Kinetic Study of the Chromium(II) Reduction of the Pentaamminecobalt(III) Complexes of Carbamate, Cyanamide, Urea, and *N*-Cyanoguanidine

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Abstract: The pentaamminecobalt(III) complexes of urea, *N*-cyanoguanidine, and cyanamide have been prepared and characterized. The kinetics of the chromium(II) reductions of these complexes and of the analogous carbamate complex have been studied. The rate constants (M^{-1} sec^{-1}), ΔH^* (kcal mol^{-1}), and ΔS^* (cal mol^{-1} deg^{-1}) for reduction of the carbamate, urea, and *N*-cyanoguanidine complexes, respectively, are: 2.4 (25.8°), 11.4, −19; 1.9×10^{-2} (24.6°), 10.6, −31; 2.9×10^{-2} (24.6°), 8.3, −37. The reduction of the carbamate complex was found to give O-bonded $(H_2O)_5CrO_2CNH_2^+$, not the N-bonded product as had previously been reported. It was found that the carbamate ligand could be protonated in aqueous acid. The proton dissociation constant of the protonated form is 0.105 M (25.8°, 1 M $LiClO_4$-$HClO_4$). The urea and *N*-cyanoguanidine complexes gave only $Cr(OH_2)_6^{3+}$ as a chromium(III) product of the reduction. The cyanamide complex is a weak acid, $K_a = 6.6 \times 10^{-4}$ M (24.6°, 1 M $LiClO_4$). The complex is reduced only through its conjugate base, for which $k = 3.3 \times 10^3$ M^{-1} sec^{-1} (24.6°, 1 M $LiClO_4$-$HClO_4$), $\Delta H^* = 4.3$ kcal mol^{-1}, and $\Delta S^* = -28$ cal mol^{-1} deg^{-1}. The results of the chromium(II) reductions are consistent with the previous proposal that bridged electron transfer does not occur through an $-NH_2$ group.

In a previous paper[1] evidence was presented which suggested that bridged electron transfer would not occur readily through a ligand $-NH_2$ group. It was proposed that the groups in the bridging molecule attached to the oxidizing agent and the reducing agent must have a lone pair of electrons available for bonding and must also be part of a conjugated system. The $-NH_2$ group has only one unshared electron pair and therefore cannot satisfy both of these criteria simultaneously. In order to test the generality of this prediction and to learn more about other specific electronic effects in electron-transfer reactions, the chromium(II) reductions have been studied for the pentaamminecobalt(III) complexes of urea, carbamate, *N*-cyanoguanidine ($N{\equiv}C{-}N{=}C(NH_2)_2$), and cyanamide ($N{\equiv}C{-}NH_2$).

All of these complexes except the carbamate would be predicted to be reduced by outer-sphere electron transfer. The kinetic studies have borne out this prediction. In the case of the cyanamide complex bridged electron transfer apparently does occur through the conjugate base of cyanamide.

The chromium(II) reduction of the carbamato complex has previously been reported[2] to proceed through the $-NH_2$ group with production of a nitrogen-bonded chromium(III) product. Since this is contrary to the above predictions one purpose of this work was to make a detailed study of this reaction.

Experimental Section

Reagents. All solutions were prepared with water redistilled from alkaline permanganate in an all-glass apparatus. Reagent grade lithium perchlorate (G. F. Smith Chemical Co.) was dissolved in water and filtered through a 5-μ Millipore filter (Millipore Filter Corp.) and standardized by determining the amount of hydrogen ion released from a Dowex 50-X8 ion-exchange column.

Chromous perchlorate solutions were prepared by dissolving electrolytic chromium (99.999% purity, United Mineral & Chemical Corp.) in dilute perchloric acid. The chromium(II) content of the solutions was determined periodically by mixing an aliquot of the chromous solution with an excess of standard ferric ammonium sulfate solution. The excess ferric ion was determined by addition of potassium iodide and titration of the iodine liberated with a standard sodium thiosulfate solution. Solutions for chromium(II) reductions were deoxygenated by purging with nitrogen and purified by passing through two solutions of chromous chloride over zinc amalgam, or with high-purity argon. The solutions were handled using standard syringe techniques.

Preparation of Complexes. $((NH_3)_5CoOC(NH_2)_2)(ClO_4)_3$. The O-bonded urea complex was prepared as described previously.[3] It was found in a series of preparations that the yield is increased substantially if the heating time is reduced from 1 hr to 0.75 hr. The visible spectrum of the urea complex shows maxima at 514 nm (ε 67.4 M^{-1} cm^{-1}) and 350 nm (ε 54.2). The ε values were incorrectly reported in ref 3. *Anal.* Calcd for $((NH_3)_5CoOC(NH_2)_2)(ClO_4)_3$: C, 2.39; H, 3.79; N, 19.5. Found: C, 2.39; H, 3.74; N, 19.2.

$((NH_3)_5CoO_2CNH_2)(ClO_4)_2$. The carbamatopentaamminecobalt(III) complex was prepared according to the method described by Sargeson and Taube,[4] except that aquopentaamminecobalt(III) nitrate and potassium cyanate were used instead of the perchlorate salt of the complex and NaNCO. The resulting complex was recrystallized three times by dissolution in a minimum volume of warm water (∼50°), followed by addition of an equal volume of a saturated sodium perchlorate solution. This ensured that all the nitrate was replaced by perchlorate, as confirmed by the absence of NO_3^- peaks in the infrared spectrum. In 1.0 M $LiClO_4$ the visible spectrum of the complex shows peaks at 353 nm (ε 61.8 M^{-1} cm^{-1}) and 505 nm (ε 77.9 M^{-1} cm^{-1}). In 1.0 M perchloric acid a protonated species predominates which shows absorption maxima at 349 nm (ε 51.8 M^{-1} cm^{-1}) and 507 nm (ε 67.4 M^{-1} cm^{-1}). *Anal.* Calcd for $((NH_3)_5CoO_2CNH_2)(ClO_4)_2$: C, 2.98; H, 4.25; N, 20.8. Found: C, 3.18; H, 4.33; N, 20.6.

$((NH_3)_5CoNCNC(NH_2)_2)(ClO_4)_3$. Cyanamide,[5] H_2NCN, is extremely sensitive to heat and will polymerize violently at temperatures above its melting point (40°). Solutions of cyanamide are very sensitive to traces of alkali which cause dimerization to *N*-cyanoguanidine. (The common name of this compound is "dicyandiamide"; however, as pointed out by Fieser,[6] *N*-cyanoguanidine is the correct name.) The sample of cyanamide used in this preparation had stood for 2 years at room temperature. It was

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

[2] R. T. M. Fraser, *Inorg. Chem.*, 3, 1561 (1964).

[3] R. J. Balahura and R. B. Jordan, *ibid.*, 9, 1567 (1970).

[4] A. M. Sargeson and H. Taube, *ibid.*, 5, 1094 (1966).

[5] "Cyanamide," American Cyanamid Co., Process Chemicals Department, Wayne, N. J.

[6] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 229.

completely fused in the bottle suggesting that it was mainly in the dimeric state. This was subsequently confirmed by ir and nmr spectra.

Cyanamide (15 g, Eastman Organic Chemicals), which was mostly *N*-cyanoguanidine as noted above, 15 g of aquopentaamminecobalt(III) perchlorate, 10 g of 5A molecular sieve, and ~100 ml of solvent trimethyl phosphate were heated for 1 hr on a steam bath. During this time the solution changed from orange-red to deep red to bright orange in color. The solution was cooled and filtered from the molecular sieve and the complex precipitated with excess (~1000 ml) *sec*-butyl alcohol. The complex was recrystallized three times by dissolution in warm water and addition of solid sodium perchlorate. The visible absorption spectrum showed maxima at 266 nm (ϵ 1710 M^{-1} cm^{-1}), 348 (ϵ 123), and 487 (ϵ 116) in water and 1.0 *M* perchloric acid. *Anal.* Calcd for $((NH_3)_5CoNCNC(NH_2)_2)(ClO_4)_3$: C, 4.56; H, 3.61; N, 23.9. Found: C, 4.92; H, 3.85; N, 24.0.

$((NH_3)_5CoNCNH_2)(ClO_4)_3$. The ligand used was supplied by Cyanamid of Canada as Aero Cyanamide-100 in the form of pellets and kept refrigerated at all times. In a typical preparation 25 g of cyanamide pellets, 15 g of aquopentaamminecobalt(III) perchlorate, and 20 g of 3A molecular sieve were mixed with 150–200 ml of dimethylacetamide and heated on a steam bath for 1 hr. The resulting solution was cooled, filtered and 1500 ml of *sec*-butyl alcohol added to precipitate the complex. Trimethyl phosphate was also used as solvent with the same results. The crude complex was first recrystallized from warm water yielding two main fractions. The least soluble fraction was a mixture of the *N*-cyanoguanidine complex and an as yet uncharacterized compound, and the soluble fraction contained the desired cyanamide complex along with ~10% impurity of the *N*-cyanoguanidine complex and the unknown compound. Fractional recrystallization of this latter mixture nine times finally yielded the cyanamide complex in ~95% purity, the remaining 5% being the *N*-cyanoguanidine complex. In 1.0 *M* perchloric acid the visible absorption spectrum shows peaks at 339 nm (ϵ 65.3 M^{-1} cm^{-1}) and 480 nm (ϵ 73.7 M^{-1} cm^{-1}), whereas in water the peaks are at 304 nm (ϵ 347 M^{-1} cm^{-1}) and 486 nm (ϵ 77.1 M^{-1} cm^{-1}). In 1.0 *M* sodium acetate the visible absorption showed maxima at 304 nm (ϵ 965 M^{-1} cm^{-1}) and 521 nm (ϵ 108 M^{-1} cm^{-1}). *Anal.* Calcd for $((NH_3)_5CoNCNH_2)(ClO_4)_3$: C, 2.48; H, 3.51; N, 20.2. Found: C, 2.41; H, 3.54; N, 20.0.

Determination of the Ionization Constants. The equilibrium constant for the proton dissociation from $(NH_3)_5CoO_2CNH_3^{3+}$ to give $(NH_3)_5CoOCNH_2^{2+}$ was determined spectrophotometrically at 24.8° and at a wavelength of 290 nm. Varying amounts of standardized perchloric acid were added to solutions of $((NH_3)_5CoO_2CNH_2)(ClO_4)_2$ and with enough lithium perchlorate to adjust the ionic strength to 1.0 *M*. The spectra were measured with a Bausch and Lomb 505 spectrophotometer fitted with a thermostated cell compartment. The data were treated following the procedure given by Albert and Sergeant.[7]

The dissociation constant of the cyanamide complex was measured at 24.6, 34.8, and 43.8° by pH titration. A weighed amount of $((NH_3)_5CoNCNH_2)(ClO_4)_3$ was dissolved in 25.0 ml of 1.0 *M* lithium perchlorate and titrated with 0.010 *M* sodium hydroxide also in 1.0 *M* $LiClO_4$. The pK_a was obtained from the pH at half neutralization since, for the range of pH's involved, this should be a good approximation. The pH measurements were made on a Beckman Expandomatic pH meter standardized at pH 4 and 7.

Kinetic Measurements. Deoxygenated solutions were handled using standard syringe techniques with rubber serum caps sealing all containers.

For reactions run under pseudo-first-order conditions (reductant in at least 15-fold excess over oxidant) the observed 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 absorbancies at time *t* and after the reaction is complete.

The reduction of the carbamate complex was carried out under second-order conditions in a number of cases. A plot of log $\{1 - (1 - (b/a))(A_0 - A_\infty)/(A_t - A_\infty)\}$ *vs.* time gives a slope of $(b - a)k_2/2.303$, where A_0, A_t, and A_∞ have the usual meaning, *b* is the initial chromium(II) concentration, *a* is the initial cobalt complex concentration, and k_2 is the specific rate constant for reduction.

The reactions were followed by observing the decrease in absorbance at the longest wavelength maximum of the cobalt(III) complex. All rates were measured using a Bausch and Lomb precision spectrophotometer.

The temperature was controlled using a Colora constant-temperature bath connected to a Rho circulating cooler (for temperatures below 20°) and a Thermistemp temperature controller (Model 71) with the thermistor probe in the cell holder of the spectrophotometer. Periodic checks of the temperature were made during a series of kinetic runs by measuring the temperature of the solution in the optical cell with a thermometer.

Ion-Exchange Separation of Reaction Mixtures. Reaction mixtures were ion exchanged at 5° using Dowex 50W-X12 cation-exchange resin. The resin was pretreated with $HClO_4$, distilled water, 50% acetone, ethanol, and distilled water in order to remove all traces of organic material. Elution was carried out with a solution 0.5 *M* in $NaClO_4$ and 0.1 *M* in $HClO_4$. The eluting solution was added first in about one-quarter strength and the concentration gradually increased after separation had occurred. The average time spent on the column was approximately 90 min.

The products were characterized spectrophotometrically on a Cary Model 14 spectrophotometer. All extinction coefficients were based on the chromium concentration which was determined spectrophotometrically as chromate. For chromium(III) solutions that contained Co^{2+}, the resulting chromate solution was filtered through two 5-μ Millipore filters to remove the cobalt oxide.

Physical Measurements. The proton magnetic resonance spectra were obtained using a Varian A56/60 spectrometer. All spectra were recorded in deuterated dimethyl sulfoxide and the chemical shifts are reported with respect to the DMSO peak at τ 7.48. All complexes were the perchlorate salts. The infrared measurements were made in potassium bromide disks and Nujol mulls using a Perkin-Elmer 421 grating spectrophotometer.

Results

All of the compounds have been characterized by CHN analysis, but this does not differentiate between the linkage isomers which are possible for several of the ligands studied. Infrared, nmr, and visible spectroscopy have been used to try and determine which linkage isomer is present. Generally a single spectroscopic method does not give a definitive isomer assignment, but the cumulative results provide a strong indication of the isomer involved. In addition, the acid–base properties and pK_a values are useful in deciding how the ligand is bonded to the cobalt atom.

Infrared Spectra. The infrared spectrum of the urea complex shows the characteristic urea pattern[8] in the 1600-cm^{-1} region with the C=O stretching frequency at ~1640 cm^{-1}.[9] The overall shifts are consistent with oxygen coordination.[8]

The carbamato complex has been characterized previously.[4] The C=O stretch occurs at 1560 cm^{-1},[9] shifted by ~150 cm^{-1} to lower frequency than the C=O stretch in ethyl carbamate (urethane).[10]

The characteristic C≡N stretching frequencies of the cyanamide and *N*-cyanoguanidine complexes are given in Table I along with the corresponding frequency for the free ligands. Also included in Table I are the C≡N frequencies for several complexes known to be coordinated through the nitrile group. In all cases the C≡N stretching frequency increases upon coordination. This behavior is also observed for nitrile complexes of $(NH_3)_5Ru^{3+}$.[11] The changes in stretching frequency provide the first indication that the cyanamide and *N*-cyanoguanidine are bonded to cobalt through the nitrile

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[7] A. Albert and E. P. Sergeant, "Ionization Constants of Acids and Bases," Wiley, New York, N. Y., 1962.

[8] R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, 79, 1575 (1957).

[9] Measured in the deuterated complex since coordinated NH_3 has a broad absorption in the 1600-cm^{-1} region.

[10] S. Pinchas and D. Ben-Ishai, *J. Amer. Chem. Soc.*, 79, 4099 (1957).

[11] R. E. Clark and P. C. Ford, *Inorg. Chem.*, 9, 227 (1970).

Table I. Stretching Frequencies, ν(C≡N) for Nitriles

Ligand	Stretching frequency,[a] cm^{-1} Complexed	Free ligand	Ref
N-Cyanoguanidine	2200, 2260 (s)	2115, 2165 (s), 2210	This work
Cyanamide[b]	2310	2210–2250	This work
1,4-Dicyanobenzene	2235,[c] 2290	2230	*d*
4-Cyanophenol	2280	2235	*d*
Acetonitrile	2320	2267[e]	*f*

[a] Identical results were obtained using KBr disks or Nujol mulls. [b] The conjugate base has ν(C≡N) at 2150 cm^{-1}. [c] This is assigned to the uncoordinated C≡N from comparison to the free ligand. [d] Detailed results on these complexes will be published elsewhere. [e] L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen, London, 1968, p 68. [f] R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966).

as shown in structures I and II, and not through the amino group.

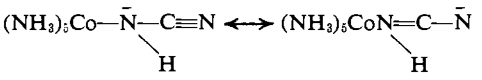
$$(NH_3)_5CoN{\equiv}C{-}NH_2{}^{3+} \quad (NH_3)_5CoN{\equiv}C{-}N{=}C(NH_2)_2{}^{3+}$$

I II

$$(NH_3)_5CoN{\equiv}C{-}\bar{N}H^{2+} \longleftrightarrow (NH_3)_5Co\bar{N}{=}C{=}NH^{2+} \qquad (1)$$

IIIa IIIb

The C≡N stretch in the conjugate base of the cyanamide complex occurs at 2150 cm^{-1}, shifted to lower frequency as expected if resonance form IIIb makes a significant contribution in the conjugate base. If cyanamide were bonded through the NH$_2$ then resonance structures IVa and IVb can be drawn for the conjugate base. However, IVb would not be favored because it involves movement of electron density away from the cobalt(III) atom. Therefore, a relatively small change in the C≡N stretching frequency would be expected for bonding through the amino group. It is also possible, however, that if cyanamide were bonded through NH$_2$, then tautomerism to give III might occur in the conjugate base.



$$(NH_3)_5Co{-}\bar{N}(H){-}C{\equiv}N \longleftrightarrow (NH_3)_5CoN(H){=}C{-}\bar{N} \qquad (2)$$

IVa IVb

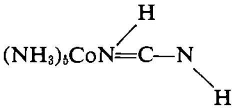
Proton Magnetic Resonance Spectra. The observed proton chemical shifts for the carbamato, urea, *N*-cyanoguanidine, and cyanamide complexes are given in Table II. It has been noted previously[3] that the chemical shift difference between the cis and trans NH$_3$ protons is τ 1.0–1.5 for an O-bonded ligand and τ 0–0.6 for an N-bonded ligand. The results in Table II conform to this empirical rule.

Table II. Proton Chemical Shift Data[a]

Complex	Cis NH$_3$	Trans NH$_3$	NH$_2$[b]
$(NH_3)_5CoO_2CNH_2{}^{2+}$	6.24	7.42	4.79
$(NH_3)_5CoOC(NH_2)_2{}^{3+}$	6.10	$\sim$7.5[c]	3.37
$(NH_3)_5CoNCNC(NH_2)_2{}^{3+}$	6.18	6.62	2.68
$(NH_3)_5CoNCNH_2{}^{3+}$	6.33	6.83	1.87

[a] All shifts are given in τ units relative to the solvent DMSO peak at τ 7.48. Spectra were measured on the perchlorate salts in DMSO-d_6. [b] Free-ligand -NH$_2$ shifts are at τ 4.36, 3.41, and 4.70 for urea, *N*-cyanoguanidine, and cyanamide, respectively, also measured in DMSO-d_6. [c] The trans NH$_3$ is hidden by the solvent peak.

The fact that all the NH$_2$ protons in the *N*-cyanoguanidine complex are equivalent shows that the ligand is bonded through the nitrile nitrogen. However, for the cyanamide complex the nmr spectrum does not help in differentiating the linkage isomers, although it does eliminate V since two different N–H protons, with a 1:12 integration relative to the cis NH$_3$ protons would be observed.



$$(NH_3)_5CoN(H){=}C{-}N{-}H$$

V

The presence of only one NH$_2$ resonance in the spectrum of the urea complex further confirms that the urea is O-bonded.

Protonation Equilibrium of $(NH_3)_5CoO_2CNH_2{}^{2+}$. As noted in the Experimental Section, the visible spectrum of the carbamato complex changes on going from neutral to acidic solution. The changes are reversible and are not associated with hydrolysis. Similar observations have been made by Barrett[12] in the acetatopentaamminecobalt(III) system. In this case the changes were attributed to protonation of the acetate ligand with an equilibrium constant for proton dissociation of 4.0 *M* (25°, 1.0 *M* LiClO$_4$–HClO$_4$). Likewise, in the less analogous $(H_2O)_5CrO_2C_2H_3{}^{2+}$ system, Deutsch and Taube[13] observed a protonation equilibrium with a dissociation constant of 3.25 *M* at 25° and ionic strength 4.0 *M*. However, in neither case was it possible to decide which of the ligand oxygens was being protonated.

A similar protonation is assumed for the carbamate ligand, and in this case it is possible to infer at least which of the ligand atoms is protonated. It was found that the carbamate -NH$_2$ protons did not exchange with D$_2$O in neutral or basic solution; however, in acidic D$_2$O exchange does occur and the NH$_2$ pmr is broadened. This shows that the -NH$_2$ proton exchange is acid catalyzed and provides evidence that protonation of the complex occurs on the -NH$_2$ group of the carbamate ligand.

The equilibrium constant for the reaction

$$(NH_3)_5CoO_2CNH_3{}^{3+} \overset{K_a}{\rightleftharpoons} (NH_3)_5CoO_2CNH_2{}^{2+} + H^+ \qquad (3)$$

has been determined spectrophotometrically at 25.8° and 290 nm. It is easily shown that a plot of $(\epsilon_1 - \epsilon_{obsd})/[H^+]$ *vs.* ϵ_{obsd} should be linear with slope $K_a{}^{-1}$ and intercept (ϵ_2/K_a), where ϵ_1 and ϵ_2 are the molar extinction coefficients of unprotonated and protonated complexes, and ϵ_{obsd} is obtained from the measured absorbance and total complex concentration at a particular hydrogen ion concentration. The resulting plot is linear, as shown in Figure 1, and gives $K_a = 0.105\ M$ and $\epsilon_2 = 7.7\ M^{-1}\ cm^{-1}$.

Proton Dissociation from Cyanamidopentaamminecobalt(III). Figure 2 shows the change in the visible spectrum of the cyanamide complex when the pH is changed from ~8 to 0. The changes are attributed to the reaction

$$(NH_3)_5Co(NCNH_2)^{3+} \rightleftharpoons (NH_3)_5Co(NCNH)^{2+} + H^+ \qquad (4)$$

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(12) M. Barrett, Ph.D. Thesis, Department of Chemistry, Stanford University, 1968.

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

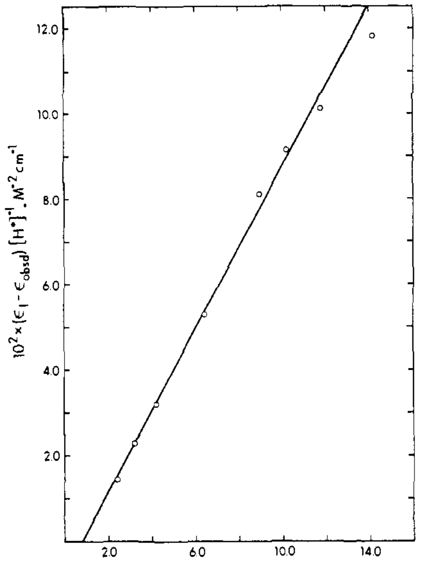


Figure 1. Spectrophotometric determination of the acid dissociation constant of $(NH_3)_5CoO_2CNH_3^{3+}$ at 290 nm, 25.8°, and ionic strength 1.0 *M*. ϵ_1 is the molar extinction coefficient of the unprotonated species.

The equilibrium constant was determined by potentiometric titration in 1 *M* $LiClO_4$ with sodium hydroxide. The p*K*'s at 24.6, 34.8, and 43.8° were found to be 5.18, 4.95, and 4.74, respectively. The enthalpy and entropy are 10.0 ± 0.5 kcal mol^{-1} and 10 ± 2 cal mol^{-1} deg^{-1}.

In all titrations the equivalent weight was determined to be 520 compared to a theoretical value of 486. This indicates about 6–7% of the *N*-cyanoguanidine complex is present as an impurity, as noted in the Experimental Section.

Coordination to $(NH_3)_5Co^{3+}$ has changed the pK_a of cyanamide (at 25°) from 10.27[5] to 5.18 or about 5 p*K* units. This change in p*K* provides some evidence for formulating the complex as the linkage isomer $(NH_3)_5Co{-}N{\equiv}C{-}NH_2$, since for the nitrogen-bonded ligands sulfamate[14] and formamide[1] the p*K* of the NH_2 protons changes by >10 and >13[15] units, respectively. The acidity of the cyanamide $-NH_2$ protons is increased on coordination, presumably because of increased H_2N to C π bonding over that present in the free ligand.[16]

On the other hand it might be argued that the large change in visible spectrum on formation of the conjugate base is more consistent with NH_2 coordination. However, the $N{=}C{=}NH^-$ ligand is isoelectronic with N_3^- and NCO^- and it is not unreasonable, therefore, that it gives a spectrum similar to those of the $(NH_3)_5Co^{3+}$ complexes of these ions. The spectrum of the $N{\equiv}C{-}NH_2$ complex is similar to that of other nitrile ligand complexes such as those with acetonitrile and terephthalonitrile.

Reactions of Coordinated Cyanamide. The nature of the linkage isomer of the cyanamide complex remains somewhat uncertain, although all indications are that it is $(NH_3)_5CoN{\equiv}C{-}NH_2^{3+}$. It was felt that this assignment could be more firmly established by studying some reactions of coordinated cyanamide.

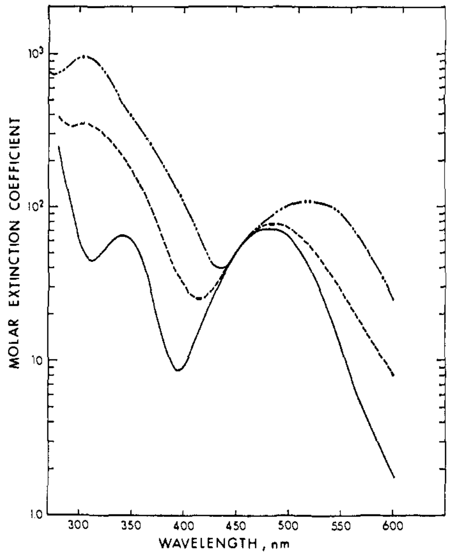


Figure 2. Visible spectra of $((NH_3)_5CoNCNH_2)(ClO_4)_3$ in 1 *M* $HClO_4$ (—), H_2O (pH ~3.7; - - -), and 1 *M* sodium acetate (pH ~8.2; · · ·).

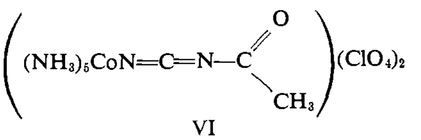
Initially the reaction with nitrous acid was studied. It was thought that this might give $(NH_3)_5CoNC^{2+}$ and N_2O as products; however, the reaction actually proceeds as a normal nitrosation

$$(NH_3)_5CoNCNH_2^{3+} + HNO_2 \xrightarrow{\text{pH 4}} (NH_3)_5CoNCO^{2+} + N_2 + H_3O^+$$

A solution containing 0.02 g of $NaNO_2$ and 0.10 g of $((NH_3)_5CoNCNH_2)(ClO_4)_3$ in 6 ml of H_2O at pH 4 (sodium acetate–acetic acid buffer) was allowed to stand at room temperature for 20 min and then solid $NaClO_4$ was added to precipitate the product. The $((NH_3)_5CoNCO)(ClO_4)_2$ product was characterized by its visible, nmr, and infrared spectra and also by its hydrolysis reaction to $Co(NH_3)_6^{3+}$ in 0.1 *M* HCl.[3]

The nitrosation is assumed to proceed by reaction of NO^+ with the $-NH_2$ group of cyanamide. This reaction may generate $(NH_3)_5CoNC^{3+}$ as an intermediate which reacts with water to give the cyanato product. It is also possible that direct oxygen atom transfer from NO^+ to cyanamide may occur to give $(NH_3)_5CoNCO^{2+}$ as the immediate product.

The acylation of coordinated cyanamide by acetic anhydride has also been observed. This reaction proceeds smoothly and appears to be complete in a few minutes when 0.2 ml of acetic anhydride is added to 0.55 g of $((NH_3)_5CoNCNH_2)(ClO_4)_2$ and ~15 drops of *N*,*N*-dimethylbenzylamine dissolved in 5 ml of *N*,*N*-dimethylformamide. The product was isolated by addition of *sec*-butyl alcohol to the reaction solution. The product (VI) was characterized by its nmr spectrum (in DMSO-d_6), which showed CH_3 protons at τ 8.17, cis NH_3 protons at τ 6.38, and trans NH_3 protons at τ 6.88. The product showed no NH_2 proton resonance and did not



$$\left((NH_3)_5CoN{=}C{=}N{-}C\begin{matrix}{\overset{\displaystyle O}{/\!\!/}}\\ {\searrow} CH_3\end{matrix}\right)(ClO_4)_2$$

VI

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[14] L. L. Po and R. B. Jordan, *Inorg. Chem.*, 7, 526 (1968).

[15] Only lower limits can be given because the p*K* of the ligand is not actually measurable in aqueous solution and is assumed to be >15.

[16] H. F. Henneike and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 5112 (1968).

change color on changing from neutral to basic conditions, both properties which distinguish it from the cyanamide complex. The infrared spectrum shows a strong peak at 2220 cm^{-1} as might be expected for an -N=C=N- system as in the *N*-cyanoguanidine complex (Table I).

The observation that the acylation reaction proceeds so easily is indicative of the $(NH_3)_5CoN{\equiv}C{-}NH_2$ linkage isomer. The reaction at a coordinated NH_2 is expected to be sterically unfavorable, but it is not impossible. The nitrosation reaction, however, provides strong evidence for the proposed linkage isomer since the NH_2 isomer should yield $(NH_3)_5CoOH_2^{3+}$ as a product rather than the observed $(NH_3)_5CoNCO^{2+}$.

Chromium(II) Reduction. Kinetics and Product Analysis. The reductions of the urea and *N*-cyanoguanidine complexes were shown to consume 1 mol of chromium(II)/mol of cobalt(III) complex. Solutions initially containing a 4:1 ratio of reductant to oxidant were analyzed for excess chromium(II) after ten half-times for reaction.

The stoichiometries of the reduction of the carbamate and cyanamide complexes were also found to be 1:1, since the visible spectrum showed no unreacted cobalt(III) complex in solutions containing initial 1:1 ratios of oxidant to reductant. In addition, the rate constant obtained for the carbamate complex under second-order conditions was in good agreement with those obtained under conditions pseudo first order in chromium(II).

The rate of reduction of the carbamate complex was found to increase with decreasing acid concentration, eventually leveling off at low [H+] as shown in Figure 3. This behavior is consistent with the reaction scheme

$$
\begin{aligned}
&(NH_3)_5CoO_2CNH_3^{3+} \overset{K_a}{\rightleftharpoons} (NH_3)_5CoO_2CNH_2^{2+} + H^+\\
&(NH_3)_5CoO_2CNH_2^{2+} + Cr^{2+} \xrightarrow{k_1} \text{products}\\
&(NH_3)_5CoO_2CNH_3^{3+} + Cr^{2+} \xrightarrow{k_2} \text{products}
\end{aligned}
\qquad (5)
$$

If the first reaction is assumed to be a rapid preequilibrium, then the rate law for reduction is

$$
-\frac{d\ln[(NH_3)_5CoO_2CNH_2]}{dt} = \left[\frac{k_1K_a + k_2[H^+]}{K_a + [H^+]}\right][Cr^{2+}] = k_{obsd}[Cr^{2+}] \qquad (6)
$$

A nonlinear least-squares[17] fit of the k_{obsd} values in Table III to the expression indicated by eq 6 gave best-fit values of k_1, k_2, and K_a shown in Table IV. The rate constant k_2 is too small to be reliably established.

The K_a calculated from the kinetic study is in reasonable agreement with the value measured spectrophotometrically. The kinetic values at 8.0 and 15.0° are considered to be the most reliable, since at 25.8° most of the kinetics were done under second-order conditions.

The chromium(III) product of reduction of the carbamate complex has been characterized by ion-exchange chromatography and by its visible spectrum. The product shows ion-exchange properties typical of a dipositive ion and generally is eluted along with the cobalt(II) ion. It should be noted that only 65% of the total expected product has been obtained in the 2+ charged species. The remainder appears to be $Cr(OH_2)_6^{3+}$, which may result from hydrolysis on the ion-exchange column or may be a direct product of the reduction.

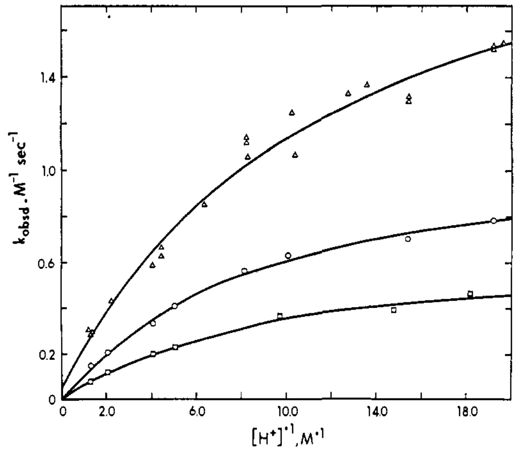

Figure 3. Dependence of the reduction rate of $(NH_3)_4CoO_2CNH_2^{2+}$ by Cr^{2+} on [H+], ionic strength 1.0 *M* ($LiClO_4$-$HClO_4$): Δ, 25.8°; ○, 15.0°; □, 8.0°.

Table III. Kinetic Data for the Reduction of $(NH_3)_5CoO_2CNH_2^{2+}$ by Chromium(II) at 25.8°, Ionic Strength 1.0 *M* ($LiClO_4$–$HClO_4$)

[Oxidant][a] × 10^3	[Reductant][a] × 10^3	[H+][a]	k_{obsd}, M^{-1} sec^{-1}
1.94	21.9	0.815	0.305
2.00	38.7	0.811	0.284
2.00	38.7	0.811	0.298
2.30	7.7	0.440	0.431
2.40	7.7	0.440	0.435
2.00	41.0	0.247	0.583
2.20	8.2	0.223	0.663
2.15	7.7	0.223	0.629
2.70	7.9	0.157	0.855
2.10	7.9	0.121	1.06
2.45	8.3	0.121	1.12
2.70	8.3	0.121	1.14
2.45	8.3	0.097	1.07
2.30	7.9	0.098	1.25
1.27	7.1	0.078	1.33
2.46	7.8	0.074	1.37
1.42	5.3	0.065	1.32
1.25	5.3	0.065	1.30
1.32	5.3	0.052	1.52
1.28	5.3	0.052	1.54
1.00	4.1	0.051	1.55

[a] Initial concentrations in molar units.

Table IV. Kinetic Parameters for Reduction of $(NH_3)_5CoO_2CNH_2^{2+}$ by Chromium(II) at Ionic Strength 1.0 *M* ($LiClO_4$–$HClO_4$)

Temp, °C	K_a,[a] *M*	k_1,[a] M^{-1} sec^{-1}	k_2,[a] M^{-1} sec^{-1}
8.0	0.111 ± 0.010	0.68 ± 0.06	−0.01 (−0.05–0.13)
15.0	0.113 ± 0.010	1.15 ± 0.05	−0.01 (−0.05–0.03)
25.8	0.085 ± 0.007[b]	2.42 ± 0.11	0.05 (−0.03–0.13)
Δ*H**, kcal mol^{-1}		11.4 ± 0.4	
Δ*S**, cal mol^{-1} deg^{-1}		−18.6 ± 2	

[a] Error limits approximate the 95% confidence limit. [b] A value of 0.105 was determined spectrophotometrically.

A sample of the chromium(III) product free of cobalt(II) was obtained, from a reaction solution initially containing 0.0189 *M* cobalt(III), 0.023 *M* chromium(II),

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[17] Nonlinear least-squares program, IBM Share Library, SDA 3094.

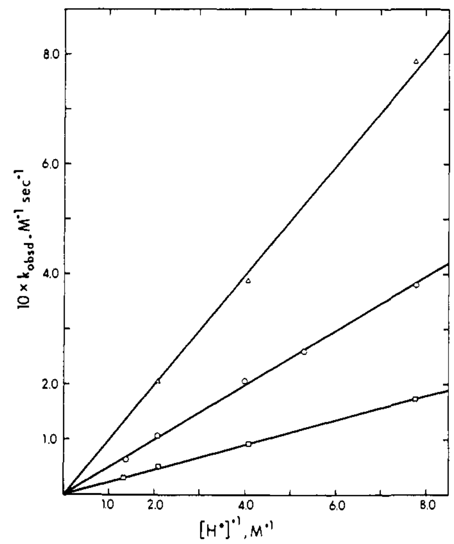

Figure 4. Dependence of the reduction rate of $(NH_3)_5CoNCNH_2{}^{3+}$ by Cr^{2+} on $[H^+]$, ionic strength 1.0 *M* ($LiClO_4$–$HClO_4$): Δ, 43.8°; O, 34.8°; □, 24.6°.

and 0.815 *M* perchloric acid, by discarding the first part of the product band eluted from the ion-exchange column. The spectrum of the product shows maxima at 568 nm (ϵ 23.9 M^{-1} cm^{-1}) and 414 nm (ϵ 21.0 M^{-1} cm^{-1}). In a number of other cases with cobalt(II) present the maxima were at the same positions, but the extinction coefficients were about 5% higher. The chromium(III) product was hydrolyzed at 50° to give $Cr(OH_2)_6{}^{3+}$ as identified by its visible and ultraviolet spectra with maxima at 572 nm (ϵ 13.2 M^{-1} cm^{-1}), 408 (ϵ 15.2), and 255 (ϵ 6.6).

The spectrum of the chromium(III) product of the reduction is typical of those of other chromium(III) carboxylate complexes,[18] and the product is assumed to be $(H_2O)_5CrO_2CNH_2{}^{2+}$. If the carbamate ligand were N-bonded it would be expected to have a spectrum similar to that of $(H_2O)_5CrNH_3{}^{3+}$ [19] and possibly to hydrolyze to the ammine complex as well.

The reduction of the cyanamide complex was found to follow the rate law

$$-\frac{d\ln[(NH_3)_5CoNCNH_2{}^{3+}]}{dt} = (k'/[H^+])[Cr^{2+}] = k_{obsd}[Cr^{2+}] \quad (7)$$

The kinetics were determined with a large (15-fold) excess of chromium(II) and H^+ to obtain k_{obsd}. Plots of k_{obsd} *vs.* $[H^+]^{-1}$ are linear as shown in Figure 4. The value of k' was determined from the slope of the lines in Figure 4. It should be noted that no significant intercept could be detected for these lines.

The rate law is consistent with the reaction scheme

$$\begin{gathered}(NH_3)_5CoNCNH_2{}^{3+} \overset{K_a}{\rightleftharpoons} (NH_3)_5CoNCNH^{2+} + H^+ \\ (NH_3)_5CoNCNH^{2+} + Cr^{2+} \xrightarrow{k_{cy}} \text{products}\end{gathered} \quad (8)$$

If it is assumed that the first step is a rapid equilibrium, then

$$-\frac{d\ln(NH_3)_5CoNCNH_2{}^{3+}]}{dt} = \frac{k_{cy}K_a}{K_a + [H^+]}[Cr^{2+}] \quad (9)$$

K_a has been determined as described previously and is always less than $[H^+]$, therefore, comparing eq 7 and 9, $k' = k_{cy}K_a$. Values of k', K_a, and k_{cy} are summarized in Table V.

Table V. Kinetic Parameters for Reduction of $(NH_3)_5CoNCNH_2{}^{3+}$ by Chromium(II) at Ionic Strength 1.0 *M* ($LiClO_4$–$HClO_4$)

Temp, °C	$10^5 \times K_a$,[a,b] *M*	$10^2 \times k'$,[b] sec^{-1}	$10^{-3} \times k_{cy}$, M^{-1} sec^{-1}
24.6	0.66	2.20	3.33
34.8	1.12	4.93	4.40
43.8	1.82	9.93	5.46
ΔH^*, kcal mol^{-1}		4.3 ± 1	
ΔS^*, cal mol^{-1} deg^{-1}		−28 ± 3	

[a] Determined by potentiometric titration at 1.0 *M* ionic strength. [b] Errors are estimated to be ±10% on K^a and ±5% on k'.

The chromium(III) product of the reduction of the cyanamide complex appears to be $Cr(OH_2)_6{}^{3+}$. This seems unusual in that the rate law and large specific rate constant k_{cy} both indicate a bridging mechanism. In a kinetic run with initial concentrations of 5.0 × 10^{-3} *M* chromium(II), 3.9 × 10^{-3} *M* cobalt(III), and 4.8 × 10^{-2} *M* H^+ the complete spectrum was scanned at various intervals. Good isosbestic behavior was observed for >95% reaction with isosbestic points at 652, 543, 419, and 381 nm. Ion-exchange analysis after complete reaction of a solution with the same composition gave a product with wavelength and extinction coefficient maxima identical with those of $Cr(OH_2)_6{}^{3+}$. There was no evidence for any chromium(III) cyanamide product.

The reductions of the urea and *N*-cyanoguanidine complexes followed the rate law

$$-\frac{d\ln[\text{cobalt(III) complex}]}{dt} = k''[Cr^{2+}] \quad (10)$$

The rate data for these two complexes are given in Table VI. The activation parameters are given in Table VII.

Table VI. Kinetic Data for Reduction of $(NH_3)_5CoOC(NH_2)_2{}^{3+}$ and $(NH_3)_5CoNCNC(NH_2)_2{}^{3+}$ by Chromium(II) at Ionic Strength 1.0 *M* ($LiClO_4$–$HClO_4$)

Temp, °C	[Oxidant][a] × 10^3	[Reductant][a] × 10^2	$[H^+]$[a]	$10^2 \times k$, M^{-1} sec^{-1}
		Urea[c]		
24.6	2.07	3.32	0.240	1.93
24.6	2.17	3.32	0.478	1.93
24.6	2.05	3.32	0.764	1.93
24.6	1.95	3.07	0.248	1.89[b]
34.8	2.05	3.32	0.240	3.45
34.8	2.15	3.32	0.478	3.42
45.0	2.19	3.50	0.240	6.46
45.0	2.22	3.50	0.478	6.46
		N-Cyanoguanidine[c]		
24.6	1.57	3.00	0.248	2.92
24.6	1.47	3.21	0.189	2.81
24.6	1.47	6.42	0.200	2.86
34.8	1.48	3.32	0.248	4.63
34.8	1.48	3.32	0.486	4.70
34.8	1.48	3.32	0.724	4.70
43.8	1.51	3.21	0.189	6.79
43.8	1.51	3.21	0.189	6.79
43.8	1.51	3.21	0.486	6.79

[a] Concentrations are initial values in molar units. [b] The spectrum was scanned during this run and showed isosbestic points at 394, 428, and 603 nm. [c] ΔH^* and ΔS^* values are given in Table VII.

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(18) E. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964).

(19) J. H. Espenson and D. W. Carlyle, *Inorg. Chem.*, **5**, 586 (1966).

Table VII. Kinetic Parameters for Chromium(II) Reduction of Some $(NH_3)_5CoX$ Complexes

Complex	k,[a] M^{-1} sec^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal mol^{-1} deg^{-1}	Ref
$(NH_3)_5CoOC(NH_2)_2{}^{3+}$	1.9×10^{-2}	10.6	−31	This work
$(NH_3)_5CoNCNC(NH_2)_2{}^{3+}$	2.9×10^{-2}	8.3	−37	This work
$(NH_3)_5CoOCHNH_2{}^{3+}$	8.5×10^{-3}	10.7	−32	1
$(NH_3)_5CoOCHN(CH_3)_2{}^{3+}$	6.7×10^{-3}	10.6	−33	1
$(NH_3)_5CoNHCHO^{2+}$ [b]	1.7	12.0	−17	1
$(NH_3)_5CoO_2CH^{2+}$	7.2	8.3	−27	12
$(NH_3)_5CoO_2CNH_2{}^{2+}$	2.4	11.4	−19	This work
$(NH_3)_5CoO_2CCH_3{}^{2+}$	0.35	8.2	−33	12
$(NH_3)_5CoNCNH^{2+}$	3.3×10^{3}	4.3	−28	This work

[a] Values given are all for within 1° of 25°. The exact temperatures are given in the references. The ionic strength is 1.0 M unless otherwise stated. [b] Ionic strength 0.92 M.

The chromium(III) product was investigated again by scanning the reaction solutions and by ion exchange. Scan runs with chromium(II) in either two- or tenfold molar, excess over cobalt(III) showed good isosbestic behavior and the final product spectrum did not change with time (up to 24 hr). Ion-exchange analysis showed that the product was $Cr(OH_2)_6{}^{3+}$ identified by its visible spectrum.

Discussion

The systems studied in this work were largely designed to test our previous proposal that bridged electron transfer would not occur through an $-NH_2$ group. It is assumed that the necessary conditions for bridged transfer are the presence of a nonbonding lone pair of electrons on the atom forming the bridge to the reducing agent and a conjugated system between the bridging group atoms attached to the reducing agent and the oxidizing agent. Therefore two non-σ-bonding pairs of electrons are required on the ligand atom attached to the reducing agent. Since an $-NH_2$ group has only one lone pair, it cannot simultaneously bond to the reducing agent and be part of a conjugated system.

The results reported here lend further support to the above proposal. The urea and *N*-cyanoguanidine complexes are both reduced by an outer-sphere mechanism as evidenced by the low specific rate constant, comparison to outer-sphere reduction of O-bonded formamide and *N*,*N*-dimethylformamide complexes and failure to detect any chromium(III) product other than $Cr(OH_2)_6{}^{3+}$.

The fact that the cyanamide complex is only reduced as its conjugate base further supports the ideas outlined above. Removal of a proton from cyanamide gives the ligand $(N{\equiv}C{-}N{-}H)^-$, in which the N—H nitrogen has a free electron pair and another electron pair in conjugation with the rest of the ligand.

The carbamate system was studied in order to check the previous report[2] that chromium(II) reduction gave an N-bonded chromium(III) product. This result clearly conflicts with predictions based on the proposed conditions for bridged transfer. It should be noted that the hydrogen ion dependence of the rate law found in the present study is opposite to that reported previously[2] since the rate shows closer to an inverse rather than direct dependence on hydrogen ion concentration. In addition no evidence has been found for an N-bonded chromium(III) product, either as a reactive intermediate or as the stable final product. Unless N- to O-bonded linkage isomerism is very fast it must be concluded that the carbamate complex is reduced through bridging to an oxygen of the carbamate ligand.

It is not possible to decide which of the two carbamate oxygens is involved in the bridge from these results. Previous work on the formamide complexes[1] has shown that the carbonyl oxygen is the one used. In the present study the results on the urea complex support this proposal. Urea has a carbonyl oxygen directly bonded to cobalt and should not have any greater steric hindrance than the carbamate complex, yet urea is reduced by an outer-sphere mechanism. Therefore, a carbonyl or carboxylate oxygen atom directly bonded to cobalt does not act as a good bridging atom.

Rate constants and activation parameters for several systems are summarized in Table VII. It may be noted that the ΔH^* and ΔS^* are very similar for all the O-bonded systems which proceed without ligand transfer. This is not surprising perhaps, in view of the structural similarity of all these ligands. The reduction of the *N*-cyanoguanidine complex has a significantly lower ΔH^* and more negative ΔS^* than that of the O-bonded systems.

It may be noted that ΔH^* and ΔS^* values, at least at 1 M ionic strength, are not necessarily greatly different for the systems which proceed with or without ligand transfer. It is clear that these parameters are not useful in distinguishing between inner- and outer-sphere chromium(II) reductions.

The reduction of the carbamate complex appears unusual in comparison to the acetate. The ΔH^* is higher, the ΔS^* more positive, and the latter is the dominant factor in making the reduction rate constant larger at 25°. The simplest argument would predict that carbamate is the most basic ligand and therefore should form the most stable bridge to chromium(II) and have the lower ΔH^*, the exact opposite of what is observed. The high ΔH^* might be attributed to chelate formation between chromium(II) and the remote O and N atoms of carbamate. The necessity to rotate about the $C{-}NH_2$ bond and break any π bonding between these atoms would contribute to the ΔH^*. Nmr studies have shown that there is restricted rotation in the carbamate ligand since the $-NH_2$ resonance splits into two peaks below −20° (100 MHz) in DMF-d_7.[20]

The reduction of the conjugate base of cyanamide is kinetically quite different from all the other systems. This indicates that bridged electron transfer is occurring, although the expected chromium(III) product has not been obtained. The latter result may be due to rapid hydrolysis of the initial product; however, this would not be expected from the relatively slow hydrolysis of most complexes of $Cr(OH_2)_5{}^{3+}$. The ligand $N{=}C{=}N{-}H^-$ is isoelectronic with and probably structurally similar to the azide ion. The activation parameters have not been determined for the chromium(II) reductions of $(NH_3)_5CoN_3{}^{2+}$, but the rate constant, $\sim 3 \times 10^5$ M^{-1} sec^{-1} at 25°,[21] indicates that the value of 3.3×10^3 M^{-1} sec^{-1} observed for $(NH_3)_5CoN{=}C{=}NH^{2+}$ is not surprisingly large.

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(20) R. J. Balahura, manuscript in preparation.

(21) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, **86**, 1019 (1964).