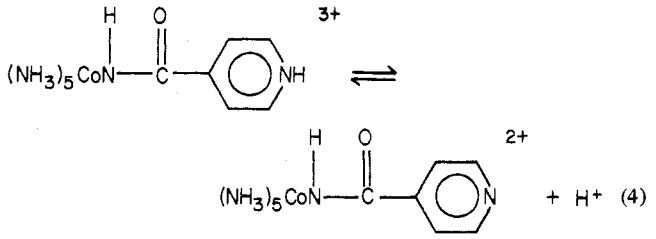
(2) R. J. Balahura, *Can. J. Chem.*, in press.

(3) R. J. Balahura and R. B. Jordan, *J. Amer. Chem. Soc.*, 92, 1533 (1970).

perchlorate was prepared by dissolving high-purity chromium metal in perchloric acid and also by reducing chromium(III) perchlorate with zinc amalgam. All solutions were handled using standard syringe techniques under an argon atmosphere.

Ion-Exchange Separation of Reaction Mixtures. Chromatographic separations were carried out using Dowex 50W-X2 in a cold room maintained at approximately 1°. Chromium concentrations were determined spectrophotometrically as chromate, ϵ 4815 M^{-1} cm^{-1} at 372 nm.

Determination of Ionization Constants. The acid dissociation constant for the reaction



was determined potentiometrically by titrating 0.01 M solutions of the acid with 0.1 M KOH. For the 2-carboxamido complex an apparent pK_a was evaluated spectrophotometrically at 301 nm and 1.0 M ionic strength maintained with $LiClO_4$. The pK_a values were evaluated using the methods outlined by Albert and Serjeant.[4]

Kinetic Measurements. The rates of reduction of the 3- and 4-carboxamido complexes were followed by monitoring the decrease in absorbance at the longest wavelength peak of the cobalt(III) complex (485 nm). For the 2-carboxamido complex the rate data were obtained using a Durrum stopped-flow spectrophotometer. Absorbance–time data were obtained at 485 nm (decrease of cobalt(III) peak) as well as at 400 and 550 nm (increase in absorbance due to production of chromium(III) product).

All reactions were carried out under pseudo-first-order conditions (reductant in a 15–20-fold excess over oxidant). The rate constant was determined from the slope of a plot of log $(A_t - A_\infty)$ *vs.* time, where A_t and A_∞ are the absorbances at time t and after the reaction was complete.

The temperature of the solution in the spectrophotometer cell was controlled by pumping water from a Colora constant-temperature bath through special blocks which housed the cells. The temperature of the bath was regulated with a thermistor probe inserted in the block which housed the cell. A similar arrangement was used to thermostat the drive syringes and observation chamber on the stopped-flow apparatus.

Physical Measurements. Electronic spectra were obtained using a Beckman Acta CIII spectrophotometer. pH measurements were made with a Radiometer Model 26 pH meter.

Results

Acid Dissociation Constants. Potentiometric determinations of the pK_a values at 25° for the reaction shown in eq 4 yielded values of 3.57 ± 0.06 and 3.66 ± 0.10 for the 3- and 4-carboxamido complexes, respectively. For the 2-carboxamido complex the pK_a's at 25, 35, and 43° are 2.31 ± 0.1, 2.20 ± 0.1, and 2.16 ± 0.1, respectively. The apparent pK_a of the 2-carboxamido complex at μ = 1.0 M ($LiClO_4$) was measured spectrophotometrically and was found to be 2.95 ± 0.2 at 25°.

Chromium(II) Reductions. Stoichiometry. The stoichiometry of the reduction of the 2-carboxamidopyridine complex was determined by analysis for Co(II) produced[5] from reaction mixtures in which the Co(III) complex was in excess with respect to the reductant. For five experiments with 9 × 10^{-5} mol of cobalt(III) complex and 7.6 × 10^{-5} mol of Cr(II) at varying acidities, the average ratio of Co(II) produced to Cr(II) used was 0.98 ± 0.02.

The reduction of the 3- and 4-carboxamidopyridine complexes also involved 1 mol of chromium(II) per mole of cobalt(III). In this case, the total chromium(III) products were collected using cation-exchange chromatography and total chromium was determined as chromate.

3- and 4-Carboxamidopyridine Complexes. The reduction of the 3- and 4-carboxamido complexes was independent of hydrogen ion concentration and followed the rate law

$$\frac{-\mathrm{d} \ln [\mathrm{Co(III)\ complex}]}{\mathrm{d}t} = k[\mathrm{Cr}^{2+}] \qquad (5)$$

Experimental conditions and results are presented in Table I. The kinetic parameters are summarized in Table II.

It should be pointed out that at high temperatures the rate of reduction of these complexes seemed to decrease with increasing acid concentration. However, the changes were so small that the rate law could not be obtained unambiguously. Thus, the rate constants shown in Table II are averages at a particular temperature which are generally accurate to about 5% except for the 3-carboxamido data at 35.5° which are accurate to only about 10%.

In order to investigate the products of the reduction, repetitive scans from 700 to 300 nm were made during the course of the reaction. For the 3-carboxamido complex, scans with Cr^{2+} to Co^{3+} ratios of 1:1 and 6:1 each at [H$^+$] =

Table I. Kinetic Data for the Reduction of 3- and 4-Carboxamidopyridinopentaamminecobalt(III) by Chromium(II)[a]

T, °C	$10^3 \times$ [Co(III)], M	$10^2 \times$ [Cr^{2+}], M	[H$^+$], M	k, M^{-1} sec^{-1}
	3-Carboxamidopyridine Complex			
25.1	4.0	6.8	0.158	0.0163
	7.0	6.8	0.156	0.0166
	6.4	6.8	0.158	0.0166
	3.2	3.4	0.163	0.0163
	6.8	7.8	0.170	0.0165
	6.6	6.8	0.548	0.0165
35.5	1.9	5.6	0.076	0.0324
	1.9	5.6	0.763	0.0273
	2.2	5.6	0.222	0.0312
44.3	2.5	5.6	0.076	0.0525
	2.0	5.6	0.118	0.0494
	2.4	5.6	0.763	0.0460
	2.4	5.6	0.222	0.0513
	4-Carboxamidopyridine Complex			
25.1	6.2	8.5	0.144	0.0786
	6.8	8.5	0.144	0.0786
	5.9	8.5	0.144	0.0786
	6.0	8.5	0.473	0.0757
	6.1	8.5	0.473	0.0757
	6.2	8.5	0.264	0.0772
	3.4	4.2	0.144	0.0778
	6.2	12.7	0.145	0.0778
	6.1	12.7	0.145	0.0746
35.5	2.0	2.8	0.069	0.127
	2.2	2.8	0.881	0.119
	2.5	2.8	0.881	0.116
	1.0	2.8	0.028	0.132
	2.2	2.8	0.215	0.126
44.3	2.0	2.8	0.215	0.176
	1.9	2.8	0.881	0.165
	1.1	2.8	0.028	0.198
	0.9	2.8	0.069	0.185
	0.5	2.8	0.028	0.197

[a] Ionic strength is 1.0 M with $LiClO_4$. The individual rate constants are accurate within 5%.

Table II. Summary of Kinetic Parameters for the Chromium(II) Reduction of 2- and 3-Carboxamidopyridinopentaamminecobalt(III)

Complex	k(25°), M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
3-Carboxamidopyridine	0.0165	10.3 ± 2	−32 ± 8
4-Carboxamidopyridine	0.0786	8.6 ± 2	−35 ± 8

(4) A. Albert and E. Serjeant, "The Determination of Ionization Constants," Chapman and Hall, London, 1971.
(5) R. K. Kitson, *Anal. Chem.*, 22, 664 (1950).

Table III. Kinetic Data for the Reduction of 2-Carboxamidopyridinopentaamminecobalt(III) by Chromium(II)[a]

T, °C	$10^4 \times$ [Co(III)], M	$10^2 \times$ [Cr^{2+}], M	[H^+], M	k_{obsd}, M^{-1} sec^{-1}
25.5	6.6	2.4	0.067	3000
	11	2.5	0.108	1820
	6.7	2.4	0.192	1075
	7.1	2.5	0.359	558
	6.7	1.2	0.359	540
	6.7	2.4	0.693	214
34.6	6.6	2.2	0.095	2900
	6.6	2.2	0.322	890
	6.6	2.0	0.806	370
43.2	6.7	2.2	0.095	3700
	6.7	2.2	0.322	1180
	6.7	2.2	0.806	500

[a] Ionic strength is 1.0 M with $LiClO_4$. The individual rate constants are accurate to within 5%.

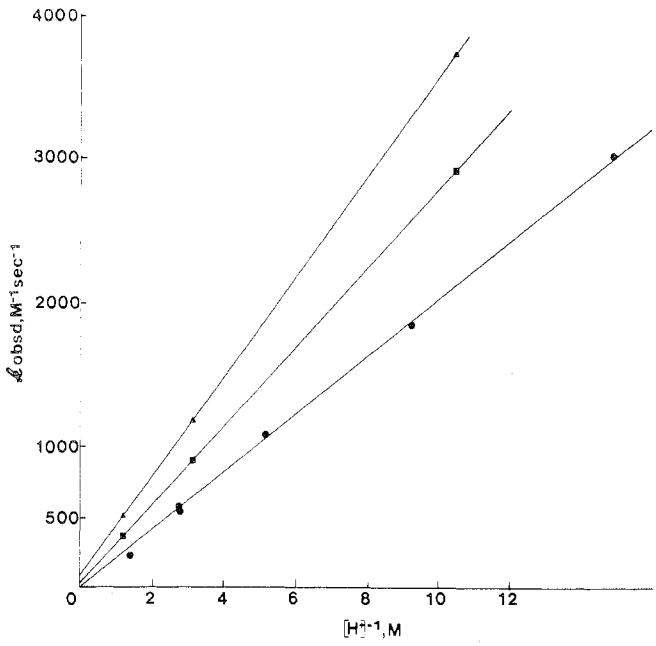


Figure 1. Dependence of the reduction rate of 2-carboxamidopyridinopentaamminecobalt(III) by chromium(II) on [H^+] [$\mu = 1.0$ M ($LiClO_4$)]: •, 25.5°; ■, 35.0°; ▲, 43.3°.

0.1 and 0.5 M indicated that a chromium(III) product was formed which hydrolyzed to $Cr(OH_2)_6^{3+}$. The spectra showed that the initial chromium(III) product had wavelength maxima very near those of $Cr(OH_2)_6^{3+}$, with apparent extinction coefficients of 20 M^{-1} cm^{-1}. For the 4-carboxamido complex at high acid concentration the same behavior was observed. However, at low acid concentration and a Cr^{2+} to Co^{3+} ratio of 1:1, the only chromium(III) product observed had wavelength maxima at lower wavelength than those of the hexaaquochromium(III) ion. In addition, this chromium(III) complex did not hydrolyze as rapidly as the predominant complex obtained at high acid. Attempts were made to isolate the various chromium(III) products by cation exchange of reaction mixtures on Dowex 50W-X2 in the Li-ion form. For the 3-carboxamido complex a mixture of [Cr^{2+}] = 0.020 M, [Co^{3+}] = 0.020 M, and [H^+] = 0.13 M was allowed to react for 165 min, after which the solution was air-oxidized, diluted, and charged onto the ion-exchange column. Only one band was isolated and the spectrum was consistent with that of $Cr(OH_2)_6^{3+}$. The same result was obtained at [H^+] = 0.90 M. Apparently the initial chromium(III) product was hydrolyzed on the column before it could be isolated. A similar analysis of the 4-carboxamido complex with [Co^{3+}] = 0.025 M, [Cr^{2+}] = 0.026 M, and [H^+] = 0.13 M and a reaction time of 30 min gave approximately 90% of a violet-pink chromium product which was removed from the column with 1.0 M $NaClO_4$ and 10^{-3} M $HClO_4$. The visible spectrum of this complex had maxima at 555 and 401 nm with extinction coefficients of 18.9 and 21.6 M^{-1} cm^{-1}, respectively. When the analysis was repeated with [H^+] = 0.90 M, essentially no violet band was detected and the only isolatable product was $Cr(OH_2)_6^{3+}$. Again, just as for the 3-carboxamido product analysis, this chromium product appears to hydrolyze rapidly on the ion-exchange column.

Table IV. Summary of Kinetic Parameters for Reduction of 2-Carboxamidopyridinopentaamminecobalt(III) by Chromium(II)[a]

T, °C	$10^3 K_a$, M	Slope, sec^{-1}	$10^{-5} k'$, M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
25.5	1.55	205	1.31	1.3 ± 0.5	−31 ± 2
35.0	1.91	275	1.44		
43.3	2.19	344	1.57		

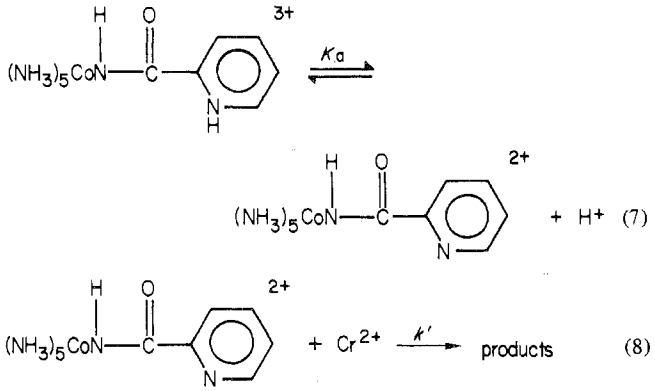
[a] The errors include estimates for K_a as well as the slope.

2-Carboxamidopyridine Complex. The reduction of the 2 derivative was strongly dependent on the hydrogen ion concentration. The reduction followed the rate law

$$\frac{-d \ln [Co^{3+}]}{dt} = \frac{k[Cr^{2+}]}{[H^+]} = k_{obsd}[Cr^{2+}] \quad (6)$$

The rate data are given in Table III. A plot of k_{obsd} *vs.* [H^+]$^{-1}$ is shown in Figure 1.

A mechanism consistent with the inverse hydrogen ion dependence is



The rate law derived for the above mechanism gives

$$k_{obsd} = \frac{k'K_a}{K_a + [H^+]} \quad (9)$$

Since $K_a \ll [H^+]$

$$k_{obsd} = \frac{k'K_a}{[H^+]} \quad (10)$$

The values of k' calculated from the slopes in Figure 1 and the measured equilibrium constants are given in Table IV along with the calculated activation parameters.

Spectra of reaction solutions with Cr^{2+} to Co^{3+} ratios of 1:1 and at varying acidities indicated that the product was not the hexaaquochromium(III) ion. Ion exchange of reaction mixtures gave a small amount of $Cr(OH_2)_6^{3+}$ and predominantly a violet-pink chromium(III) complex which was eluted off the column *after* $Cr(OH_2)_6^{3+}$ but with an apparent 3+ charge. The visible spectrum obtained by elution with 2.0 M $LiClO_4$ and 10^{-3} M $HClO_4$ had maxima (extinction coeffi-

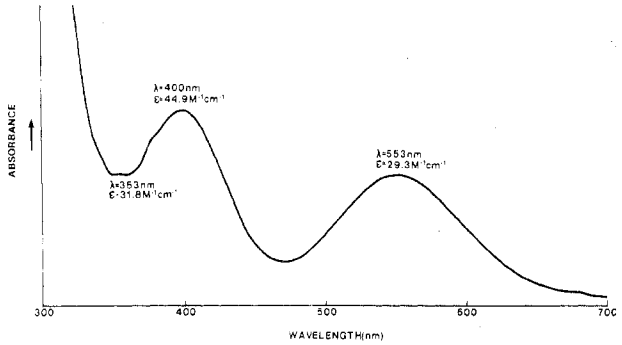


Figure 2. Visible spectrum of the chromium(III) product of the reduction of 2-carboxamidopyridinopentaamminecobalt(III) by chromium(II).

cient) at 553 (29.3), 400 (44.9), and 353 nm (31.8 M^{-1} cm^{-1}). The spectrum of this complex is shown in Figure 2. Repeated attempts to remove the "anomalous" shoulder at ~380 nm and the small peak at 353 nm by further chromatography were unsuccessful. It was, therefore, concluded that we were dealing with one pure complex and not a mixture.

The ion-exchange method was also used to determine the percentage of the ligand transferred from cobalt to chromium. Solutions with varying ratios of chromium(III) ion to cobalt(III) complex at several acidities were allowed to react and charged onto cation-exchange columns. The total amount of violet-pink complex discussed above was separated and removed from the column and the percentage transfer determined. Some representative results are shown in Table V. Difficulty was encountered in removing all of the complex from the ion-exchange column and the results are taken to indicate virtually 100% transfer. It should also be pointed out that for the high acidities the solution of cobalt(III) complex had to be heated to approximately 40° to effect complete dissolution.

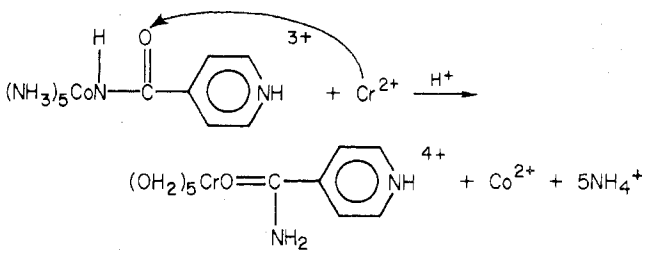
The chromium(III) complex described above is also quite stable toward release of ligand. No aquation was observed after 3 days at 45°, $[H^+] = 0.1$ M, and $\mu = 1.0$ M ($LiClO_4$).

This pink-violet product was also prepared by treating a solution of picolinamide and silver perchlorate with chromous ion. After addition of the chromous ion, the solution was decanted and filtered through 0.25-μ Millipore filters and charged onto a column of Dowex 50W-X8 in the hydrogen ion form. Elution with a solution of 0.25 M $NaClO_4$ and 0.05 M $HClO_4$ separated three bands. The first moved down the column with the characteristics of a 3+ ion and was shown to be $Cr(OH_2)_6^{3+}$. This band was followed closely by a pink-violet band with an apparent 3+ charge. This band was removed from the column with a solution 2.0 M in $LiClO_4$ and 0.001 M in $HClO_4$. The remaining band was left at the top of the column and probably was the result of reduction of picolinamide by Cr^{2+}. The pink-violet band comprised about 80% of the total products and corresponded to the product obtained *via* reduction of the 2-carboxamidopyridine complex.

The reduction of this complex was also attempted. However, only chromium(II)-catalyzed aquation was observed followed by rapid reduction of the picolinamide produced.

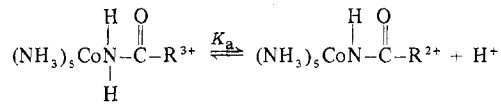
Discussion

Since the reduction of the 3- and 4-carboxamido complexes is independent of hydrogen ion concentration but produces a chromium(III) product other than $Cr(OH_2)_6^{3+}$, attack of the reductant likely takes place at the adjacent carbonyl oxygen as shown for the 4 isomer



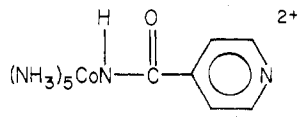
The initial chromium(III) product formed is identical with that obtained by Taube and Nordmeyer from reduction of the nicotinamide and isonicotinamide complexes where the ligands are initially coordinated through the pyridine nitrogen. Furthermore, for the 4-carboxamido complex a second chromium(III) product was obtained which resulted from reaction of the initial product with Cr^{2+}. The values of the peak maxima and extinction coefficients obtained for this complex in ref 1 [λ_{max} (ϵ_{max}): 555 (18.6) and 401 nm (20.9 M^{-1} cm^{-1})] are virtually identical with those obtained here [555 (18.9) and 401 nm (21.6 M^{-1} cm^{-1})]. The production of the latter complex is acid dependent and in qualitative agreement with the results of Taube and Nordmeyer.[1]

Previous work[3,6] on the chromium(II) reductions of coordinated amide complexes has yielded a rate law strongly inverse in hydrogen ion concentration. The source of this inhibition is the preequilibrium involving the ionization of the coordinated nitrogen

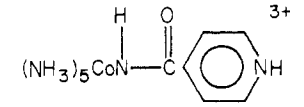


The pK_a's for the above reaction lie in the range 1-3 pK_a units. The deprotonation provides a path for the inner-sphere electron transfer through the O=C–N–Co linkage. In the case of the carboxamidopyridine complexes the acid-base properties are associated with dissociation of a proton from the uncoordinated pyridine nitrogen as shown in eq 4. For these complexes the coordinated nitrogen is much too acidic to become protonated and electron transfer by attack at the carbonyl oxygen is not inhibited as discussed above. It should be pointed out, however, that at high temperatures, the observed rate constant decreases slightly with increasing acid concentration. This could be due to the first effect discussed above. Unfortunately this effect was not large enough for a rate constant to be obtained for this path.

Direct evidence for protonation at the pyridine nitrogen has been obtained from proton magnetic resonance measurements. For the 4-carboxamidopyridine complex, the conjugate base



had a broad resonance at τ 1.30 and a doublet at τ 2.23, 2.33 due to the pyridine protons. However in the acid form of the complex



the peaks were shifted downfield and the expected AA'XX' pattern was obtained with peaks at τ 0.83, 0.93 and 1.68,

(6) R. J. Balahura and L. Hutley, *Can. J. Chem.*, **51**, 3712 (1973).

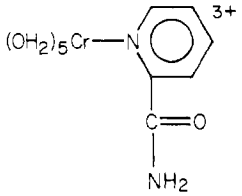
Table V. Ion-Exchange Analysis for the Chromium(III) Product Formed in the Reaction of 2-Carboxamidopyridinopentaamminecobalt(III) with Chromium(II)

$[H^+]$, *M*	[Co(III)], *M*	[Cr(II)], *M*	% ligand transferred
0.13[a]	0.013	0.017	75
0.13[a]	0.013	0.017	72
0.16[a]	0.020	0.037	92
0.31[a]	0.020	0.011	70
0.78[b]	0.013	0.017	86
0.87[b]	0.012	0.017	87

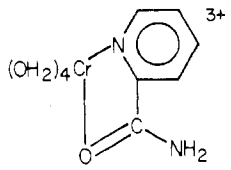
[a] 25°. [b] ~40°.

1.78, respectively. These observations are consistent with protonation at the remote pyridine nitrogen.

The reduction of the 2-carboxamido complex occurs through the 2+ conjugate base. In this case two possible modes of attack are possible. The reductant can attack at the deprotonated pyridine nitrogen to form



as the product. The reductant could also be chelated in the transition state and form the chelated product

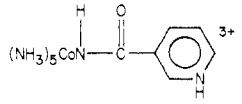
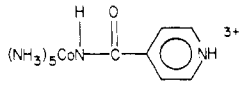
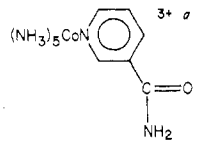
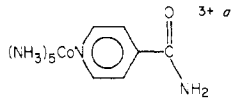
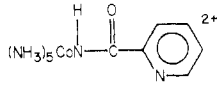


The above product might explain the "high" values of the extinction coefficients obtained for the visible spectrum. Chelation could also explain in part the fast rate of reduction.

The kinetic parameters for the systems studied here as well as other relevant data are gathered in Table VI. The similarity in the kinetic parameters for the reduction of the 3-[7] and 4-carboxamido complexes to those obtained for the nicotinamide complex suggests that the complexes reported herein also react *via* a resonance-transfer mechanism. The fact that the 4 derivative reacts 5 times faster than the 3 derivative could simply be a reflection of the fact that conjugative effects are transmitted across para positions of the pyridine ring more effectively than across the meta positions. Stereochemically, the carboxamido complexes $(NH_3)_5CoNHC(=O)R^{2+}$ where $R \neq H$ all have the same overall configuration with the carbonyl oxygen pointing down between two of the cis ammines.[6] Thus the rates of reduction of these complexes for a wide range of R groups might be expected to show little variation. In fact, the rates would simply reflect small changes in steric requirements due to the R groups. This type of behavior has been observed for reduction of the carboxylatopentaamminecobalt(III) complexes $(NH_3)_5CoO_2CR^{2+}$, for a large variety of R groups, and the rates have been correlated with Taft's steric substituent parameters.[8]

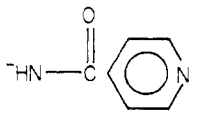
The reduction of the isonicotinamide complex has been postulated to occur *via* a radical ion mechanism by remote

Table VI. Summary of Kinetic Parameters for Reduction of Pyridine Complexes of $(NH_3)_5Co^{3+}$ by Chromium(II)

Complex	$k(25°), M^{-1}$ sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
	1.7×10^{-2}	10.3	−32
	7.8×10^{-2}	8.6	−35
	3.3×10^{-2} (i.s.) 1.4×10^{-2} (o.s.)	10 9	−31 −36
	17.4	3.9	−40
	1.31×10^{5}	1.3	−31

[a] Reference 1; i.s. = inner sphere; o.s. = outer sphere.

attack of the reductant. An analogous process in the case of the 4-carboxamido complex would require prior dissociation of the pyridine proton followed by attack of the reductant at the pyridine nitrogen. However, the deprotonated form of the complex contains the



ligand which would be much more difficult to reduce than free isonicotinamide. Thus, energetically, attack at the adjacent carbonyl oxygen with a resonance-transfer mechanism is probably favored. The same arguments apply to the 3-carboxamido complex reduction.

The kinetic parameters for reduction of the 2-carboxamido complex strongly indicate that this complex is reduced by a different mechanism than the 3 and 4 analogs. It is tempting to rationalize the low $\Delta H^{\ddagger}$ in terms of the radical ion mechanism. However, attempted reduction of the product from this reaction led only to chromium(II)-catalyzed aquation contrary to expectations of an equilibrium similar to that observed for the products of the isonicotinamide reduction. Also, since only reduction of the 2+ complex is observed, the ligand bears a negative charge and would not be expected to be easily reduced with respect to the neutral species. Although chelation in the transition state might be expected to cause an increase in the rate of reduction, the increase of 10^7 seems too large to be attributed to this process. The kinetic data presently available for this and related systems do not permit an unambiguous explanation for this large rate increase.

Acknowledgment. The author wishes to thank the National Research Council of Canada for financial support of this research.

Registry No. I, 51176-01-3; II, 51103-05-3; III, 51103-06-4; Cr(II), 22541-79-3.

(7) The low rate constant for reduction of the 3-carboxamido complex, as well as the ion-exchange results, indicates that part of the reaction may be occurring through an outer-sphere path.

(8) J. C. Chen and E. S. Gould, *J. Amer. Chem. Soc.*, 95, 5539 (1973).