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Preparation, Characterization, and Chromium(II) Reduction of Pentaammine(phenanthroline-2-carboxamido-*N*)cobalt(III) Perchlorate

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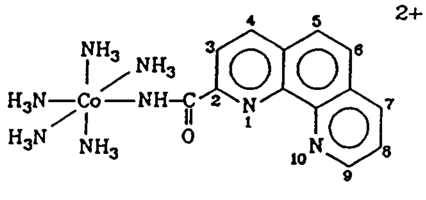
The reduction of pentaammine(phenanthroline-2-carboxamido-*N*)cobalt(III) by chromium(II) proceeds by formation of a binuclear intermediate followed by intramolecular electron transfer. The observed rate constant can be expressed as $k_{obs} = K_pk_{et}[Cr^{2+}]/(1 + K_p[Cr^{2+}])$, where K_p is the formation constant of the binuclear species and k_{et} is the intramolecular electron-transfer rate constant within the binuclear intermediate. At 25 °C, $I = 1.0$ M ($LiClO_4$), $K_p = 28$ M^{-1}, $\Delta H° = 4.4 \pm 2$ kcal mol^{-1}, $\Delta S° = 22 \pm 5$ cal mol^{-1} deg^{-1}, $k_{et} = 140$ s^{-1}, $\Delta H^* = 2.6 \pm 0.4$ kcal mol^{-1}, and $\Delta S^* = -40 \pm 6$ cal mol^{-1} deg^{-1}. Complete ligand transfer is observed, and the initial chromium(III) product is a chelate involving the carboxamido oxygen and one of the phenanthroline nitrogens. The subsequent reactions of this complex are also described.

Introduction

It is generally recognized that homogeneous electron-transfer reactions between metal centers can be divided into several discrete steps along the reaction pathway.[1] The notable mechanistic steps involve formation of a binuclear intermediate with the original valencies unchanged (K_p) followed by intramolecular electron transfer (k_{et}) to form the product binuclear complex. Depending on the identity of the metal ions, further reactions can occur. In most studies the individual steps are not separable and an overall second-order rate constant, K_pk_{et}, is obtained.[2] However, for systems where formation of the binuclear intermediate is favorable (large K_p) or the binuclear intermediate has been "presynthesized", values of K_p and/or k_{et} have been determined.[3-14] Most of these reactions involve pentaamminecobalt(III) complexes of aromatic nitrogen heterocycles as the acceptor and either ruthenium(II) or iron(II) complexes (both π-donors) as the electron donor. One of the few cases where both K_p and k_{et} have been determined for a σ-donor involved the reaction of pentaammine(3-cyano-2,4-pentanedionato-*N*)cobalt(III) with chromium(II).[14] For the Ru(II) and Fe(II) reactions there is no orbital symmetry barrier between the donor and acceptor ligand, and electron transfer is expected to be from metal ion to metal ion.[15] In the case of Cr(II) as donor, a symmetry mismatch (σ to π) exists, and in some cases electron transfer is thought to be stepwise with reduction of the acceptor ligand rate-determining.[16,17] It is important then to determine k_{et} for Cr(II)–Co(III) systems in order to probe the detailed mechanism of these reactions. It is especially appropriate since the much-studied reductions of $(NH_3)_5CoL^{m+}$ complexes[18] by Cr(II) give second-order rate constants which are a composite of K_p and k_{et}.

In this work we wish to report the determination of the intramolecular rate constant for electron transfer in the reaction of chromium(II) with the following phenanthroline complex:



It was anticipated that the reductant would interact strongly with the pendant phenanthroline.[19]

Experimental Section

All solutions used in kinetic studies were prepared with water which was treated on a Milli-Q water system (Millipore Ltd.). Perchloric acid solutions were prepared by dilution of 70% doubly distilled perchloric acid (G. Frederick Smith Chemical Co.) and standardized with sodium hydroxide solution. Lithium perchlorate solutions were prepared by dissolving reagent grade lithium perchlorate in water and filtering through a 5-μm filter. These solutions were standardized by passing an aliquot over an Amberlite cation-exchange resin and titrating the liberated acid. Chromium(II) perchlorate solutions were prepared from deoxygenated chromium(III) perchlorate solutions by reduction over zinc–mercury amalgam. Chromium(II) solutions were standardized by reduction of excess standard iron(III) ammonium sulfate and subsequent determination of the excess iron(III) by titration with sodium thiosulfate in the presence of iodide.

Safety Note! *Perchlorate salts of metal complexes with organic ligands are potentially explosive.* Only small amounts of material should be prepared, and these should be handled with caution.

Syntheses. 2-Cyano-1,10-phenanthroline.[20] A solution of 10 g of 1,10-phenanthroline in 60 mL of glacial acetic acid was heated to 70–75 °C and 6 mL of 30% hydrogen peroxide added. The solution was maintained at this temperature for 3 h, at which time another 6 mL of 30% H_2O_2 was added and heating continued for another 3 h. Acetic acid was removed by rotoevaporation to a volume of 15 mL. At this point, 15 mL of water was added and the volume reduced to 10 mL. The resulting black syrupy mixture was neutralized with a minimum of solid sodium carbonate. The 1,10-phenanthroline 1-oxide was extracted from the resulting paste with two 500-mL portions of chloroform. The combined chloroform extracts were reduced to dryness, and the product was dissolved in 300 mL of chloroform. This solution was dried over sodium sulfate,

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decolorized, and filtered. The yellow filtrate was evaporated to dryness, leaving 6–7 g of 1,10-phenanthroline 1-oxide (mp 180–184 °C).

The 1,10-phenanthroline 1-oxide (3 g) and 3 g of potassium cyanide were dissolved in 50 mL of water, and the solution was stirred vigorously while 3 mL of benzoyl chloride was slowly added. The mixture was allowed to react for 30 min, during which time a brown-yellow precipitate formed. The precipitate was collected and recrystallized from ethanol, giving long tan needles of 2-cyano-1,10-phenanthroline (mp 230–235 °C).

Pentaammine(phenanthroline-2-carboxamido-*N*)cobalt(III) Perchlorate, $[Co(NH_3)_5(NHCO\text{-}phenH)](ClO_4)_3$. A solution containing 1 g of 2-cyano-1,10-phenanthroline and 3 g of pentaammine(trifluoromethanesulfonato)cobalt(III) trifluoromethanesulfonate[21] in 30 mL of tetramethylsulfone was stirred at 50–55 °C for 3 h. During this time the color of the solution changed from red to orange. The tetramethylsulfone was removed by extraction with vigorous stirring with approximately 1 L of diethyl ether. The resulting thick orange-red syrup was dissolved in 1 L of deionized water, and the solution was charged onto a column of CM-sephadex C-25-120 cation-exchange resin. Elution with increasing concentrations of sodium chloride (0.10–0.25 M) separated two orange bands with elution characteristics of +2 ions. The first band (minor product) was removed from the column with 0.15 M NaCl and precipitated from solution (pH ~ 6) by adding solid sodium perchlorate. The crystals were filtered, washed with 95% ethanol and diethyl ether, and air-dried by suction. This complex was subsequently shown to be triammine(1,10-phenanthroline-2-carboxamido-N,N,N^1)cobalt(III) perchlorate. Anal. Calcd for $[Co(NH_3)_3(NHCO\text{-}C_{12}H_7N_2)](ClO_4)_2$: C, 29.4; H, 3.20; N, 15.8. Found: C, 28.7; H, 3.25; N, 15.3.

The second band was eluted from the column with 0.25 M NaCl, and the solid was precipitated from 0.10 M $HClO_4$, filtered, washed with diethyl ether, and air-dried. This product proved to be pentaammine(phenanthroline-2-carboxamido-*N*)cobalt(III) perchlorate. Anal. Calcd for $[Co(NH_3)_5(NHCO\text{-}C_{12}H_8N_2)](ClO_4)_3\cdot 2H_2O$: C, 22.2; H, 3.99; N, 16.0. Found: C, 21.6; H, 3.92; N, 15.8.

1,10-Phenanthroline-2-carboxamide. Chromium(II) reduction or acid hydrolysis of $[Co(NH_3)_5(NHCO\text{-}phenH)]^{3+}$ gives the free 1,10-phenanthroline-2-carboxamide ligand. The compound precipitates in the protonated form as the perchlorate salt in 0.03–1.0 M $HClO_4$. The infrared spectrum gave a broad band at 1090 cm^{-1} characteristic of perchlorate. The perchlorate salt decomposed at 325 °C (melting point of neutral ligand at 304.5–305.5 °C). Anal. Calcd for $C_{13}H_{10}N_3ClO_5$: C, 48.2; H, 3.09; N, 13.0. Found: C, 48.4; H, 3.34; N, 13.4.

Kinetic Measurements. All reactions were carried out anaerobically under an atmosphere of high-purity argon. Kinetic measurements were made under pseudo-first-order conditions on a Dionex stopped-flow spectrophotometer. Absorbance versus time data were collected either using a DASAR analog–digital data storage and retrieval system or a computer and rate constants determined using the OLIS Kinfit routines (On-Line Instrument Systems, Jefferson, GA). Solutions were handled using standard syringe techniques.

Product Analysis. Product analyses were performed by charging reaction products onto columns of SP-sephadex cation-exchange resin and eluting with suitable concentrations of sodium perchlorate which contained 0.0030 M $HClO_4$. The products were characterized spectrophotometrically. Extinction coefficients and total chromium were determined as chromate at 372 nm ($\epsilon = 4815\ M^{-1}\ cm^{-1}$).[22]

The stoichiometry of the reduction reaction was determined by reacting the complex with excess chromium(II) and then analyzing for the remaining Cr(II).

Instrumentation. Ultraviolet and visible absorbance spectra were obtained on a Beckman Acta CIII UV–visible spectrophotometer at 25 °C. Infrared spectra were measured using a Perkin-Elmer 1330 spectrometer with KBr disks. Nuclear magnetic resonance spectra were recorded on Bruker WH-400 or AM-250 instruments. Proton chemical shifts were assigned relative to TMS or deuterium hydrogen oxide (HOD). Measurements of pH were made on a Radiometer Model PHM26 instrument fitted with a G202C glass electrode.

Table 1. Spectral Properties of Cobalt(III) Carboxamido Complexes[a]

complex	λ_{max}, nm (ϵ_{max}, $M^{-1}\ cm^{-1}$)
(a) Visible Region	
$[Co(NH_3)_5(NHCO\text{-}H]^{2+}$	348 (81.3), 484 (68.4)
	340 (58.2),[b] 478 (62.2)[b]
$[Co(NH_3)_5(NHCO\text{-}C_6H_4\text{-}4\text{-}CN]^{2+}$	345 (117), 484 (83.2)
	342 (87.6),[b] 478 (73.7)[b]
$[Co(NH_3)_5(NHCO\text{-}phen]^{2+}$	480 (83.3)
	480 (86.0)[b]
$[Co(NH_3)_3(NHCO\text{-}phen)]^{2+}$	460 (118)
(b) Ultraviolet Region	
$[Co(NH_3)_5(NHCO\text{-}phen)]^{2+}$	230 (3.9×10^4), 271 (3.4×10^4)
	228 (3.4×10^4),[b] 276 (2.8×10^4)[b]
$[Co(NH_3)_3(NHCO\text{-}phen)]^{2+}$	239 (1.9×10^4), 266 (1.5×10^4), 276 (1.5×10^4)
$[Co(phen)_3]^{3+}$	273 (2.0×10^4)
	229 (3.7×10^4), 276 (2.8×10^4)
1,10-phen-2-carboxamide	227 (3.3×10^4),[b] 280 (3.1×10^4)[b]

[a] pH 7 except where noted. [b] In 1 M $HClO_4$.

Results and Discussion

Characterization of the Complexes. The synthetic method did not yield the pentaammine(1,10-phenanthroline-2-cyanide-*N*)cobalt(III) complex, as was clearly evident by the absence of a nitrile stretching frequency in the infrared spectrum. The two compounds isolated were both complexes of 1,10-phenanthroline-2-carboxamido in which the original nitrile substituent has been hydrolyzed to the amide. This was not entirely unexpected since nitrile-bound complexes of cobalt(III) are notoriously susceptible to hydrolysis under mild conditions.[23-26] Thus during the synthesis and purification the initially formed nitrile-bound complex would be expected to be rapidly hydrolyzed to the carboxamido complex by external attack of small amounts of hydroxide ion. Under these conditions the tridentate species could also be formed from the latter compound.

$$[Co(NH_3)_5(NC\text{-}phen)]^{3+} + OH^- \xrightarrow{H_2O} [Co(NH_3)_5(NHCO\text{-}phen)]^{2+}$$

major product

$$[Co(NH_3)_5(NHCO\text{-}phen)]^{2+} \rightarrow [Co(NH_3)_3(NHCO\text{-}phen)]^{2+} + 2NH_3$$

minor product

The minor product has been characterized by X-ray crystallography and the tridentate coordination of 1,10-phenanthroline-2-carboxamido confirmed.[27] The metal ion is bonded in the meridional conformation to the ligand through the two ring nitrogens and the deprotonated carboxamide nitrogen in the 2-position. The cation has a distorted octahedral geometry with the Co–N-carboxamido bond bent toward the ligand. The distortion in the molecule is also apparent from the bond lengths between the cobalt and the phenanthroline nitrogens. The cobalt–phenanthroline bond lengths are significantly different from one another (1.858(3) and 2.013(4) Å) with the bond to the nitrogen adjacent to the carboxamido group being shorter. The cobalt–nitrogen bond distances in other phenanthroline complexes[28-30] range from 1.919 to 2.05 Å, but in all cases the two cobalt–nitrogen bonds are almost identical in length in any given compound.

The electronic spectral properties of the two complexes are listed in Table 1 along with those of related compounds. There

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Table 2. Chemical Shift and Coupling Constants of the Aromatic Protons in 1,10-Phenanthroline and Phenanthroline Complexes[a]

compd	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9
1,10-phenanthroline[b]	9.32	7.91	8.61	8.09	8.09	8.61	7.91	9.32
$[Co(en)_2(phen)]^{3+}$	9.19	8.28	9.09	8.43	8.43	9.09	8.28	9.19
$[Co(NH_3)_3(NHCO\text{-}phen)]^{2+}$		8.31	9.07	8.46	8.43	8.97	8.20	9.04
		$J_{34} = 8.4$		$J_{5,6} = 9.0$			$J_{7,8} = 8.2$ $J_{8,9} = 5.2$	
$[Co(NH_3)_5(NHCO\text{-}phen)]^{2+}$		8.37	8.62	8.08	8.08	8.57	7.85	9.14
		$J_{3,4} = 8.3$					$J_{7,8} = 8.0$ $J_{8,9} = 4.4$	
$[Co(NH_3)_5(NHCO\text{-}phen)]^{2+}$ + TFA		8.89	8.60	8.45	8.45	9.46	8.45	9.46

[a] Solvent is DMSO-d_6; shifts measured with respect to TMS in ppm; J in Hz; TFA = trifluoroacetic acid. [b] Reference 39. [c] Balahura, R. J. Unpublished results.

are two important features in the spectrum of $[Co(NH_3)_5(NHCO\text{-}phen)]^{2+}$: (1) there is no change in the visible spectrum on going from pH 7 to pH 0. (2) In the ultraviolet region there is a distinct difference in the spectra recorded at neutral and acidic pH. This latter change is completely reversible. A similar reversible change in the spectrum of the free ligand is also observed on acidification. The changes in the UV spectrum with pH are consistent with the equilibrium

$$[Co(NH_3)_5(NHCO\text{-}phenH)]^{3+} \rightleftharpoons [Co(NH_3)_5(NHCO\text{-}phen)]^{2+} + H^+ \qquad K_a$$

where protonation–deprotonation occurs at one of the phenanthroline nitrogens. If protonation were occurring at the bound nitrogen or carboxamido oxygen, a large shift to lower wavelengths would be expected upon formation of the conjugate acid[31–33] (Table 1a). The K_a was determined spectrophotometrically according to the equation

$$(\epsilon_{obs} - \epsilon_{RH})[H^+] = \epsilon_R K_a - K_a \epsilon_{obs}$$

where ϵ_{RH} and ϵ_H are the extinction coefficients of the protonated and deprotonated complexes and ϵ_{obs} is the extinction coefficient of an equilibrium mixture of the two complexes at a given acid concentration. The pK_a obtained was 3.3 ± 0.3 for several determinations using dilute HCl solutions. Potentiometric titration of the acid form of the complex gave a value of 3.61 ± 0.03. For free phenanthroline the approximate pK_a is 5,[34,35] and it is thought that the proton is shared between the two nitrogen atoms. On the basis of electronic effects, the 2-substituent on 1,10-phenanthroline-2-carboxamido should favor protonation at the remote N in the free ligand and at N-10 in the complex.

The proton magnetic resonance spectrum of $[Co(NH_3)_3(NHCO\text{-}phen)]^{2+}$ shows that the amine protons appear as two singlets at 2.94 and 4.64 ppm which integrate for 6 and 3 protons. These have been assigned to the axial and equatorial amines. The carboxamido NH appears as a singlet at 4.80 ppm. For $[Co(NH_3)_5(NHCO\text{-}phen)]^{2+}$, the four *cis*-$NH_3$'s appear at 3.63 ppm while the *trans*-NH_3 is at 3.47 ppm. The shift difference between the *cis* and *trans* resonances of 0.16 ppm is clearly characteristic of an N-bonded carboxamido ligand bound in the sixth coordination site.[36]

The aromatic protons of phenanthroline absorb in the range 7.5–9.5 ppm. The chemical shifts and coupling constants of the aromatic protons in the complexes are given in Table 2. These peaks have been assigned by comparison with the spectra of other phenanthroline complexes[37–39] and a number of rules elucidated by Kahl et al.[40] The spectrum of $[Co(en)_2phen]^{3+}$, in Table 2, shows that coordination of the phenanthroline nitrogens causes a general downfield shift of the aromatic protons. Somewhat unexpected is the relatively small change in the signal for the H-2,9 protons upon coordination. The electron-withdrawing effect of cobalt(III) might be expected to deshield these protons (ortho to the heterocyclic nitrogen), causing a downfield shift. Miller and Prince[39] suggest that upfield shifts in the 2 and 9 protons upon coordination might be attributed to shielding of these positions by the metal d-electrons. The $[Co(NH_3)_3(NHCO\text{-}phen)]^{2+}$ complex displays a similar spectrum with the H-3 proton shifted downfield from the H-8 signal and the H-4 signal shifted downfield from that of H-7 due to the electron-withdrawing effect of the carboxamido function. In this spectrum the H-5 and H-6 protons are partially resolved into two doublets. Once again, an anomalous shift in the H-9 signal upon coordination was observed.

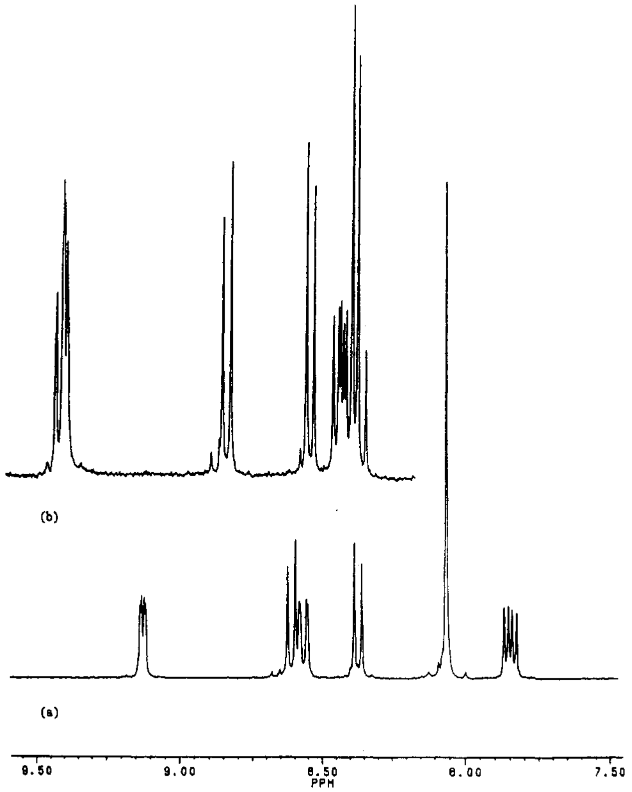

Figure 1. Proton magnetic resonance spectra of (a) $[Co(NH_3)_5(NHCO\text{-}phen)]^{2+}$ and (b) $[Co(NH_3)_5(NHCO\text{-}phenH)]^{3+}$ in DMSO-d_6.

The aromatic region of the spectrum of the $[Co(NH_3)_5(NHCO\text{-}phen)]^{2+}$ complex is shown in Figure 1a. Protons 7–9 should all appear as a doublet of doublets. The doublet of doublets exhibiting the largest couplings should be H-8. The doublet of doublets which is broadened to some extent is that proximate to the

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Table 3. Analysis of the Products of the Chromium(II) Reduction of $[Co(NH_3)_5(NHCO\text{-}phenH)]^{3+}$

(a) Initial Reaction[a]

10^5 mol of Co(III)	10^5 mol of Cr(II)	10^5 mol of $[CrO_4]^{2-}$	% ligand transfer	electronic spectral data: λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})
3.96	3.42	3.32	97.2	560 (78.3), 284 (2.1×10^4), 228 (2.4×10^4)
4.01	3.60	3.27	90.8	560 (82.5), 284 (2.2×10^4), 228 (2.5×10^4)
3.77	3.32	3.32	100	560 (78.3), 284 (2.0×10^4), 228 (2.3×10^4)

(b) Complete Reaction[b]

		electronic spectral data: λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})	
10^5 mol of Co(III)	10^5 mol of Cr(II)	ligand (1+ ion)[c]	$[(OH_2)_4Cr(OH)_2Cr(OH_2)_4]^{4+}$
1.24	11.1	280 (3.1×10^4), 227 (3.2×10^4)	410 (22.5), 580 (17.0)
2.54	11.1	280 (3.1×10^4), 228 (3.1×10^4)	410 (20.4), 580 (17.4)

[a] Deficit of Cr(II). [b] Excess of Cr(II). [c] Extinction coefficients calculated on the assumption that 100% of the ligand was liberated.

Table 4. Kinetic Data for the Reduction of $[Co(NH_3)_5(NHCO\text{-}phenH)]^{3+}$ by Chromium(II)[a]

T, °C	$10^4[Co^{3+}]$, M	$10^2[Cr^{2+}]$, M	$[H^+]$, M	$k_{obs}(1)$, s^{-1}	$k_{obs}(2)$, s^{-1}
25.8	0.0700	0.138	0.100	5.61	
	4.04	0.403	0.100	13.9	
	3.26	0.688	0.100	25.0	0.0439
	3.96	1.37	0.100	46.3	0.0971
	4.04	2.15	0.100	60.9	
	4.18	2.69	0.100	55.5	0.191
	4.04	3.50	0.100	66.6	0.316
	4.18	4.04	0.100	63.3	0.329
	3.26	0.688	0.0510	25.0	0.105
	3.26	0.688	0.200	23.8	0.0216
	3.96	1.37	0.050	49.0	0.189
	3.96	1.37	0.200	45.0	0.0437
	3.34	2.75	0.0500	52.6	0.490
	2.86	0.404	0.0300		0.0926
	2.86	0.673	0.0300		0.167
	2.86	1.35	0.0300		0.272
	2.86	3.50	0.0300		0.952
16.1	3.67	0.683	0.100	17.5	0.0370
	3.67	1.37	0.100	30.5	0.0575
	3.67	2.18	0.100	44.2	0.103
	3.67	2.73	0.100	50.6	0.137
	3.67	4.10	0.100	60.1	0.199
	3.67	5.46	0.100	64.9	0.301
35.4	4.07	0.683	0.100	36.7	0.694
	4.07	1.37	0.100	64.9	0.143
	4.07	2.18	0.100	83.3	0.263
	4.07	2.73	0.100	104	0.338
	4.07	4.10	0.100	103	0.549
	4.02	5.46	0.100	101	0.699

[a] $I = 1.0$ M ($LiClO_4$).

quadrupolar nitrogen or H-9. Protons 3 and 4 should appear as doublets since they are on the substituted ring of phenanthroline and the couplings should be large. Thus, they are distinguishable from protons 5 and 6 which should also be doublets but with a smaller coupling. H-3 was distinguished from H-4 by a long-range COSY experiment.

Addition of acid to $[Co(NH_3)_5(NHCO\text{-}phen)]^{2+}$ results in a general downfield shift of the aromatic resonances (see Figure 1b). The largest shift occurs in the signals of the 7 and 8 protons, while the corresponding 4 and 3 protons are affected to a lesser extent. This suggests that the phenanthroline nitrogen adjacent to the 9-position is preferentially protonated. Identical results were obtained from the proton spectra of 2-cyano-1,10-phenanthroline and 1,10-phenanthroline-2-carboxamide in the neutral and protonated forms. Note that the proton spectrum of $[Co(NH_3)_3(NHCO\text{-}phen)]^{2+}$ is insensitive to the addition of acid. This is as predicted since the phenanthroline nitrogens are unavailable for protonation in this complex. The proton spectrum of $[Co(NH_3)_5(NHCO\text{-}phen)]^{2+}$ was also obtained in D_2O and D_2O plus TFA; identical results were obtained. Finally, a C-13 study of $[Co(NH_3)_5(NHCO\text{-}phen)]^{2+}$ and its protonated form has unambiguously confirmed the site of protonation as N-10.[19]

Kinetics of the Chromium(II) Reduction. The stoichiometry of the reduction of $[Co(NH_3)_5(NHCO\text{-}phenH)]^{3+}$ by Cr^{2+} was determined using molar ratios of reductant to oxidant of 1:1, 2:1, and 5:1. The analysis was carried out for reaction times corresponding to completion of the initial reduction as well as for subsequent slower reactions of the chromium(III) products. An average of six determinations showed that 1.06 ± 0.05 mol of chromium(II) is consumed/mol of the cobalt(III) complex reacted.

The reduction of $[Co(NH_3)_5(NHCO\text{-}phenH)]^{3+}$ by Cr^{2+} initially gives a purple chromium(III) product with a visible absorption band at 584 nm ($\epsilon \sim 65$ M^{-1} cm^{-1}) and UV bands at 291 and 230 nm. The fate of the purple complex is dependent on the relative concentrations of Cr^{2+}. With a deficit of Cr^{2+} with respect to the initial cobalt(III) concentration, the peak at 584 nm slowly ($\sim 10^{-4}$ s^{-1}) gives a new maximum at 560 nm ($\epsilon = 80$ M^{-1} cm^{-1}). This change occurs with isosbestic points at 598 and 429 nm. This reaction also shows an inverse dependence on $[H^+]$. With Cr^{2+} in excess, the initial Cr(III) product formed undergoes a further reaction with Cr^{2+}. At initial cobalt(III) concentrations of approximately 10^{-3} M and a 5-fold excess of Cr(II), the absorption band at 580 nm from the first chromium(III) product disappears, and a white precipitate forms. This precipitate was identified as the perchlorate of the protonated form of 1,10-phenanthroline-2-carboxamide (see Experimental Section). This chromium(II)-catalyzed reaction can be followed spectrally in the UV, where, at low cobalt(III) concentrations, precipitation of ligand does not occur. The initial spectrum after reduction exhibits maxima at 289 and 230 nm. This spectrum is converted to one with peaks at 282 and 228 nm with isosbestic points observed at 289, 259, and 223 nm. This latter spectrum has been identified as that of the protonated form of 1,10-phenanthroline-2-carboxamide. Since the stoichiometry of the initial reaction is 1 Cr(II) per 1 Co(III) and remains the same for the excess Cr(II) determinations, it follows that the reaction of the initial Cr(III) product with excess Cr(II) is a redox reaction with no net change in the chromium(II) concentration.

The nature of the chromium(III) products was investigated by cation-exchange chromatography after all reactions were complete for varying ratios of chromium(II):cobalt(III). These experiments are summarized in Table 3. With Cr^{2+} in deficiency with respect to cobalt(III), column chromatography gave a single purple chromium(III) product with elution characteristics of a +3 ion. The total yield of this complex, based on chromium(III), was essentially 100% of the initial chromium(II) used (see first three entries in Table 3). If the chromatographic separation was carried out as rapidly as possible without waiting for the initial chromium(III) product to convert to the final product, two bands were obtained. The new band was converted to the other on the column. The final spectrum after conversion was the same as that obtained above. When Cr^{2+} is in excess with respect to Co(III), three products are separated by chromatography. A colorless band was eluted as a +1 ion, and the UV spectrum confirmed it was the protonated form of the free ligand. A second faint blue band eluted as a +3 ion and was identified as $[Cr(OH_2)_6]^{3+}$. The third

Scheme 1

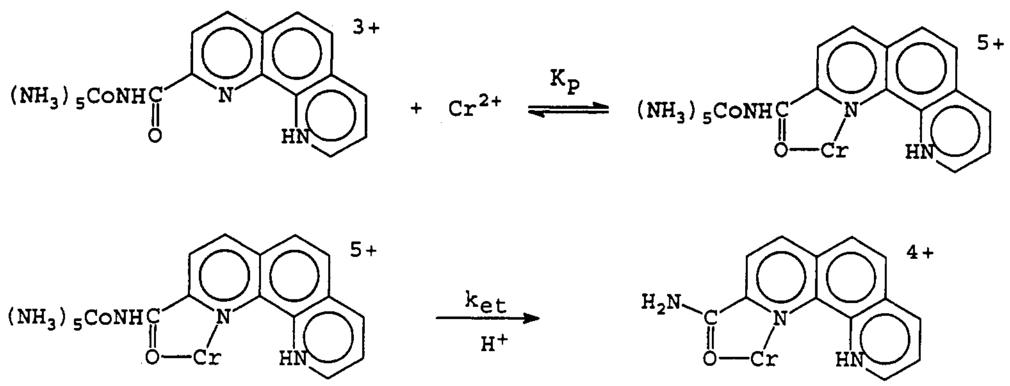

Table 5. Rate Constants and Activation Parameters for the Chromium(II) Reduction of [CO(NH$_3$)$_5$(NHCO-phenH)]$^{3+}$ [a]

	T, °C	k_{et}, s^{-1}	K_p, M^{-1}
	16.1	120 ± 3	25 ± 1
	25.8	140 ± 5	28 ± 1
	35.4	160 ± 5	44 ± 1
ΔH^*, kcal mol^{-1}	2.1 ± 0.4		
ΔS^*, cal mol^{-1} deg^{-1}	−42 ± 5		
ΔH, kcal mol^{-1}	5.1 ± 2		
ΔS, cal mol^{-1} deg^{-1}	24 ± 8		

[a] I = 1.0 M (LiClO$_4$).

product was green and eluted as a +4 ion. This species was [Cr$_2$(OH$_2$)$_8$(OH)$_2$]$^{4+}$ (see Table 3).

The kinetics of the Cr^{2+} reduction of [Co(NH$_3$)$_5$(NHCO-phenH)]$^{3+}$ were determined at 280 nm (ligand band), 380 nm (chromium(III) product band), and 480 nm (cobalt(III) band). All three wavelengths yield comparable kinetic data. Kinetic data for the initial reduction (k_{obs}(1)) are given in Table 4. A plot of k_{obs} versus [Cr^{2+}] clearly shows that as the concentration of chromium(II) increases, the observed rate constant shows less than a first-order dependence on [Cr^{2+}] (see Figure 2) and is independent of [H$^+$]. A mechanism consistent with this behavior is given in Scheme 1. This mechanism gives the rate law (1),

$$k_{obs} = k_{et}K_p[\mathrm{Cr}^{2+}]/(1 + K_p[\mathrm{Cr}^{2+}]) \qquad (1)$$

where k_{et} is the intramolecular electron-transfer rate constant and K_p is the equilibrium constant for formation of the binuclear intermediate. Equation 1 can be rearranged to give eq 2. Plots

$$1/k_{obs} = 1/K_pk_{et}[\mathrm{Cr}^{2+}] + 1/k_{et} \qquad (2)$$

of k_{obs}^{-1} vs [Cr^{2+}]$^{-1}$ are linear as expected, and the values of k_{et} and K_p obtained are collected in Table 5. The solid lines in Figure 2 are calculated from the least-squares parameters in Table 4. The kinetic data for the Cr(II)-catalyzed reaction (k_{obs}(2)) are also given in Table 4. The second reaction was first-order in [Cr^{2+}] and inverse first-order in [H$^+$]. A mechanism consistent with the observations is given in Scheme 2. This mechanism gives the rate law (3). Under the conditions where [H$^+$] ≫ K_a,

$$k_{obs} = kK_a[\mathrm{Cr}^{2+}]/(K_a + [\mathrm{H}^+]) \qquad (3)$$

(3) reduces to (4), which is consistent with the data. The second-

$$k_{obs} = kK_a[\mathrm{Cr}^{2+}]/[\mathrm{H}^+] \qquad (4)$$

order rate constants obtained from plots of k_{obs} versus [Cr^{2+}] at three different acid concentrations were plotted against [H$^+$]. The slope of the straight line obtained gives kK_a = 0.80 s^{-1} at 25 °C.

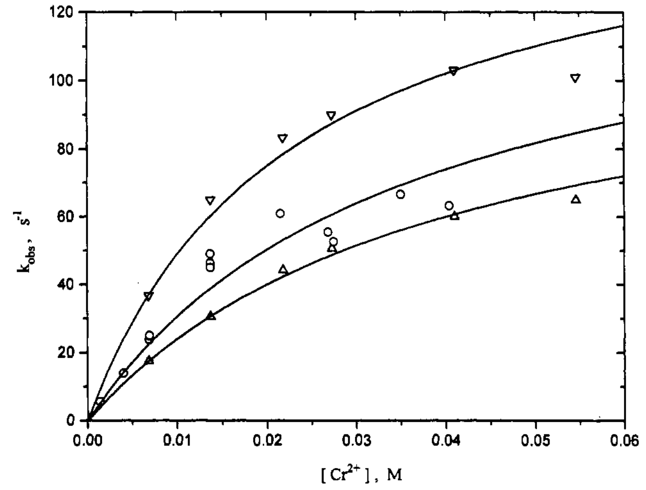

Figure 2. Plot of the observed rate constant versus [Cr^{2+}] for data set 1 in Table 4.

Before the details of the mechanism outlined in Scheme 1 are considered, it should be pointed out that the data are also consistent with formation of a "dead end" complex and reaction between the uncomplexed reactants.[41] However, outer-sphere reactions between Cr^{2+} and pentaamminecobalt(III) complexes are generally several orders of magnitude slower than those observed in this study[42] and thus we consider Scheme 1 the most reasonable.

Several possibilities exist for reductant attack on the oxidant. One involves attack of reductant at the carbonyl oxygen followed by electron transfer giving [(H$_2$O)$_5$CrOCNH$_2$phenH]$^{4+}$ as the initial product. This is not favored since saturation kinetics are observed. The latter behavior is expected only for the formation of reasonably stable precursor complexes such as metal chelates. Furthermore, the visible spectra of pentaaquachromium(III) O-bonded complexes have been shown to exhibit λ_{max} (ϵ_{max}) values which closely resemble those for Cr(H$_2$O)$_6^{3+}$ (λ_{max} = 408 (15.6) and 578 nm (13.4 M^{-1} cm^{-1})).[43] Thus, the observed maximum at 584 nm with high extinction coefficient, ϵ = 65 M^{-1} cm^{-1}, is not consistent with O-bonded monodentate coordination. Extinction coefficients greater than 20–30 M^{-1} cm^{-1} are observed for chelated Cr(III) species[44,45] and support the present formulation. The product analysis from the chromium(II) reduction of [Co(NH$_3$)$_3$(NHCO-phen)]$^{2+}$, which gives only monodentate O-bonded chromium(III) in an inner-sphere reaction, further supports this scheme (vide infra).

A second possibility involves attack of chromium(II) at the phenanthroline nitrogens, resulting in a stable chelate. However,

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(42) Balahura, R. J.; Purcell, W. L. *J. Am. Chem. Soc.* **1976**, *98*, 4457.
(43) Laswick, J. A.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3564.
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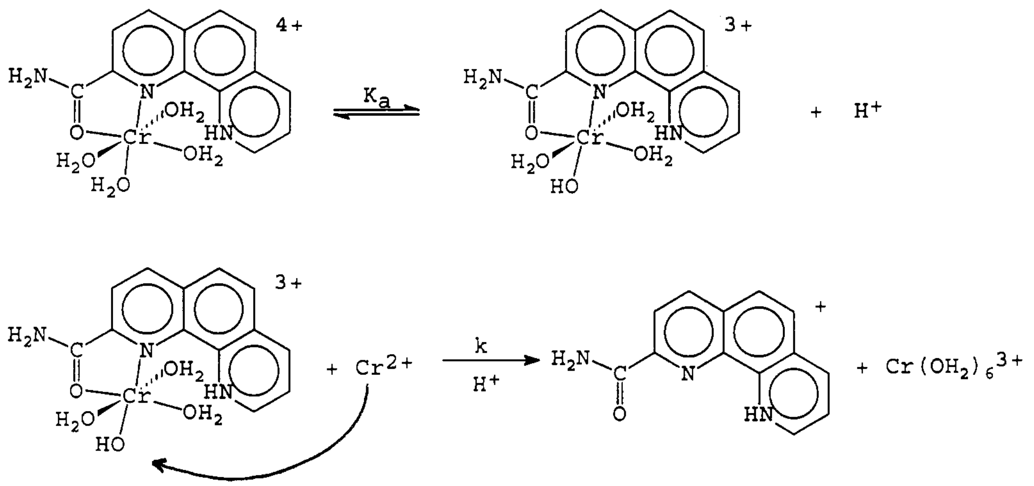
Scheme 2



we have shown that an acid–base equilibrium exists at this site and would then expect the rate of reduction to show an inverse acid dependence at the acid concentrations used. Since no dependence on [H^+] was observed, this second possibility has also been ruled out.

The mechanism shown in Scheme 1 involving one phenanthroline nitrogen and the carboxamido oxygen in chelate formation is unusual but does account for all the observations. Molecular models illustrate that a metal center can form a five-membered chelate with the carbonyl oxygen and one phenanthroline nitrogen. This type of chelate might be preferred over the phenanthroline N,N-bonded chelate by chromium(II) since the latter has a preference for hard donor atoms such as oxygen.

Because of the rigid structure of 1,10-phenanthroline, bonding of just one phenanthroline nitrogen is not normally observed. However, a few instances of monodentate-bonded phenanthroline ligands have been proposed.[40,46–49] The most compelling evidence was presented by Bushnell, Dixon, and Khan, who carried out a crystal structure determination on the complex [$PtCl(PEt_2)_2$(phen)]BF_4.[49] The Pt–N bond lengths suggest one covalently bonded nitrogen and one uncoordinated nitrogen (Pt–N_1 = 213.7 pm and Pt–N_2 = 284.3 pm). These authors also suggest that the complex exhibits fluxional behavior in solution, with the phenanthroline very rapidly exchanging its point of attachment to platinum.

Finally, a study of the kinetics of substitution of the aqua ions of Fe(II), Co(II), and Ni(II) onto [$Co(NH_3)_5$(NHCO-phenH)]$^{3+}$ showed that the substitution reactions were independent of the hydrogen ion concentration and indicated coordination at the carboxamido oxygen and the adjacent phenanthroline nitrogen.[19]

A preliminary investigation of the chromium(II) reduction of [$Co(NH_3)_3$(NHCO-phen)]$^{2+}$ was carried out to aid in the interpretation of the reduction of the pentaammine complex. The reduction was first-order in [Cr^{2+}] and independent of [H^+]. The data are collected in Table 6. The second-order rate constant was 540 ± 20 $M^{-1}\,s^{-1}$ at 25 °C, and I = 1.0 M ($LiClO_4$). Although we could not isolate the initial chromium(III) product, a spectral scan with approximately 1:1 molar ratio of Cr(II):Co(III) gave a spectrum with λ_{max} (ϵ_{max}) at 410 nm (~27 $M^{-1}\,cm^{-1}$) at 578 nm (~29 $M^{-1}\,cm^{-1}$). For an inner-sphere reaction, the structure of the cobalt(III) complex requires attack at the free carboxamido oxygen to form the monodentate oxygen-coordinated Cr(III) product. The spectral data obtained are consistent[16,50] with the formulation of the product as [$Cr(OH_2)_5(OC(NH_2)$-phenH)]$^{4+}$.

Table 6. Kinetic Data for the Reduction of [$Co(NH_3)_3$(NHCO-phen)]$^{2+}$ by Chromium(II)[a]

$10^4[Co^{3+}]$, M	$10^3[Cr^{2+}]$, M	[H^+], M	k_{obs}, s^{-1}
2.76	6.30	0.100	2.81
2.76	12.6	0.100	6.25
2.76	25.2	0.100	13.6
2.76	37.8	0.100	20.8
6.80	12.6	0.0500	6.49
6.80	12.6	0.200	6.25

[a] T = 25.1 °C; I = 1.0 M ($LiClO_4$).

Table 7. Thermodynamic Parameters for the Formation of Precursor Complexes

complex	K_p, M^{-1}	ΔH, kcal mol^{-1}	ΔS, cal mol^{-1} deg^{-1}
[$(NH_3)_5CoNC(acac)Cr^{II}$]$^{4+}$ [a]	58	-7.1	-14
[$(NH_3)_5Co(NHCOphenH)Cr^{II}$]$^{5+}$ [b]	28	5.1	24
[$(NH_3)_5Co(NTA)Fe^{II}$]$^{2+}$ [c]	1.15 × 10^6	1.5	-23
[$(NH_3)_5Ru(4\text{-vpy})Cu^{I}$]$^{3+}$ [d]	1300	-9.7	-18

[a] Reference 14. [b] This work. [c] Reference 3. [d] Reference 51.

The formation constant K_p and the thermodynamic parameters ΔH and ΔS are compared to those from some similar systems in Table 7. The value of 28 M^{-1} for K_p in the present system seems reasonable when compared to the formation constant obtained from the chromium(II) reduction of [$(NH_3)_5CoNC(acac)$]$^{2+}$ (K_p = 58 M^{-1}).[14] In the latter case the hard chromium(II) bonds to the two hard oxygen donors of the β-diketone. Formation of the precursor complex is also enhanced in the latter system by the electrostatic attraction of the delocalized negative charge at the remote acac moiety. In the present system only a stabilizing effect due to chelate formation is expected, and a small K_p is predicted. Because of the lability of chromium(II), very few measurements of ligand complexation have been made.

Enthalpies of formation of these complexes are expected to be small[51] or negative because energy lost upon dissociation of Cr(II)-bound H_2O is compensated by the formation of bonds in the precursor complex. The value of 5.1 kcal mol^{-1} obtained for ΔH in this work is consistent with these considerations.

The entropies of formation of metal chelates of this type are governed predominantly by two opposing factors. An increase in translational entropy is expected if one considers that the reaction results in a change from a two-particle system to a three-

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Table 8. Rate Constants and Activation Parameters for Intramolecular Electron-Transfer Reactions

complex	k_{et}, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}
$[(NH_3)_5CoNC(acac)Cr^{II}]^{4+}$ [a]	735	8.4	−17
$[(NH_3)_5Co(NHCOphenH)Cr^{II}]^{5+}$ [b]	140	2.1	−42
$[(NH_3)_5Co(NTA)Fe^{II}]^{2+}$ [c]	0.115	18.7	0
$[(NH_3)_5Ru(4\text{-}vpy)Cu^{I}]^{3+}$ [d]	0.24	15.1	−10

[a] Reference 14. [b] This work. [c] Reference 3. [d] Reference 51.

particle system with the release of two water molecules upon substitution. However, a decrease in entropy of solvation is predicted with the concentration of positive charge in the precursor complex. The electrostatic interaction between the precursor complex and the polar solvent should result in a net increase in the order of the system. The relatively large positive value of ΔS (24 cal mol^{-1} deg^{-1}) obtained suggests that the translational effect is more important in this system.

The rate parameters for a number of intramolecular electron-transfer reactions are listed in Table 8. The value of 140 s^{-1} obtained for the complex $[(NH_3)_5CoNHCOphenHCr]^{5+}$ is of the same order of magnitude as that obtained for $[(NH_3)_5CoNCacacCr]^{4+}$ (k_{et} = 735 s^{-1}). In another study,[52] an estimate of 600 s^{-1} was made for the intramolecular electron-transfer rate in $[(NH_3)_5CoNTACr]^{3+}$ (NTA = nitrilotriacetic acid). However, in this study, saturation kinetics were not observed and an accurate determination was not possible. Furthermore, due to the flexibility of the bridging ligand and the presence of a saturated group between reductant and oxidant in the precursor complex, a bridged outer-sphere mechanism cannot be ruled out. Due to the limited data available in Co(III)–Cr(II) redox systems, no trends can be ascertained.

The entropy of activation obtained for the intramolecular electron transfer in this study is unusually negative (−42 cal mol^{-1} deg^{-1}). It has been suggested[51] that a large negative entropy is indicative of nonadiabatic electron transfer. The fact that there is a symmetry mismatch involved in the reduction (σ-orbitals in the metal and π-orbitals in the ligand) may support this supposition.

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