Moreover, even for those Cu(II) complexes having $g_\perp > g_\parallel$ (unpaired electron in a d_{z^2} orbital), the resonance can be seen at room temperature.[18]

Additionally, the small g factor anisotropy observed at 77° is not consistent with rotational broadening at room temperature. The small g-factor anisotropy (small spin–orbit interaction) indicates that the unpaired electron resides in a nondegenerate state, hence a rapid spin lattice relaxation seems unlikely since such a mechanism requires a spin–orbit perturbation.

The possibility remains that the Rh(0) species at room temperature in this concentration range is dimerized and the resultant $S = 1$ signal broadened by the spin–spin interaction. The magnitude of D^* (Table I) estimated assuming $g = 2.00$ is sufficient to rationalize such broadening. Cyclic voltammetry[9,10] did not indicate the presence of a dimer, for either the phen or dip complex. However, the adsorption and precipitation of the phen complexes made detection of such a dimer species difficult. Indeed, a dipole–dipole type dimer species with a reduction potential similar to that of the monomer here would likely not be distinguished even in the voltammetry of the dip complexes where adsorption is not significant.

The magnitude of the g anisotropy for the monomeric $[Rh(dip)_2]^0$ ($g_\perp = 2.01$, $g_\parallel = 1.98$) and $[Rh(phen)_2]^0$ ($g_\perp = 2.01$, $g_\parallel = 1.97$) is much less than that of a typical d^9 Cu(II) system.[17,18] Consequently the Rh(0) species cannot be considered a d^9 crystal field complex. Consideration of the complex as a ligand localized complex containing dip^{-1} or $phen^{-1}$ is obviously not appropriate since the dip^{-1} species has an isotropic g factor.[19] Therefore, the Rh(0) complexes are best considered as delocalized orbital complexes, i.e., metal containing heterocycles.

Such an electronic structure accounts for the relative stability of the $[Rh(dip)_2]^+$ and $[Rh(dip)_2]^0$ and the phen analogues and is consistent with the "distorted planar" trans type structure determined by x-ray diffraction for the $[Pd(dip)_2]^{2+}$ complex,[20,21] isoelectronic with the $[Rh(dip)_2]^+$ and $[Rh(phen)_2]^+$ species.

References and Notes

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# Reduction of Pentaamminecobalt(III) Complexes of Aromatic Nitriles by Chromium(II)

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Abstract: The reductions of the pentaamminecobalt(III) complexes of 3-formylbenzonitrile, 4-formylbenzonitrile, furanacrylonitrile, cinnamonitrile, and acetoxybenzonitrile by chromium(II) have been studied. The reductions all follow the rate law $-(d \ln (Co^{3+})/dt) = k[Cr^{2+}]$. The 3-formyl complex has a specific rate constant of 77 ± 8 M^{-1} s^{-1} at 25° and $\mu = 0.5$ M. The 4-formyl derivative is reduced at a rate of $2.5 \pm 0.2 \times 10^5$ M^{-1} s^{-1} at 25° and $\mu = 0.5$ M. In the latter system the reductant attacks the remote formyl carbonyl oxygen producing the intermediate A_3 which has been detected spectrally. The $(NH_3)_5Co^{3+}$ complex of 4-formylbenzonitrile is 30% hydrated in aqueous solution, and the dehydration reaction has also been studied. The furanacrylonitrile, cinnamonitrile, and acetoxybenzonitrile complexes are reduced by an outer-sphere process with rate constants 0.020 ± 0.002, 0.022 ± 0.004, and 0.021 ± 0.003 M^{-1} s^{-1} at 25° and $\mu = 0.5$ M, respectively. The results are discussed in terms of the reducibility of the ligands and the stabilities of the precursor complexes. Comparison to analogous carboxylato complexes is also made.

The reductions of $(NH_3)_5CoN{\equiv}CR^{3+}$ complexes by chromium(II) have been shown to occur by remote attack of the reductant when suitable binding groups are available on the R group. For example, the reduction of

$$(NH_3)_5CoN{\equiv}C{-}\text{C}_6\text{H}_4{-}\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \quad {}^{3+}$$
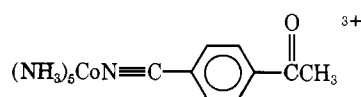
proceeds by attack of chromium(II) at the remote acetyl oxygen.[1] The study of nitrile complexes is considerably simplified with respect to the analogous carboxylato complexes since there is no adjacent position available to bind chromium(II) or protons. In the latter case it is thought that protonation of the adjacent carboxylato oxygen reduces the energy of the empty π antibonding orbitals thus allowing a more facile reduction process.[2]

We have investigated the reduction of 3-, and 4-formylbenzonitrile coordinated to $(NH_3)_5Co^{3+}$ via the nitrile nitrogen in order to compare the results with those obtained for the analogous carboxylato-coordinated ligands. The reduction of the 4-formyl derivative is complicated by the hydration–dehydration equilibrium shown below
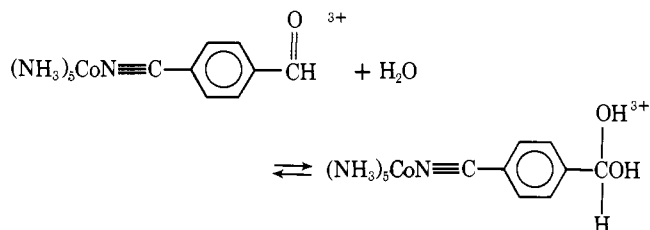

A number of other nitriles were also studied since the ligands lend themselves to an ordering of reducibility or energy of the lowest empty π antibonding orbital by either polarographic or theoretical methods.

Experimental Section

Reagents were prepared and standardized as previously described.[3] Nitriles were purchased from the Aldrich Chemical Co. and used as received. Elemental analyses were performed by M-H-W Laboratories, Garden City, Mich.

Preparation of Complexes. The preparation and characterization of the 3- and 4-cyanobenzaldehyde complexes have been described.[4] Similar preparative methods were used in the preparation of the furanacrylonitrile and cinnamonitrile complexes as well as the 4-cyanophenol complex which served as the starting material for the 4-acetoxybenzonitrile complex (see below). Physical data for the various complexes as perchlorate salts are given below.

Furanacrylonitrile (FAN) Complex. Anal. Calcd for [Co-$(NH_3)_5(C_7H_5NO)](ClO_4)_3$: C, 15.0; H, 3.60; N, 15.0. Found: C, 15.7; H, 3.90; N, 14.8. The infrared spectrum of the complex shows a peak at 2290 cm^{-1} assigned to a coordinated nitrile. The corresponding peak for the free ligand appears at 2210 cm^{-1}. The visible spectrum in water showed a peak at 472 nm with an extinction coefficient of 147 M^{-1} cm^{-1}. The ^{1}H NMR spectrum in Me$_2$SO-d_6 has the following resonances: trans NH$_3$, τ 6.65; cis NH$_3$'s, 6.26; H$_a$, 3.88 (center of doublet); H$_b$, 2.33 (center of doublet); H$_c$, 2.90 (center of multiplet); H$_d$, 3.35 (center of multiplet); and H$_e$, 2.15 (center of multiplet). The letters refer to the structure shown below. The coupling constant for H$_a$ and H$_b$ is 16 Hz indicating a trans arrangement of H$_a$
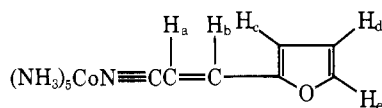

and H$_b$ with respect to the double bond.

Cinnamonitrile (CIN) Complex. Anal. Calcd for [Co-$(NH_3)_5(C_9H_7N)](ClO_4)_3$: C, 18.9; H, 3.90; N, 14.7. Found: C, 18.7; H, 3.90; N, 14.6. The nitrile stretching frequency for the complex appears at 2290 cm^{-1} and for the free ligand at 2220 cm^{-1}. The visible spectrum in H$_2$O shows a band at 470 nm with an extinction coefficient of 103 M^{-1} cm^{-1}. The ^{1}H NMR spectrum for
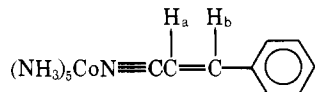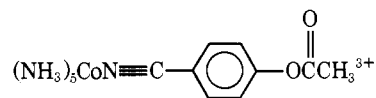

gave: trans NH$_3$, τ 6.61; cis NH$_3$'s, 6.20; aromatic protons, 2.45 (center of multiplet); H$_a$, 3.37 (center of doublet); and H$_b$, 2.07 (center of doublet). The coupling constant for H$_a$ and H$_b$ is 16.5 Hz indicating a trans structure with respect to the double bonds.

4-Acetoxybenzonitrile Complex. This complex was prepared by acylation of the 4-cyanophenol complex
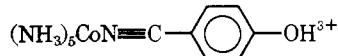
in dimethylformamide using acetic anhydride. Anal. Calcd for [Co(NH$_3$)$_5$(C$_9$H$_7$NO$_2$)](ClO$_4$)$_3$: C, 17.9; H, 3.70; N, 13.9. Found: C, 18.5; H, 3.80; N, 14.0. The complex shows a nitrile stretching

frequency at 2290 cm^{-1} and a carbonyl stretching frequency at 1760 cm^{-1}. The visible absorption band in water appears at 468 nm with an extinction coefficient of 75.9 M^{-1} cm^{-1}. The ^{1}H NMR for

gave: trans NH$_3$, τ 6.56; cis NH$_3$'s, 6.18; aromatic protons, 2.24 (center of quartet); and CH$_3$, 7.72.
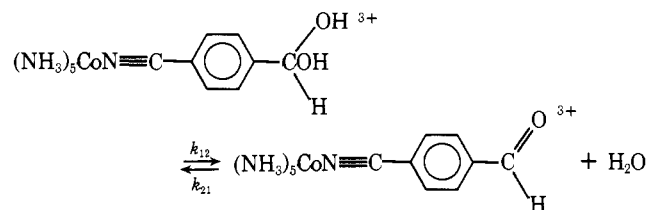
The physical data presented for the above complexes indicate that all the ligands are coordinated through the nitrile nitrogen. The complexes also undergo facile hydrolysis to coordinated carboxamides in dilute base, indicative of nitrile coordination.

Kinetic Measurements. The reduction of the 3- and 4-formylbenzonitrile complexes was studied by observing the change in absorbance both at 280 and 470 nm. Kinetic runs were performed on a Durrum Model D-110 stopped-flow spectrophotometer. The remaining complexes were studied using a Beckman Acta CIII spectrophotometer equipped with temperature control equipment.
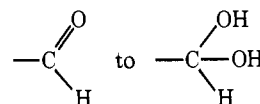
Results

Stoichiometry and Products. The stoichiometry for the reduction of the 3- and 4-formyl complexes was determined by analysis for cobalt(II) produced when cobalt(III) was in excess of chromium(II) at varying acidities. The ratio of cobalt(II) produced to chromium(II) initially present was found to be 0.99 ± 0.03 and 1.01 ± 0.01 for the 3- and 4-formyl complexes, respectively. For the slower reacting complexes total Cr^{3+} products produced were collected from ion exchange of product solutions which involved one to one mole ratios of chromium(II) to cobalt(III) complex. The only Cr^{3+} product detected was Cr(OH$_2$)$_6$$^{3+}$.

4-Formylbenzonitrilepentaamminecobalt(III). Initial reduction studies indicated that hydration of the 4-formyl group was a complicating factor. A comparison of the absorbance changes observed to those expected from the initial concentrations showed that only approximately 30% of the expected change was observed. In addition, at a given hydrogen ion concentration, the observed rate constant was apparently independent of chromium(II) concentration. Such behavior would be consistent with the existence of the equilibrium

where ~70% of the carbonyl form is rapidly reduced by chromium(II) and the process being followed is the rate of dehydration of the remaining 30%.

Evidence for the above equilibrium was obtained from proton magnetic resonance measurements on the chloride salt in D$_2$O. Such a spectrum, shown in Figure 1, clearly shows the presence of both the aldehyde and *gem*-diol forms of the complex. The formyl proton in the unhydrated form is shifted from τ −0.06 to 3.88 in the hydrated form. This is consistent with a change from

The benzenoid protons in the unhydrated form give an A$_2$B$_2$ pattern centered at τ 1.83 whereas in the *gem*-diol an A$_2$X$_2$ pattern is observed, centered at τ 2.09. Integration of the C–H proton at τ −0.06 and 3.88 indicates the presence of 25% of the *gem*-diol in agreement with the above analysis from the kinetic studies. When the ^{1}H NMR spectrum is run in Me$_2$SO-d_6 only

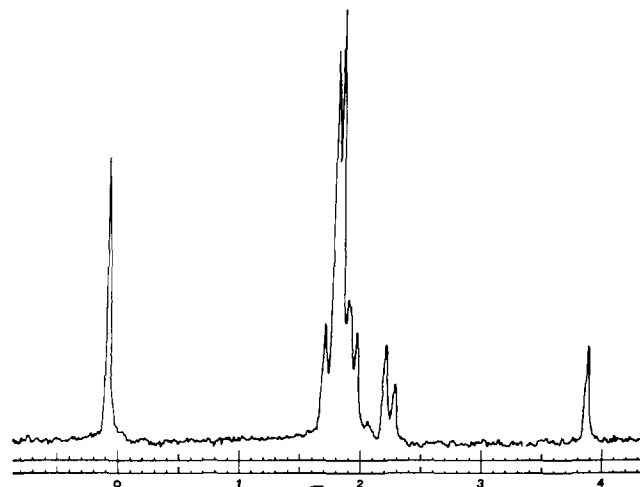**Figure 1.** Proton magnetic resonance spectrum of 4-formylbenzonitrilepentaamminecobalt(III) trichloride in D_2O at 100 MHz.

Table I. Rate of Dehydration[a] of

[Cr^{2+}], M $\times$ 10^2	[H$^+$], M	k_{dehyd},[b] M^{-1} s^{-1}
0.10	0.050	35.8
2.0	0.050	35.4
2.1	0.050	36.4
5.2	0.050	32.0
5.2	0.050	32.0
10	0.050	34.4
5.2	0.075	33.2
0.099	0.100	36.7
0.49	0.100	31.6
2.1	0.100	34.7
3.8	0.100	35.5
5.2	0.100	32.5
5.2	0.125	32.8
5.2	0.150	31.9
0.10	0.400	32.8
0.43	0.400	31.0

[a] T, 25.2 °C; λ 470 nm; μ = 0.5 M (LiClO$_4$); [Co(III)] = 3.0–4.0 $\times$ 10^{-4}. [b] k_{dehyd} = k_{obsd}/[H$^+$].

the carbonyl form of the complex is observed. The C–H resonance is at τ −0.17 and the aromatic protons are essentially a singlet at τ 1.77. Addition of acidified D_2O causes hydration with the *gem*-diol C–H proton appearing at τ 4.14.

The kinetic data describing the dehydration of the *gem*-diol at 25.2 °C are given in Table I.[5] A plot of k_{obsd} vs. [H$^+$] gave a straight line indicating a rate law of the type k_{obsd} = k_0 + k_{12}[H$^+$]. The k_0 term is small with respect to k_{12}[H$^+$] and could not be assigned a value. The data in Table I clearly indicate that the reaction is independent of [Cr^{2+}]. At 25.0 °C, k_{12} = 32 ± 7 M^{-1} s^{-1} with $\Delta H^{\ddagger}$ equal to 14.8 ± 0.9 kcal mol^{-1} and $\Delta S^{\ddagger}$ equal to −2 ± 3 eu.
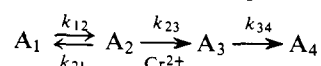
The equilibrium constant

$$K_{hyd} = \frac{[\text{aldehyde form}]}{[\text{\textit{gem}-diol form}]}$$

was obtained from the absorbance-time plots obtained for the experiments listed in Table I. Comparison of the initial absorbance expected theoretically vs. the actual absorbance observed at 470 nm gave a K_{hyd} of 2.7 ± 0.3 (27 ± 2% hydrate) and K_{hyd} = 3.1 ± 0.2 (24 ± 2% hydrate) at 25.3 and 34.7 °C, respectively. This analysis assumes that the extinction coefficients of aldehyde and *gem*-diol forms of the complex are identical at 470 nm.[6] Integration of the formyl group proton from the NMR in D_2O obtained at ~30° gives a K_{hyd} of 3.0 with 25% hydrate present.

Studies at very low chromium(II) concentrations permitted the observation of the reduction of the carbonyl form of the complex. The data, given in Table II, follow the rate law
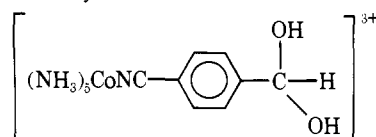
$$\frac{-d \ln (Co^{3+})}{dt} = k[Cr^{2+}]$$

At 25.2 °C the specific rate constant for reduction is (2.5 ± 0.2) $\times$ 10^5 M^{-1} s^{-1}. When the reduction was monitored at 470 or at 260 nm only a decrease in absorbance was observed corresponding to reduction. However, at 280 nm, an initial increase in absorbance was observed followed by a decrease. Also, depending upon the acid concentration used, the equilibrium between the aldehyde and hydrate forms of the complex was a complicating factor. The system observed at 280 nm can be represented by the reaction sequence
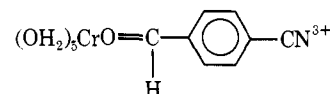
$$A_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} A_2 \xrightarrow[Cr^{2+}]{k_{23}} A_3 \xrightarrow{k_{34}} A_4$$

where A_1 and A_2 are the hydrated and unhydrated forms of the complex, respectively, A_3 is an intermediate with probable structure

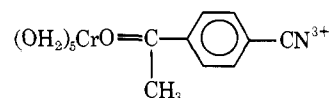and A_4 is $Cr(OH_2)_6^{3+}$ The equations derived for the above reaction sequence are given in the Appendix. With k_{12} and k_{21} known, the absorbance-time data were fit to the equations using a nonlinear least-squares program.[7] The values obtained for k_{23} (rate of reduction) were in reasonable agreement with those obtained at 260 and 470 nm where only disappearance of cobalt(III) was observed. Also, the value of 125 ± 20 s^{-1} ([H$^+$] = 0.5) for disappearance of the intermediate was reasonable in light of the value obtained for aquation[1] of

The analysis at 280 nm is hampered by the small increase in absorbance observed and the low chromium(II) concentrations necessary. At best the value of decay of the intermediate is an order of magnitude figure.

3-Formylbenzonitrilepentaamminecobalt(III). Reduction of the 3-formyl derivative followed the rate law −d ln (Co^{3+})/dt = k[Cr^{2+}]. At 25.2°, k = 77 ± 8 M^{-1} s^{-1} with $\Delta H^{\ddagger}$ equal to −2.1 ± 0.6 kcal mol^{-1} and $\Delta S^{\ddagger}$ equal to −57 ± 2 eu.[5] The reduction was studied in the ultraviolet at intervals of 5 nm between 260 and 320 nm, but no evidence for formation of intermediates was found. Good agreement was obtained for rates determined in the ultraviolet region with those obtained at 470 nm. The product of the reaction was $Cr(OH_2)_6^{3+}$ as detected spectrophotometrically after cation-exchange chromatography of reaction mixtures.

No evidence was found for hydration of the 3-CHO group either in the NMR or kinetically.

Furanacrylonitrile, Cinnamonitrile, and 4-Acetoxybenzonitrile Complexes. The rate laws for reduction are the same as those obtained for the previous complexes. At 25° the rates for reduction of the FAN, CIN, and 4-acetoxybenzonitrile complexes are 0.020 ± 0.002, 0.022 ± 0.004, and 0.021 ± 0.003 M^{-1} s^{-1}, respectively. The corresponding activation parameters are $\Delta H^{\ddagger}$ equals 9.5 ± 0.8, 8.8 ± 0.9, and 9.1 ± 1.2 kcal mol^{-1} and $\Delta S^{\ddagger}$ equals −34 ± 3, −37 ± 3, and −36 ± 4 eu,
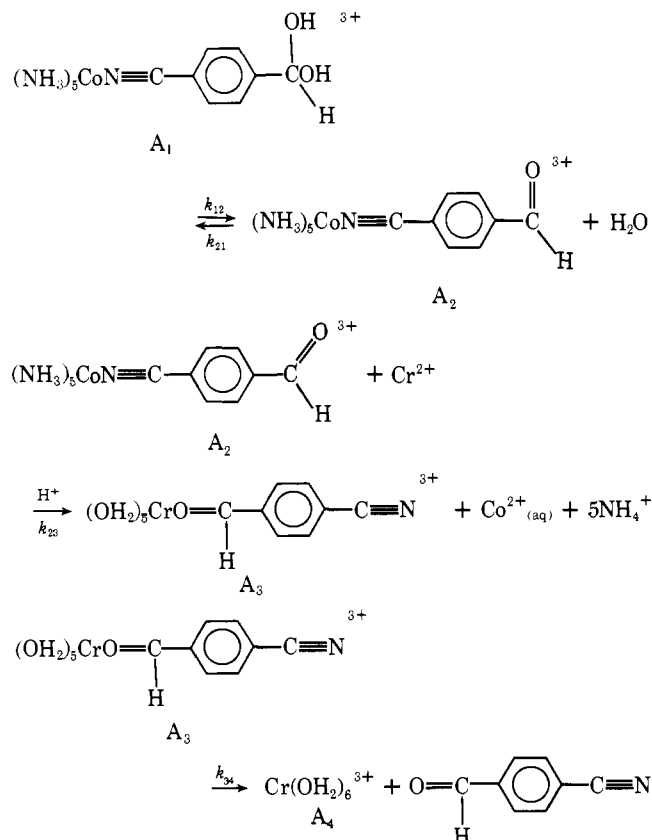
Table II. Rate Data for Reduction[a] of

$$\left[(NH_3)_5CoNC-\!\!\left\langle\bigcirc\right\rangle\!\!-\!C\!\!\begin{array}{c}O\\ \\H\end{array}\right]^{3+}$$

[Cr²⁺], M × 10⁴	[Co- (III)], M × 10⁴	[H⁺], M	k, M⁻¹ s⁻¹	λ, nm
2.0	1.8	0.050	2.5 × 10⁵	470[b]
2.0	1.8	0.050	2.6 × 10⁵	470[b]
2.0	1.8	0.050	3.3 × 10⁵	470[b]
5.0	0.5	0.020	2.7 × 10⁵	260
5.0	0.5	0.020	2.3 × 10⁵	260
5.0	0.5	0.020	3.1 × 10⁵	260
5.0	0.5	0.020	2.7 × 10⁵	260
10	1.0	0.020	2.5 × 10⁵	260
10	1.0	0.200	2.7 × 10⁵	260
10	1.0	0.200	2.3 × 10⁵	260
10	1.1	0.500	3.6 × 10⁵	280[c]
5.0	0.8	0.500	6.9 × 10⁵	280[c]
5.0	0.8	0.250	9.0 × 10⁵	280[c]

[a] By chromium(II) at 25.2 °C, μ = 0.5 M (LiClO₄). [b] Rate constants were obtained from the equation log $\{1 - [(1 - b/a)((A_0 - A_\infty)/(A_t - A_\infty))]\}$ = $((b - a)/2.303)kt + \log(b/a)$, where b = initial chromium(II) concentration, a = initial cobalt(III) concentration of the unhydrated form, and A_0, A_t, A_∞ = absorbance at times t = 0, t, and ∞, respectively. [c] Rate constants were obtained as outlined in the Appendix. The rise in absorbance was not sharp (~2.5–3.0 ms had elapsed at the maximum of the absorbance–time curve), and the rate constants were difficult to determine accurately. These runs were carried out using a 2-mm cuvette in the stopped flow, with a dead-time determined as 0.8 ms. Therefore the first half-time was not observed.

respectively.[5] In all cases the sole chromium product of the reduction is Cr(OH₂)₆³⁺.
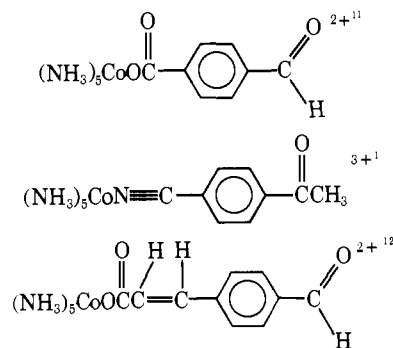
Discussion

The data for the 4-formylbenzonitrile complex are consistent with the mechanism given below. The inertness of the hydrated

$$(NH_3)_5CoN\!\!\equiv\!\!C-\!\!\left\langle\bigcirc\right\rangle\!\!-\!\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}OH\;\;^{3+}$$

A₁

$$\underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}}\;\;(NH_3)_5CoN\!\!\equiv\!\!C-\!\!\left\langle\bigcirc\right\rangle\!\!-\!C\!\!\begin{array}{c}O\\ \\H\end{array}^{3+}\;+\;H_2O$$

A₂

$$(NH_3)_5CoN\!\!\equiv\!\!C-\!\!\left\langle\bigcirc\right\rangle\!\!-\!C\!\!\begin{array}{c}O\\ \\H\end{array}^{3+}\;+\;Cr^{2+}$$

A₂

$$\overset{H^+}{\underset{k_{23}}{\longrightarrow}}\;(OH_2)_5CrO\!\!=\!\!\overset{|}{\underset{H}{C}}-\!\!\left\langle\bigcirc\right\rangle\!\!-\!C\!\!\equiv\!\!N\;\;^{3+}\;+\;Co^{2+}_{(aq)}\;+\;5NH_4^+$$

A₃

$$(OH_2)_5CrO\!\!=\!\!\overset{|}{\underset{H}{C}}-\!\!\left\langle\bigcirc\right\rangle\!\!-\!C\!\!\equiv\!\!N\;\;^{3+}$$

A₃

$$\overset{k_{34}}{\longrightarrow}\;Cr(OH_2)_6^{3+}\;+\;O\!\!=\!\!C-\!\!\left\langle\bigcirc\right\rangle\!\!-\!C\!\!\equiv\!\!N$$
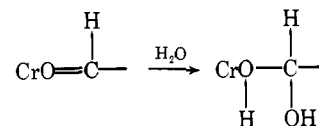
A₄ (with H below C)

form of the complex to Cr²⁺ reduction is indicated by the excellent agreement between K_{hydr} values obtained by ¹H NMR and kinetic methods and, hence, provides a method for studying the rate of dehydration of the complex. Since the carbonyl form of the complex is essentially used up as fast as it is produced, the rate of dehydration of the complex can conveniently be measured. Similar results have been observed for the Cr²⁺ reduction of the glyoxalato[8] complex of (NH₃)₅Co^III and also with the ligand 4-formylpyridine coordinated to pentaammineruthenium(II)[9] and pentacyanoiron(II).[10] For 4-formylpyridine, the ligand is essentially completely hydrated in the Ru(III) and Fe(III) complexes at equilibrium and rapid reduction to Ru(II) and Fe(II) produces a perturbation from the normal equilibrium values in the lower oxidation states where significant amounts of carbonyl form exist at equilibrium. Thus, the normal equilibrium distribution is being monitored, and k_{obsd} is a combination of hydration and dehydration terms. In the Ru(II) system the specific rate for acid catalyzed dehydration is about 45–50 M⁻¹ s⁻¹ at 25°. In the present system the acid catalyzed rate of dehydration was found to be 32 ± 7 M⁻¹ s⁻¹ at 25°. This value, along with the measured equilibrium constant of 2.7 at 25°, gives 12 M⁻¹ s⁻¹ for the rate of hydration.

The reduction was measured at very low chromium(II) concentrations at 470, 260, and 280 nm. At 280 nm the absorbance changes observed provided evidence for the existence of A₁, A₂, and A₃ in the general mechanism given. The assignment of structure A₃ to the intermediate is reasonable in light of the chromium(III) intermediates observed in the systems using

$$(NH_3)_5CoOC-\!\!\left\langle\bigcirc\right\rangle\!\!-\!C\!\!\begin{array}{c}O\\ \\H\end{array}\;\;^{2+\,11}$$

$$(NH_3)_5CoN\!\!\equiv\!\!C-\!\!\left\langle\bigcirc\right\rangle\!\!-\!C\!\!\begin{array}{c}O\\ \\CH_3\end{array}\;\;^{3+\,1}$$

$$(NH_3)_5CoOCC\!\!=\!\!C-\!\!\left\langle\bigcirc\right\rangle\!\!-\!C\!\!\begin{array}{c}O\\ \\H\end{array}\;\;^{2+\,12}$$

as oxidants.

It appears from the limited data available that the decomposition of A₃ is independent of the hydrogen ion concentration. Therefore it is likely the rate of hydrate formation

$$CrO\!\!=\!\!\overset{|}{\underset{H}{C}}-\;\;\overset{H_2O}{\longrightarrow}\;\;CrO\!\!-\!\overset{|}{\underset{OH}{C}}-$$

that is being observed. Similar arguments were used by Zanella and Taube[11] in considering the decomposition of the aldehydo–Cr(III) intermediate formed from reduction of 4-formylbenzoatopentaamminecobalt(III) by Cr²⁺.

The chromium(II) reduction of the CIN complex was expected to proceed by an outer-sphere process since no suitable binding site for chromium(II) exists. A similar outer-sphere process was anticipated for the FAN complex since remote attack was not observed with the 2-furanacrylato complex of pentaamminecobalt(III).[13] The similarity of the rate constants and activation parameters of the CIN, FAN, and 4-acetoxybenzonitrile complexes (see Table III and Results) indicates that the latter complex also proceeds by an outer-sphere process.

The rates of reduction by chromium(II) for several nitrile complexes have been collected in Table III. Note that the 3-

and 4-formylbenzonitrile complexes are reduced 275 and 40 times faster than 3- and 4-acetylbenzonitrile complexes, respectively. This may be due to the presence of lower energy empty π antibonding orbitals on the formyl substituent relative to the acetyl group. The ability of formyl groups to achieve coplanarity with the aromatic ring more readily than the acetyl group[1] may also contribute to the increased rate. For the 4-substituted ligands a remote attack path has been demonstrated. However, for the 3-derivatives no intermediates were observed but both rates are significantly faster than those normally observed for outer-sphere reactions with nitrile ligands and on this basis we favor an inner-sphere path.

An interesting feature for the chromium(II) reduction of a number of carboxylato complexes where remote attack has been shown to occur is a first-order hydrogen ion term in the rate law. It has been suggested that the proton binds at the adjacent carbonyl oxygen thereby promoting electron transfer by a chemical mechanism. Comparison of the rate laws obtained for reduction of the $(NH_3)_5Co^{3+}$ complexes with 4-formylbenzonitrile and 4-formylbenzoate supports the arguments of Taube and Gould,[2] and Zanella and Taube[11] on the location of the proton in the transition state. However, the nitrile complex is reduced about 1000 times more readily than the protonated carboxylato complex. This is probably due to the greater "reducibility" of 4-formylbenzonitrile as opposed to 4-formylbenzoic acid.

The reduction of the 3-formylbenzonitrile complex was much slower than the 4-derivative. Attempts to observe an intermediate spectrally (in the region $260 \rightarrow 320$ nm) were unsuccessful. For the range of $[Cr^{2+}]$ used (0.01-0.2 M) in the latter experiments the first-order rate constant for reduction under pseudo-first-order conditions varies from 0.77 to 15 s^{-1}. Since no intermediate was detected, a lower limit for decomposition of an intermediate would be approximately 100 s^{-1}. This value seems reasonable in light of the value (125 s^{-1}) obtained for decomposition of A_3. The rate of reduction of 77 M^{-1} s^{-1} seems too high for an outer-sphere process where the rates for reduction of nitrile complexes are in the range 0.02-0.06 M^{-1} s^{-1}. The activation parameters of -2.1 kcal mol^{-1} and -57 eu are disturbing. It may be that the negative enthalpy results from compensating temperature effects; i.e., a decrease in the association constant of the precursor complex with increasing temperature is balanced by the increase in specific rate of internal electron transfer. An unusually negative entropy term was also observed for reduction of the corresponding 3-formylcarboxylato complex by the remote path.[11]

The large difference in rate observed between 3- and 4-formyl and 3- and 4-acetyl complexes can be attributed to the difference in reducibility of the ligands.[14] For example, the polarographic half-wave potentials for 3- and 4-formylbenzonitrile are -1.63 and -1.45 V, respectively,[15] while the stability of the precursor complexes might be expected to be similar. The stability of the precursor complex can also drastically affect the rate of electron transfer as evidenced by the rates of electron transfer and the $E_{1/2}$ values for the 1,4-dicyanobenzene,[16] 4-acetylbenzonitrile, and 4-formylbenzonitrile systems. The corresponding $E_{1/2}$ values are -1.71, -1.72, and -1.45 V, respectively. Thus, the fact that the 4-acetyl complex is reduced 6000 times faster than the 4-cyano complex is attributed to the more effective donor characteristics[17] of the acetyl oxygen over the nitrile nitrogen toward chromium(II). The even greater rate for the 4-formyl complex results predominantly from a "reducibility" effect if the precursor complex stability is considered to be approximately the same as for the 4-acetyl complex.

The lability of keto and aldehydo bonds to chromium(III) has been generally observed. It appears that chromium(III)-nitrile bonds are also extremely labile. During the chromium(II) reduction of the 1,4-dicyanobenzene[16] and 4-

Table III. Kinetic Data for Reduction of Nitrile Complexes of Pentaamminecobalt(III) by Chromium(II)[a]

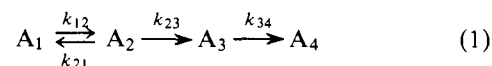| Ligand	$k^{25°}$, M^{-1} s^{-1}	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, eu	Mechanism[b]
Benzonitrile[c]	0.043	—	—	o.s.
1,2-Dicyanobenzene[d]	0.13	—	—	o.s.
1,3-Dicyanobenzene[d]	0.059	—	—	o.s.
1,4-Dicyanobenzene[c]	0.92	5.5	−40	i.s.
Furanacrylonitrile	0.020	9.5	−34	o.s.
Cinnamonitrile	0.022	8.8	−37	o.s.
Acetoxybenzonitrile	0.021	9.1	−36	o.s.
3-Acetylbenzonitrile[e]	0.28	3.2	−50	i.s. (?)
4-Acetylbenzonitrile[e]	6×10^3	−2.0	−48	i.s.
3-Formylbenzonitrile	77	−2.1	−57	i.s. (?)
4-Formylbenzonitrile	2.5×10^5	—	—	i.s.

[a] Rate constants reported at 25° are those from the best fit of the data at different temperatures to the transition state equation. [b] o.s. = outer-sphere; i.s. = inner-sphere. [c] See ref 16. [d] Unpublished results, R. J. Balahura. [e] Reference 1.

cyanopyridine[18] complexes of $(NH_3)_5Co^{3+}$, intermediate $Cr(III)-N\equiv C-$ complexes have been observed. In the former case the complex rapidly aquates whereas in the latter case further reduction occurs rapidly to destroy the nitrile–chromium bond. Finally, all attempts to synthesize $(OH_2)_5Cr^{3+}$ nitrile complexes have failed to date.

Appendix

Treatment of Kinetic Data for the 4-Formylbenzonitrile Complex. The system can be represented by the reaction sequence

$$A_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} A_2 \overset{k_{23}}{\longrightarrow} A_3 \overset{k_{34}}{\longrightarrow} A_4 \tag{1}$$

where the symbols have been defined in the text. The differential equations for eq 1 are given below where the A_i's now refer to molar concentrations.

$$-dA_1/dt = k_{12}A_1 - k_{21}A_2$$

$$-dA_2/dt = -k_{12}A_1 + k_{21}A_2 + k_{23}A_2$$

$$-dA_3/dt = -k_{23}A_2 + k_{34}A_3$$

$$-dA_4/dt = -k_{34}A_3 \tag{2}$$

These equations yield the secular equation[19]

$$\begin{vmatrix} k_{12} - \lambda & -k_{21} & 0 & 0 \\ -k_{12} & k_{21} + k_{23} - \lambda & 0 & 0 \\ 0 & -k_{23} & k_{34} - \lambda & 0 \\ 0 & 0 & -k_{34} & -\lambda \end{vmatrix} = 0 \tag{3}$$

Equation 3 has the roots

$$\lambda_1 = [(k_{12} + k_{21} + k_{23}) + \sqrt{(k_{12} + k_{21} + k_{23})^2 - 4k_{12}k_{23}}]/2$$

$$\lambda_2 = [(k_{12} + k_{21} + k_{23}) - \sqrt{(k_{12} + k_{21} + k_{23})^2 - 4k_{12}k_{23}}]/2$$

$$\lambda_3 = k_{34}$$

$$\lambda_4 = 0 \tag{4}$$

For each λ there will be a set of four values B_j which serve as particular solutions to the differential equations. Hence there will be four sets of four B_j's of which three sets will be independent.[19] Let the four B_{4r}'s equal one (if the B_{1r}'s, B_{2r}'s,

$$B = \begin{pmatrix} \dfrac{-\lambda_1(k_{34}-\lambda_1)(k_{21}+k_{23}-\lambda_1)}{k_{12}k_{23}k_{34}} & \dfrac{-\lambda_2(k_{34}-\lambda_2)(k_{21}+k_{23}-\lambda_2)}{k_{12}k_{23}k_{34}} & 0 & 0 \\ \dfrac{-\lambda_1(k_{34}-\lambda_1)}{k_{23}k_{34}} & \dfrac{-\lambda_2(k_{34}-\lambda_2)}{k_{23}k_{34}} & 0 & 0 \\ \dfrac{-\lambda_1}{k_{34}} & \dfrac{-\lambda_2}{k_{34}} & -1 & 0 \\ 1 & 1 & 1 & 1 \end{pmatrix} = \begin{pmatrix} B_{11} & B_{12} & 0 & 0 \\ B_{21} & B_{22} & 0 & 0 \\ B_{31} & B_{32} & -1 & 0 \\ 1 & 1 & 1 & 1 \end{pmatrix} \quad (5)$$

or B_{3r}'s were set equal to one, some of the B's would be infinite). Solving for the B's according to ref 19 yields the matrix (eq 5).

Once these particular solutions have been obtained (eq 5), the general solutions to the differential equations may most easily be obtained using the matrix methods as outlined by Lewis and Johnson.[20] These solutions are given in matrix notation by

$$A = BEB^{-1}A_0 \quad (6)$$

where at $t = 0$, $A_1 = A_1^0$, $A_2 = A_2^0$, $A_3 = 0$, $A_4 = 0$;

$$A = \begin{pmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \end{pmatrix} \qquad A^0 = \begin{pmatrix} A_1^0 \\ A_2^0 \\ 0 \\ 0 \end{pmatrix}$$

$$E = \begin{pmatrix} e^{-\lambda_1 t} & 0 & 0 & 0 \\ 0 & e^{-\lambda_2 t} & 0 & 0 \\ 0 & 0 & e^{-\lambda_3 t} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

and B^{-1} is the inverse matrix of B.

The final solution, i.e., integrated forms of the differential equations, is given below:

$$A_1 = \frac{[Co^{III}]_0}{(K_h+1)|B|}\{B_{11}(B_{12}-K_hB_{22})e^{-\lambda_1 t} + B_{12}(K_hB_{21}-B_{11})e^{-\lambda_2 t}\}$$

$$A_2 = \frac{[Co^{III}]_0}{(K_h+1)|B|}\{B_{21}(B_{12}-K_hB_{22})e^{-\lambda_1 t} + B_{22}(K_hB_{21}-B_{11})e^{-\lambda_2 t}\}$$

$$A_3 = \frac{[Co^{III}]_0}{(K_h+1)|B|}$$
$$\times \{B_{31}(B_{12}-K_hB_{22})e^{-\lambda_1 t} + B_{32}(K_hB_{21}-B_{11})e^{-\lambda_2 t} + B_{31}(K_hB_{22}-B_{12})e^{-\lambda_3 t} + B_{32}(B_{11}-K_hB_{21})e^{-\lambda_3 t}\}$$

$$A_4 = [Co^{III}]_0\left\{1 + \frac{1}{(K_h+1)|B|}[(B_{12}-K_hB_{22})e^{-\lambda_1 t} + (K_hB_{21}-B_{11})e^{-\lambda_2 t} + B_{31}(B_{12}-K_hB_{22})e^{-\lambda_3 t} + B_{32}(K_hB_{21}-B_{11})e^{-\lambda_3 t}]\right\} \quad (7)$$

where $[Co^{III}]_0$ = initial complex concentration, K_h = equilibrium constant for hydration (k_{12}/k_{21}), and $|B|$ = determinant of B.

The nonlinear least-squares program employed in this study provided a best fit to the experimental absorbance at 280 nm, A_{280}, given by

$$A_{280} = \epsilon_{A1}A_1 + \epsilon_{A2}A_2 + \epsilon_{A3}A_3 + \epsilon_{A4}A_4$$
$$= A_\infty + \epsilon_{A1}A_1 + \epsilon_{A2}A_2 + \epsilon_{A3}A_3 + \epsilon_{A4}(A_4 - [Co^{III}]_0) \quad (8)$$

The quantities $[Co^{III}]_0$, k_{12}, k_{21}, A_{280}, and A_∞ and t were treated as knowns and the program searched for best fit values for ϵ_{A1}, ϵ_{A2}, ϵ_{A3}, ϵ_{A4}, k_{23}, and k_{34}, where the ϵ's are molar extinction coefficients, t equals time, and A_∞ equals the absorbance at infinite time.

Supplementary Material Available: Tables of rate data (4 pages). Ordering information is given on any current masthead page.

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(15) Unpublished results, R. J. Balahura. Solvent was acetonitrile.
(16) The rate of reduction of this complex was reinvestigated using stopped flow methods in the hope of detecting an intermediate chromium(III)–nitrile complex. At 288 nm an initial rise in absorbance was observed followed by a slower decrease in absorbance. Analysis of the rise in absorbance yielded a rate constant in agreement with that found previously by R. J. Balahura, G. B. Wright, and R. B. Jordan, *J. Am. Chem. Soc.*, **95**, 1137 (1973). The decrease in absorbance can be attributed to aquation of the intermediate complex

$(OH_2)_5CrN\!\!\equiv\!\!C\!-\!\!\bigcirc\!\!-CN^{3+}$
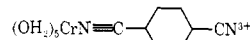
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