Table III. Least-Squares Analysis of the Temperature Dependence of the Rate Constants for the Thermolysis of $[Co(HL)_3](ClO_4)_3$ in DMF

	k_r^A	$k_r^{C,D}$	k_t	k_1	k_2
ΔH^*, kJ mol^{-1}	73.7	33.5	44.9	43.7	73.7
intercept[a]	−1.40	−2.28	26.9	7.41	19.3
R^2 [a]	0.94	0.77	0.97	0.92	0.94

[a] This intercept and correlation coefficient for the least-squares analysis of the data. Entropies of activation were not calculated.

rate constants, we assume that $k_r^C = k_r^D \gg k_r^A$ for the reasons given above. The differential dichroic absorbance as a function of time can be written as

$$\delta(t) = \Delta\epsilon_A[A]_t + \Delta\epsilon_B[B]_t + \Delta\epsilon_C[C]_t + \Delta\epsilon_D[D]_t$$

at any wavenumber for unit path length. Initial values for $\Delta\epsilon_A$ and $\Delta\epsilon_B$ were estimated from those observed in aqueous solution, i.e. about 60–70 units for $\Delta\epsilon_A$ and 80–100 units for $\Delta\epsilon_B$. $\Delta\epsilon_C$ was estimated from the experiment in which $Co(HL)_3^{3+}$ was reacted with $Co(HL)_3^{2+}$ to form C. Assuming a quantitative conversion with 100% stereoselectivity, the value for $\Delta\epsilon_C$ was calculated to be 30 units as a minimum. The value of $\Delta\epsilon_D$ is more difficult to estimate, but because the concentration of D is never very large, it was sufficient to consider it to be zero.

The rate equations above were solved as a function of time by fourth-order Runge–Kutta integration, and values for k_r^A, $k_r^C = k_r^D$, k_t, k_1, and k_2 were obtained by minimizing the sum of the squares of the deviations between the calculated and observed differential dichroic absorbance. The results are given in Tables II and III. Before discussing the results, it must be remembered that, to simplify the treatment of the data, it was assumed that complex C does not undergo racemization. Any loss of differential absorbance due to such racemization will be embedded in the data and will manifest itself through the value of k_r^C, which controls the loss of optical activity by reduction to the racemic cobalt(II) complex. For this reason the values of k_r^C will not be as accurately estimated as the other rate constants. Toward the end of the thermolysis runs, when the concentration of C is relatively large, failure to account for this racemization rate will lead to large deviations between the calculated and observed differential absorbance. The rate constants shown in Table II give good agreement between these values for the first two-thirds of the runs, after which the experimental values decay much more rapidly than does the calculated one. The fractions of the total run times for which the agreement is good are shown in Table II. The rate of reduction of A is seen to be extremely slow, but the rate of electron exchange between the complexes R and B is comparable in magnitude to other inner-sphere electron-transfer processes.[27] Despite the fact that Scheme II is a simplification of what occurs during these thermolyses, the sets of rate constants were treated by least-squares analysis to determine primarily the correlation coefficient and secondarily the activation enthalpies. The results (see Table III) indicate that k_r^A, k_t, k_1, and k_2 are reasonably significant quantities but that k_r^C and k_r^D are not, most probably for the reason discussed above. It remains to be seen if any advantage can be taken of the high stereoselectivity of this type of electron-transfer process to synthesize optically active complexes from lower valence racemic precursors.

Registry No. DMF, 68-12-2; (−)-$[Co(HL)_3](ClO_4)_3$, 97673-12-6.

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(27) Espenson, J. *Inorg. Chem.* **1965**, *4*, 121. Stritar, J. A.; Taube, H. *Inorg. Chem.* **1969**, *8*, 2281. Taube, H. "Electron Transfer Reactions of Complex Ions in Solution"; Academic Press: New York, 1970.

(28) The times in minutes and the differential absorbances in parentheses of the curves starting at the top of the band near 330 nm.

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Reactions of Chromium(II) with Fumaronitrile and Pentaamminecobalt(III)- and Pentaaquochromium(III)-Fumaronitrile Complexes

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The reaction of chromium(II) with the fumaronitrile complex of pentaamminecobalt(III) proceeds with transfer of fumaronitrile to the chromium(III) product and with a rate constant of (1.9 ± 0.2) × 10^5 M^{-1} s^{-1} (25 °C, 0.50 M $LiClO_4$–$HClO_4$). The chromium(III)–fumaronitrile complex undergoes further reduction by chromium(II), forming various organochromium(III) products. The reaction of chromium(II) with fumaronitrile was found to be $\sim 10^3$ times slower than that of the chromium(III) complex. With fumaronitrile, the main products are succinonitrile (~20%) and $(H_2O)_5Cr{-}CH(CN){-}CH_2CN{-}Cr(OH_2)_5^{5+}$ (~70%), while with the chromium(III) complex, all the organic ligand appears as organochromium species of which the main product is $(H_2O)_5Cr{-}CH(CONH_2Cr){-}CH_2CNCr(OH_2)_5^{8+}$ (~70%). The distribution and composition of the products are rationalized on the basis of a few simple principles.

This study began as a simple investigation of the electron-transfer kinetics between $(NH_3)_5Co(fumaronitrile)^{3+}$ and Cr^{2+} in order to compare fumaronitrile as a bridging ligand to analogues such as succinonitrile,[1] 1,4-dicyanobenzene,[2] and others.[3] Fumaronitrile is shown to provide a very facile electron-transfer pathway between chromium(II) and pentaamminecobalt(III). In addition it was noted that subsequent reactions between chromium(II) and fumaronitrile, either free or complexed to chromium(III), can complicate the product analysis and spectrophotometric observations. Although these are minor complications for the original goal, a thorough investigation of them was undertaken and constitutes the main portion of this work. This investigation was stimulated by the seemingly disparate results that have been obtained for the reduction of fumaric and maleic acids and their esters by chromium(II).[4-6] The nitrile presents

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(1) Kupferschmidt, W. C.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 3469.

(2) Balahura, R. J.; Purcell, W. L. *J. Am. Chem. Soc.* **1976**, *98*, 4457.

(3) Hua, H. H.; Balahura, R. J.; Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* **1978**, *12*, 3692.

(4) Malliaris, A.; Katakis, D. *J. Am. Chem. Soc.* **1965**, *87*, 3077.

(5) Sevcik, P.; Treindl, L. *Collect. Czech. Chem. Commun.* **1972**, *37*, 2725.

(6) (a) Petrou, A.; Vrachnou-Astra, E.; Katakis, D. *Inorg. Chim. Acta* **1980**, *39*, 161. (b) Petrou, A.; Vrachnou-Astra, E.; Konstantatos, J.; Katsaros, N.; Katakis, D. *Inorg. Chem.* **1981**, *20*, 1091.

0020-1669/85/1324-3357$01.50/0

Table I. Kinetic Data for the Chromium(II) Reduction of $(NH_3)_5CoNCCH{=}CHCN^{3+}$ [a]

10^4[Co(III)], M	10^4[Cr(II)], M	[H^+], M	$10^{-5}k$,[b] $M^{-1}\ s^{-1}$
0.30	3.1	0.100	2.0[c]
0.15	2.3	0.100	1.9[c]
0.15	1.5	0.250	1.8[c]
0.15	1.5	0.100	2.0[c]
0.15	1.5	0.050	2.0[c]
0.73	3.4	0.250	2.1
1.46	3.4	0.025	2.2
0.73	1.7	0.250	1.7
0.73	1.7	0.100	1.6
0.73	1.7	0.025	1.6
0.62	1.5	0.100	1.9
0.31	1.5	0.100	1.9
0.73	1.0	0.100	1.6
0.37	1.0	0.026	1.6

[a] At 25 °C in 0.50 M $LiClO_4$–$HClO_4$, monitored at 260 nm. [b] Unless otherwise noted, the data were obtained under second-order conditions and analyzed accordingly. [c] Pseudo-first-order conditions.

some advantages over the acids in that the substrate has no protolytic equilibria and chelate formation in the products is unlikely. These are offset somewhat by the lability of the chromium(III)–nitrile complexes.[7]

Experimental Section

The experimental procedures, instrumentation and analytical techniques have been described previously.[1,8]

$[(NH_3)_5CoNCCH{=}CHCN](ClO_4)_3$. A solution containing 4 g of (trifluoromethanesulfonato)pentaamminecobalt(III) trifluoromethanesulfonate,[9] 1.1 g of fumaronitrile, and 2 drops of CF_3SO_3H in 20 mL of sulfolane was allowed to react at room temperature for 48 h. The orange solution was added to a rapidly stirred mixture of 100 mL of 2-butanol in 500 mL of ether. The solid was collected by filtration and recrystallized from 30 mL of 0.1 M HCl by adding concentrated $HClO_4$. The product was chromatographed on Dowex 50W-X2 (H^+), separated from impurities by elution with 2 M NaCl (pH 4.5), and then removed from the resin by a batch method with 6 M HCl. Concentrated $HClO_4$ was added to precipitate the perchlorate salt, which was recrystallized from dilute perchloric acid, washed with ethanol and ether, and air-dried. Anal. Calcd for $[(NH_3)_5CoNCCH{=}CHCN][ClO_4]_3$: C, 9.23; H, 3.29; N, 18.84. Found: C, 9.21; H, 3.21; N, 18.67. The electronic spectrum has a maximum at 467 nm with an extinction coefficient of 74.3 $M^{-1}\ cm^{-1}$. The infrared spectrum, in Nujol, shows C≡N stretches at 2302 and 2240 cm^{-1}, compared to 2240 cm^{-1} for free fumaronitrile. In the NMR spectrum, the HC=CH protons are an AB system with chemical shifts of τ 2.70 and 3.00 and a coupling constant of 16.5 Hz, which is typical[10] for a trans arrangement around the double bond.

Results

$(NH_3)_5CoN{\equiv}CCH{=}CHCN^{3+} + Cr^{2+}$. It seems appropriate to start with this system because it is the simplest, and the product is the subject of further work described below. The kinetic data summarized in Table I are consistent with the rate law

$$\frac{-d\ \ln\ [(NH_3)_5CoNCCH{=}CHCN^{3+}]}{dt} = k[Cr^{2+}] \qquad (1)$$

with $k = (1.9 \pm 0.2) \times 10^5\ M^{-1}\ s^{-1}$ (25 °C, 0.50 M $LiClO_4$–$HClO_4$). The large value of k required that the studies be done under second-order conditions at rather low ($<3 \times 10^{-4}$ M) Cr^{2+} concentrations on the stopped-flow system.

A solution of $(NH_3)_5CoNCCH{=}CHCN^{3+}$ (1.95×10^{-3} M) in 0.10 M $HClO_4$ was treated with chromium(II) (2.15×10^{-3} M) and immediately oxidized by air and subjected to ion-exchange chromatography at 5 °C on Dowex 50W-X2. The separated products were identified as fumaronitrile, $Co(OH_2)_6^{2+}$, and $Cr(OH_2)_6^{3+}$ in yields of 98%, 101%, and 102%, respectively, based on the initial cobalt(III). These observations indicate that the reaction involves reduction of cobalt(III) to cobalt(II) with the expected 1:1 stoichiometry for cobalt(III):chromium(II). Furthermore, no chromium(III)–fumaronitrile complex is detectable on the time scale required for the ion-exchange separation.

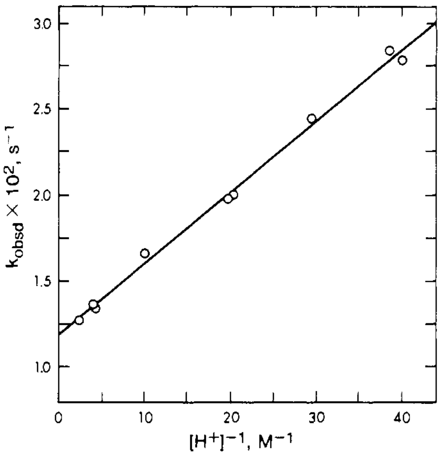
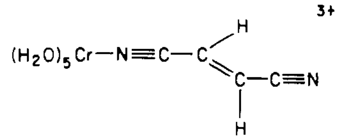


Figure 1. Variation of k_{obsd} with $[H^+]^{-1}$ for the aquation of $(H_2O)_5CrNCCH{=}CHCN^{3+}$ at 25 °C in 0.50 M $LiClO_4$–$HClO_4$.

When reaction mixtures containing a slight deficiency of chromium(II) were monitored spectrophotometrically, an initial product with an absorption maximum at 395 nm and molar extinction coefficient of ~25 $M^{-1}\ cm^{-1}$ was detected. Over a period of a few minutes the intensity of this band decreased, and the maximum shifted to 408 nm. These observations are consistent with the presence of an initial chromium(III) product with a nitrogen-bound ligand that aquates fairly rapidly to $Cr(OH_2)_6^{3+}$. The electronic spectral properties and kinetic lability of this product are consistent with its formulation as

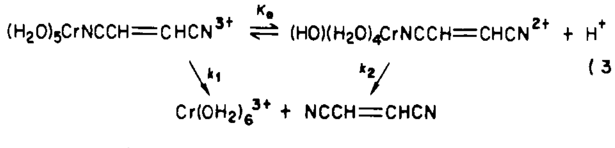


In the presence of excess chromium(II), the reactions subsequent to cobalt(III) reduction give a more complex spectrophotometric behavior. This will be dealt with in a later section of this work.

Aquation of $(H_2O)_5CrNCCH{=}CHCN^{3+}$. The reaction was monitored at 395 nm on a Cary 219 spectrophotometer by mixing $(NH_3)_5CoNCCH{=}CHCN^{3+}$ with a 10–15% deficiency of Cr^{2+}. The cobalt(III) reduction was complete before observation was started. The aquation reaction was studied between 0.025 and 0.442 M H^+, and the results give the observed pseudo-first-order rate constant as

$$k_{obsd} = a + b[H^+]^{-1} \qquad (2)$$

as shown by the plot in Figure 1. The rate law is typical for the aquation of $(H_2O)Cr^{III}X$ complexes and is consistent with the usual reaction scheme



(3)

If $K_a << [H^+]$, then this scheme predicts that

$$k_{obsd} = k_1 + k_2K_a[H^+]^{-1}$$

A least-squares analysis of the data yields $a = k_1 = (1.19 \pm 0.05) \times 10^{-2}\ s^{-1}$ and $b = k_2K_a = (4.14 \pm 0.34) \times 10^{-4}\ M^{-1}\ s^{-1}$ (25 °C, 0.5 M $LiClO_4$–$HClO_4$).

Reaction of Chromium(II) and Fumaronitrile. As noted earlier, the chromium(II) product of the initial reduction reacts in a complex way with excess chromium(II). To better understand these reactions, the chromium(II)–fumaronitrile system was in-

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[7] Jordan, D.; Kupferschmidt, W. C.; Jordan, R. B. *Inorg. Chem.* **1984**, *23*, 1986.

[8] Kupferschmidt, W. C.; Jordan, R. B. *J. Am. Chem. Soc.* **1984**, *106*, 991.

[9] Kupferschmidt, W. C.; Jordan, R. B. *Inorg. Chem.* **1982**, *21*, 2089.

[10] Williams, D. H.; Fleming, I. "Spectroscopic Methods in Organic Chemistry"; McGraw-Hill: London, 1973; Chapter 3.

Table II. Kinetic Data for the Chromium(II) Reduction of Fumaronitrile (25 °C, 0.50 M $LiClO_4$–$HClO_4$)

10^3[NCCH=CHCN], M	10^2[Cr(II)], M	$[H^+]$, M	10^3k_{obsd}, s^{-1}	k, $M^{-2}\ s^{-1}$
1.55	2.00	0.400	1.09	2.73[a]
2.03	2.99	0.354	2.73	3.05[a]
4.00	5.99	0.209	9.29	2.59[a]
2.03	2.99	0.025	2.53	2.83[a]
4.00	5.99	0.025	9.01	2.51[a]
2.50	6.56	0.100	10.9	2.53[b]
2.50	4.87	0.100	6.76	2.85[b]
0.92	1.64	0.100	0.71	2.64[b]
2.50	6.58	0.050	11.8	2.73[b]
2.50	4.95	0.050	6.47	2.64[b]
0.92	2.31	0.050	1.42	2.66[b]
0.92	3.43	0.025	3.25	2.76[b]
0.92	3.29	0.025	2.86	2.64[b]

[a] Reaction monitored at 750 nm. [b] Reaction monitored at 520 nm and analyzed by least-squares fits to A → B → C scheme.

vestigated. It is known that chromium(II) reduces carbon–carbon double bonds.[4–6] But it is obvious from the color changes from initial blue to intermediate red, after ~20 min, to final blue-green, after ~200 min, that the system is not just represented by the reaction

$$2Cr^{2+} + 2H^+ + HCCH{=}CHCN \rightarrow NCCH_2{-}CH_2CN + 2Cr^{3+} \quad (4)$$

Stoichiometry studies were carried out with initial concentrations of chromium(II) and fumaronitrile in the range 0.10 and 0.025 M, respectively, and in 0.10 and 0.48 M $HClO_4$. After 19.5 min, when the red color is fully developed, the amount of unreacted chromium(II) was determined by oxidation with iron(III) and found to conform to 2.01 ± 0.01 mol of chromium(II) consumed/mol of fumaronitrile. After 210 min, no further chromium(II) was consumed. These observations indicate that the initial reaction corresponds to reduction of the double bond with formation of intermediate chromium(III) complexes that decompose in the subsequent reaction.

The rate of the initial reaction was studied in several ways. In one type of experiment, solutions of chromium(II) and fumaronitrile at several acidities were quenched by oxidation with air after a certain time. The reaction solution was placed on a Dowex 50W-X8 column, and the amount of fumaronitrile in the initial eluent was determined. For example, solutions initially containing 3.12×10^{-2} M fumaronitrile and 6.84×10^{-2} M Cr^{2+} in 0.40, 0.20, and 0.067 M H^+ were allowed to react for 200 s, and the percentage of fumaronitrile remaining was 35.1, 35.4, and 35.6%, respectively. These, and a number of analogous runs, indicate that there is no significant [acid] dependence of the rate between 0.05 and 0.40 M H^+.

At 750 nm, chromium(II) ($\epsilon = 4.5\ M^{-1}\ cm^{-1}$) is the only absorbing species. The rate was measured from the decrease in absorbance at this wavelength, with the results summarized in Table II. Although the absorbance change is in the range of 0.1 unit, good first-order kinetic plots were obtained. An analysis of the observed rate constants indicates that the rate is second order in $[Cr^{2+}]$ and independent of $[H^+]$ between 0.025 and 0.4 M, with an average rate constant of 2.7 $M^{-2}\ s^{-1}$.

The absorbance change at 520 nm is biphasic with an initial increase during formation of the red color followed by a decrease as the color changes to blue-green. The rate constant for the first stage was determined by fitting the data to an A → B → C reaction scheme. The results agree with those at 750 nm for $[H^+]$ between 0.025 and 0.10 M, as shown in Table II. At higher acidities, the third-order rate constant seems to decrease, for example to ~2.1 $M^{-2}\ s^{-1}$ at 0.34 M H^+. This is inconsistent with the quenching and 750-nm experiments. Observations in the 350–450-nm region show that the absorbance initially increases as expected but then starts to decrease below 375 nm while still increasing above 375 nm. This effect is more apparent at higher acidity and can be attributed to an intermediate species that decomposes more rapidly at lower acidity and is then less influential on the data analysis. This may be due to decomposition of minor product III′ described later.

Table III. Electronic Spectral Data of Organochromium Products

species	λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$)[a]		
I	519 (81.1)	411 (117)	268 (4.09×10^3)
III	515 (116)	408 (137)	267 (4.08×10^3)
V	519 (97.2)	411 (128)	269 (3.87×10^3)
VI	532 (116)	408 (123)	263 (4.78×10^3)
VII	529 (155)	405 (145)	260 (6.54×10^3)

[a] Extinction coefficients are per mole of organic ligand and are based on the total chromium analysis and the Cr:ligand ratio given in the text.

In summary, the formation of the initial red color is consistent with the rate law

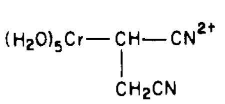
$$\frac{-d[\text{fumaronitrile}]}{dt} = 2.7[\text{fumaronitrile}][Cr^{2+}]^2 \quad (5)$$

between 0.025 and 0.400 M H^+ at 25 °C in 0.50 M $LiClO_4$–$HClO_4$.

The final organic product was recovered by extraction 10 times from water with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and evaporated to dryness, and the white product (85% recovered yield) was identified as succinonitrile by ^1H NMR and infrared spectroscopies.

Product analysis was undertaken to ascertain the nature of the highly colored complexes formed during the initial phase of the reduction. Ion-exchange separation on Sephadex SP-C25 cation-exchange resin gave the following elution pattern: a red band (I) was eluted with 0.2 M $HClO_4$; a blue band (II) was eluted with 0.2 M $HClO_4$ in 0.2 M $NaClO_4$; a second red band (III) was eluted with 0.2 M $HClO_4$ in 0.5 M $NaClO_4$; a pink band (IV) and a small purple band would not elute from the column even with 1.0 M $HClO_4$ in 3 M $NaClO_4$. However, on standing for 2 days at room temperature in 1 M $HClO_4$, the pink band (IV) decomposes to a red (V) and a blue product (IVb), which can be separated and eluted. The purple band could only be removed by conversion to chromate with alkaline hydrogen peroxide. The electronic spectral properties of the products are summarized in Table III.

The chemical nature of these products can be inferred from their ion-exchange properties, electronic spectra, and chemical reactions. The most easily eluted product has properties consistent with its formulation as



$$(H_2O)_5Cr{-}\underset{CH_2CN}{CH}{-}CN^{2+}$$

I

The electronic spectrum of I is similar to that of $(H_2O)_5CrCH_2CN^{2+}$.[8] In 0.5 M $HClO_4$ at room temperature, I shows no signs of decomposition even in the presence of dioxygen. However I reacts readily with chromium(II) to produce $Cr(OH_2)_6^{3+}$ as the sole chromium product, isolated by ion-exchange chromatography on Dowex 50W-X2 and identified by its electronic spectrum. The reaction rate is first order in $[Cr^{2+}]$ (1.5×10^{-2} to 7.52×10^{-2} M) and independent of $[H^+]$ (0.020–0.376 M) with a rate constant of $(1.19 \pm 0.03) \times 10^{-2}\ M^{-1}\ s^{-1}$ (25 °C, 0.50 M $LiClO_4$–$HClO_4$).

Species I reacts with Hg^{2+} with a rate constant of $3.2 \times 10^{-4}\ M^{-1}\ s^{-1}$ (0.50 M $HClO_4$, 25 °C). The [acid] dependence has not been studied, but I is much less reactive than $(H_2O)_5CrCH_2CN^{2+}$ toward Hg^{2+},[8] as expected from the steric and inductive effects of the $-CH_2CN$ substituent.

The blue band (II) and the decomposition product, band IVb, are identified as $Cr(OH_2)_6^{3+}$ from their electronic spectra and ion-exchange characteristics.

The red species (III) is the major initial reaction product. The high charge indicated by its ion-exchange behavior is consistent with two chromiums coordinated to the organic ligand. The

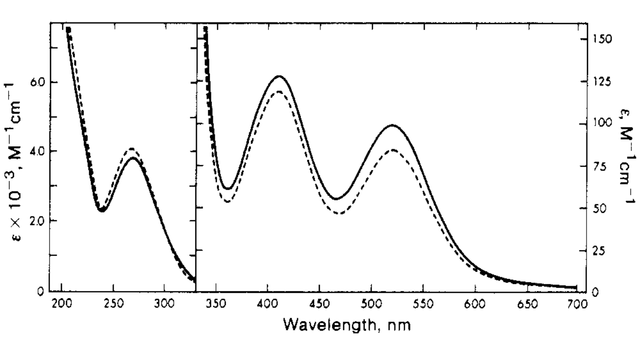
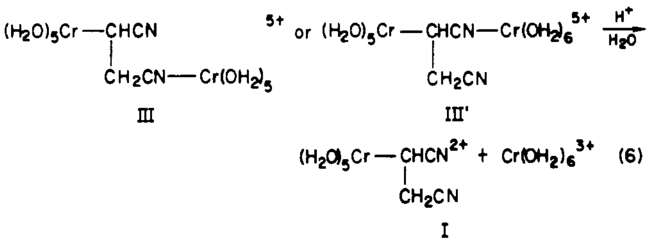


Figure 2. Electronic spectra of III (—) and V (--) at 25 °C in 0.5 M $HClO_4$.

electronic spectrum and the extinction coefficients (especially at 267 nm) indicate that there is one Cr–C bond in the ion. This species decomposes in a few hours in aqueous acid at ambient temperature. This reaction is troublesome for characterization studies but at the same time is informative because the reaction products are equivalent amounts of I and $Cr(OH_2)_6^{3+}$. These observations suggest the following formulation and reaction:



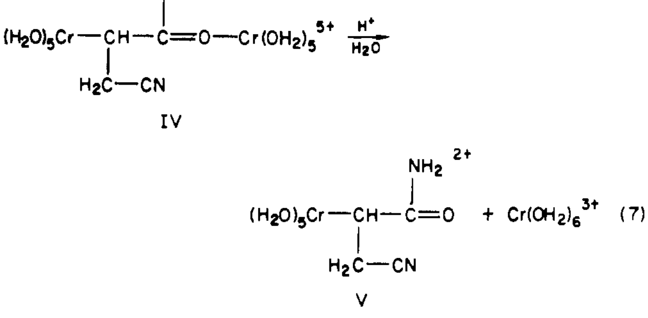
III III' I (6)

The reaction rate, monitored at 510 nm, is independent of O_2 and $[H^+]$ (0.025–0.330 M) with a first-order rate constant of $(3.60 \pm 0.09) \times 10^{-4}$ s^{-1}. This rate constant is similar to the value of 4.3×10^{-4} s^{-1} [7] for aquation of $(H_2O)_5Cr{-}NCCH_3^{3+}$, as expected if both processes involved breaking a chromium(III)–nitrile bond.

Mixtures of chromium(II) and species III show biphasic kinetic behavior when monitored at 408 nm. The observations are qualitatively consistent with aquation of III followed by chromium(II)-catalyzed decomposition of I, a reaction described above. However the analysis is complicated by the inevitable presence of some I formed by aquation of III before chromium(II) is injected. Certainly III is much less reactive than I toward chromium(II), and the rate constant for III + Cr^{2+} is $<2 \times 10^{-3}$ M^{-1} s^{-1}.

The properties of III do not permit one to decide which isomer (III or III′) is present. The similarity of the spectrum to that of I and the aquation rate to that of $(H_2O)_5CrNCCH_3^{3+}$ [7] and steric and charge-separation effects seem to favor III.

The pink complex (IV) could not be removed from Sephadex, but IV decomposes on the resin in 1 M $HClO_4$ to give equimolar amounts of $Cr(OH_2)_6^{3+}$ and a red species V, whose electronic spectrum (Table III and Figure 2) is consistent with a Cr–C bond. The red species moves more rapidly than $Cr(OH_2)_6^{3+}$ on Dowex 50W-X2 and elutes readily with 0.5 M $HClO_4$, indicative of a 2+ charge. The electronic spectrum of V is similar to that of III (Figure 2) but differs especially at 519 nm. A tentative formulation of IV and its decomposition are given by the reaction



IV V (7)

Table IV. Product Distribution from the Reaction of Chromium(II) and Fumaronitrile ($10^4 \times$ mol)[a,b]

expt type	species	0.32 M H^+ nitrile	0.32 M H^+ Cr(III)	0.051 M H^+ nitrile	0.051 M H^+ Cr(III)
	reacted	1.651	(3.30)	1.670	(3.34)
i	$Cr(OH_2)_6^{3+}$		1.821		1.713
i	IV	(0.170)	0.3398	(0.136)	0.2711
i	V	(0.044)	0.0887	(0.018)	0.0361
ii	I	(1.13)	1.125	(1.26)	1.258
iii	2+ charge	(1.28)	1.280	(1.36)	1.360
	complexed	(1.34)		(1.41)	
	$N(CH_2)_2CN$	(0.31)		(0.26)	

[a] Values in parentheses are derived from others as described in the text. [b] Initially fumaronitrile and Cr^{2+} were 1.65×10^{-2} and 3.80×10^{-2} M respectively; the reaction time was 460 s at 25 °C in 0.50 M $LiClO_4$–$HClO_4$; 60% of the initial nitrile had reacted.

Species IV is viewed as forming from III′ (see eq 6) because the two chromiums in III′ would provide more activation than in III for hydrolysis of the nitrile to the carboxamide.[11] It is implied that the N-isomer of the carboxamide, which would form by simple nitrile hydration, has undergone linkage isomerism to the O-isomer.[12] Intramolecular attack of a coordinated H_2O could bring about this same change.

The main difficulty with the formulation of IV is that it has the same 5+ charge as III, yet IV could not be eluted from Sephadex SP-C25 while III moved off easily. The charge equality of III and IV seems to be required because they both decompose to give equal amounts of 2+- and 3+-charged species. Possibly the greater localization of positive charge in IV causes it to be more strongly adsorbed than III. Protonation equilibria of the carboxamide may be a complicating feature.[13]

Finally, the purple band could not be characterized because it could not be removed from the Sephadex resin. It constitutes less than 3% of the total product, as shown below, and does not decompose to elutable products.

Quantitative studies of the product distribution are complicated by the rather rapid aquation of III (eq 5) and by the fact that III and IV give 2+-charged aquation products. Three types of product studies proved to be most useful in assessing the product distribution:

(i) The reaction was quenched with $(NH_3)_5CoN_3^{2+}$, the solution was allowed to stand at 25 °C for 5 h for aquation of III to go to completion, and then the amounts of $Cr(OH_2)_6^{3+}$, IV, and immobile purple band were determined after separation on Sephadex SP-C25.

(ii) The reaction was quenched with O_2, allowed to stand for 5 h as before, and the amount of I determined after separation on Dowex 50W-X2.

(iii) The reaction was quenched with O_2, allowed to stand for 4 days at ambient temperature, and then the total chromium in the +2 product was determined after separation on Dowex 50W-X2. In (ii), the amount of I reflects the amount of III in the original product mixture. In (iii), the amount of 2+-charged species reflects the amount of III plus IV in the original mixture. The difference between (ii) and (iii) gives the original amount of IV and should be consistent with that found in (i). The amount of $Cr(OH_2)_6^{3+}$ in (i) should be consistent with that expected from aquation of III plus that formed if there is some direct reaction

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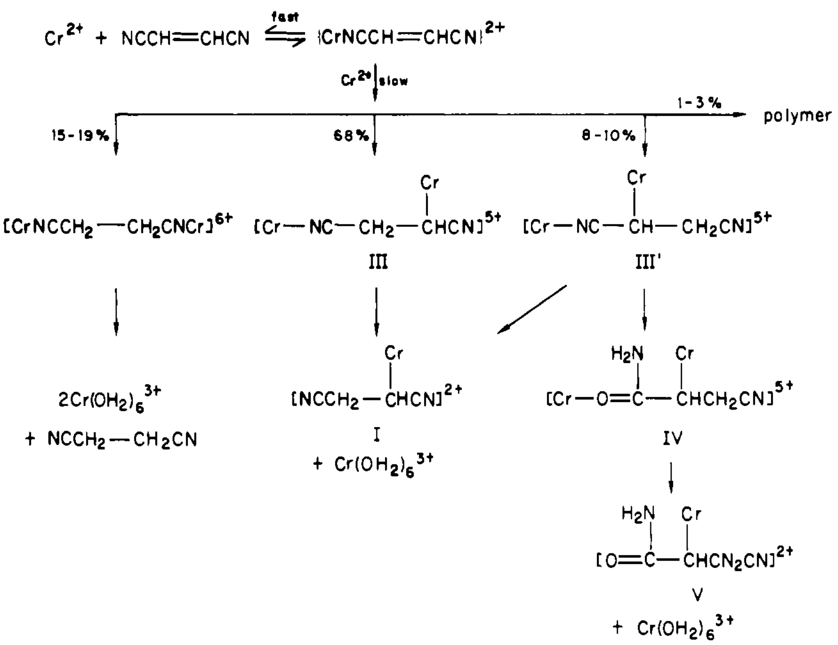
(11) Alternatively, III′ could be the parent of I (eq 6), and III could undergo attack by coordinated OH^-, on the free –CN, followed by cleavage of the original Cr–NC bond to give IV. Some precedent for intramolecular attack is provided by the Cr(III)–2-cyanopyridine system: Balahura, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 1487.

(12) Curtis et al. (Curtis, N. J.; Lawrance, G. A.; Sargeson, A. M. *Aust. J. Chem.* **1983**, *36*, 1495) have observed rapid N → O isomerism for carboxamide complexes of $(NH_3)_5Cr^{3+}$.

(13) Kita, P., private communication. $(H_2O)_5Cr{-}CH_2C(O)NH_2^{2+}$ is easily separated from $Cr(OH_2)_6^{3+}$ if the eluting acid is <0.1 M on Dowex 50W-X2, but separation is not feasible at higher acidities. The electronic spectrum of the organochromium species indicates reversible protonation occurs in the range of 0.01–0.1 M $HClO_4$.

Scheme I



to give succinonitrile + $2Cr(OH_2)_6^{3+}$. The amount of succinonitrile is determined from the amount of fumaronitrile reacted minus the total ligand recovered in organochromium species.

The product studies are summarized in Table IV. The results generally show the expected balance. For example in 0.32 M H^+, the sum of $Cr(OH_2)_6^{3+}$ resulting from succinonitrile formation (0.62×10^{-4} mol) and from aquation of I (1.13×10^{-4} mol) to give 1.75×10^{-4} mol agrees with the 1.82×10^{-4} mol found. Similarly, the sum of I in (ii) and IV in (i) ($1.125 \times 10^{-4} + 0.170 \times 10^{-4} = 1.295 \times 10^{-4}$ mol) agrees with the 1.28×10^{-4} mol of 2+-charged species found in (iii).

The changes in products with acidity appear to be minor. The total amount of nitrile complexed changes from 81% to 84% when $[H^+]$ changes from 0.32 to 0.051 M. The major product III, given by the amount of I in (ii), changes from 68% to 75% with the same change in acidity. The rate of the reaction appears independent of $[H^+]$, but such small changes might go undetected in the kinetic study. Also it is possible that some of the precursor of IV (III′) is diverted to I by a path more favorable at lower acidity. This possibility is included in Scheme I, which can be used to rationalize the product distribution and proposed structures.

Reaction of Chromium(II) and $(H_2O)_5CrNCCH{=}CHCN^{3+}$. As shown above, the reaction of Cr^{2+} and $(NH_3)_5CoNCCH{=}CHCN^{3+}$ is fast and yields cobalt(II) and $(H_2O)_5CrNCCH{=}CHCN^{3+}$. The latter product can aquate, but with Cr^{2+} in excess at moderate concentrations reduction of the coordinated fumaronitrile is observed. The kinetics of the reaction have proven difficult to study. The Cr^{2+} concentration must be high enough to allow reduction to dominate over aquation of the chromium(III) reactant. But then the reaction is too rapid to quench in a controlled way to determine unreacted fumaronitrile. Observations at 410, 520, and 750 nm show a wavelength dependence of the apparent rate. It seems probable that hydrolytic reactions of products are interfering, as suggested in the similar studies on free fumaronitrile. Between 0.025 and 0.10 M $[H^+]$ and 0.95×10^{-2} and 2.96×10^{-2} M $[Cr^{2+}]$, the rate determined from the absorbance increase at 520 nm is approximately[14] given by

$$\text{rate} \approx 2.2 \times 10^3[(H_2O)_5CrNCCH{=}CHCN^{3+}][Cr^{2+}]^2 \qquad (8)$$

The main point is that reduction of coordinated fumaronitrile is $\sim 10^3$ times faster than that of the free ligand, as seen by a comparison of eq 5 and 8.

To ascertain the reaction products, a solution of $(NH_3)_5CoNCCH{=}CHCN^{3+}$ was allowed to react with ~20% excess (3:1) Cr^{2+} for 5 min ($\sim 10t_{1/2}$). Then the solution was treated with $(NH_3)_5CoN_3^{2+}$ or O_2 and ion exchanged at 2 °C on Sephadex SP-C25 resin. The order of elution of the chromium products from the column is as follows. A small amount of a red fraction eluted with 0.2 M $HClO_4$, and the elution characteristics and electronic spectrum indicate that it is I, identified previously. A blue band eluted with 0.2 M $HClO_4$ and 0.2 M $NaClO_4$ and proved to be $Cr(OH_2)_6^{3+}$. With 0.2 M $HClO_4$ in 0.5 M $NaClO_4$ a small amount of red product eluted and was qualitatively identified as III. A purple band (VI) was eluted with 0.2 M $HClO_4$ and 0.8 M $NaClO_4$. The elution properties indicate that it is a dichromium species, and on this basis the absorption maxima and molar extinction coefficients are given in Table III. The major product (VII) was a red-purple fraction eluted with 1 M $HClO_4$ in 2 M $NaClO_4$. As shown later this is a trichromium species, with absorption maxima and molar extinction coefficients given in Table III. Finally a purple band (VIII) could not be eluted with 1 M $HClO_4$ in 4 M $NaClO_4$, did not decompose on standing to elutable products, and could only be removed by conversion to chromate with alkaline hydrogen peroxide.

The major product (VII) was found to hydrolyze slowly. When VII reacted for 3 days in 1 M $HClO_4$, the hydrolysis products were separated and found to be $Cr(OH_2)_6^{3+}$ and V[15] in the molar ratio 2:1. During this reaction the absorbance decreases in the 530-nm region with an initial shift in the maximum from 529 to 532 nm after 4 h followed by a shift back to 522 nm. The biphasic character of the reaction was confirmed by observations at 240 nm in 0.10 M $HClO_4$ and 0.20 M $NaClO_4$. These data were treated by a consecutive reaction scheme and least-squares analysis to give successive rate constants of 2.0×10^{-4} s^{-1} and 3.6×10^{-5} s^{-1} at 25 °C.

Another observation is probably relevant to the characterization of the major product (VII). The initial reduction reaction is followed by significant absorbance changes at 355 and 750 nm. Since the other products are each less than 12% of the total as

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(14) Deviations from eq 8 are such that the apparent third-order rate constant appears to decrease at higher (>0.10 M) $[H^+]$ and decreases by ~20% with increasing $[Cr^{2+}]$ over the range given.

(15) The electronic spectrum of the product has maxima at 518, 411, and 269 nm with extinction coefficients of 96.7, 125 and 3.80×10^3 M^{-1} cm^{-1}, respectively. See Table III for comparison.

(16) (a) Hurst, J. K.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1178. (b) Diaz, H.; Taube, H. *Inorg. Chem.* **1970**, *9*, 1304.

(17) Davies, R.; Jordan, R. B. *Inorg. Chem.* **1971**, *10*, 2432.

Scheme II

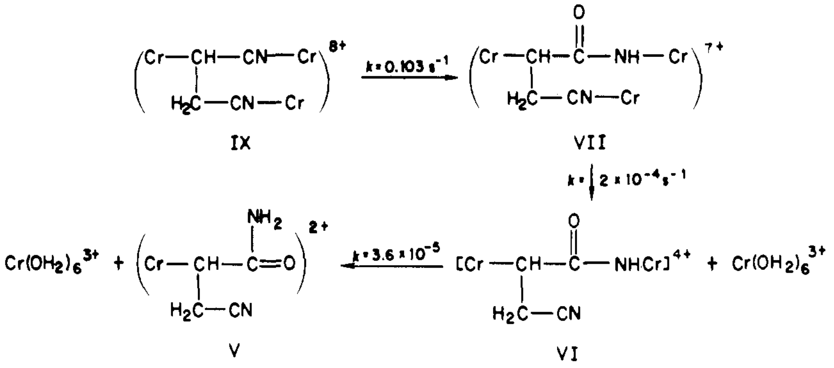


Table V. Product Distribution from the Reaction of Chromium(II) and $(H_2O)_5CrNCCH{=}CHCN^{3+}$ (10^4 × mol)[a,b]

	0.38 M H^+		0.051 M H^+	
species	nitrile	Cr(III)	nitrile	Cr(III)
reacted	1.840	(5.52)	1.740	(5.22)
I	(0.027)	0.0265	(0.038)	0.0384
III	(0.069)	0.137	(0.118)	0.236
VI	(0.213)	0.426	(0.169)	0.338
VII	(1.298)	3.895	(1.144)	3.431
$Cr(OH_2)_6^{3+}$		0.387[c]		0.468[c]
immobile	(0.273)[d]	0.546	(0.248)[d]	0.495
total	1.879	5.418	1.717	5.006
recovered	102%	98%	99%	96%

[a] Values in parentheses are derived from the others as described in the text. [b] Initially fumaronitrile complex and Cr^{2+} were 2.35×10^{-2} and 9.60×10^{-2} M, respectively; the reaction time was 110 s at 25 °C in 0.50 M $LiClO_4$-$HClO_4$. [c] These values are corrected for the $Cr(OH_2)_6^{3+}$ from unreacted $(H_2O)_5CrNCCH{=}CHCN$, 0.116×10^{-4} and 0.220×10^{-4} mol at 0.38 and 0.051 M H^+, respectively. [d] Value assumes a Cr:nitrile ratio of 2:1.

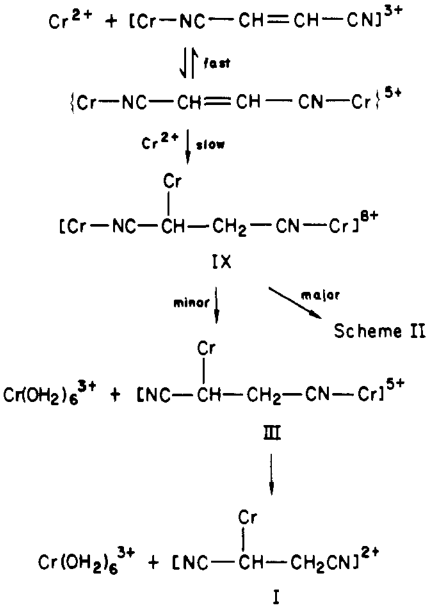
shown below, it seems most likely that this absorbance change is associated with the major product. The rate of this reaction is the same at the wavelengths noted, and is independent of $[H^+]$ (0.010–0.350 M) and of $[Cr^{2+}]$ (1.47×10^{-2} to 3.0×10^{-2} M) with a first-order rate constant of 0.103 ± 0.010 s^{-1} (25 °C, 0.50 M $LiClO_4$-$HClO_4$).

These reactivity patterns are consistent with Scheme II in which the initial reduction product IX undergoes carboxamide formation[11,12] to give VII, which in turn aquates to VI, and further aquation gives V.

The product distribution was determined after quenching with O_2 and $(NH_3)_5CoN_3^{2+}$ in parallel runs. The former reagent was used to analyze for I as well as VI, VII, and VIII, while the latter was used for $Cr(OH_2)_6^{3+}$, III, VI, VII, and VIII. The extent of reaction and amounts of comparable products agreed to better than 2% with the two quenching agents. The product amounts are summarized in Table V in terms of moles of species. The recovery of chromium and nitrile is ≥96% at both acidities. The major difference in products between the reduction of the free and coordinated nitrile is that essentially all of the nitrile is recovered as organochromium species in the latter system, while ~20% appears as free succinonitrile in the former.

For each 1 mol of products I, III, and VI there should be 2, 1, and 1 mol of $Cr(OH_2)_6^{3+}$. This predicts 0.335×10^{-4} and 0.364×10^{-4} mol of $Cr(OH_2)_6^{3+}$ at the higher and lower acidity, respectively. These values are 86% and 78%, respectively, of the amount found.

Scheme III



The major reaction product is VII at both acidities, with no other product constituting more than 12% of the total compared to the 66–71% of VII. The main change in products with acidity is the formation of more III and less VI at 0.051 M H^+. This could be explained if IX (Scheme III) undergoes aquation to III in competition with formation of VII and the aquation rate has some $[H^+]^{-1}$ dependence. This reaction would constitute less than 7% of the net reaction of IX, based on the III:VII ratio at 0.051 M H^+ and could go undetected in the kinetic study described in Scheme II. This suggestion parallels that made for the reactivity of III′ in Scheme I.

Discussion and Summary

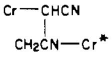
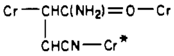
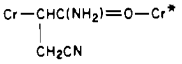
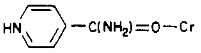
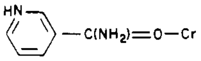
The chromium(II) reductions of free and coordinated fumaronitrile produce a multiplicity of products with variable reactivity. One is left with the impression of a very complex system; a feeling shared by the authors during much of this work. However, with the clarity of hindsight it is found that the major features of these systems can be understood on the basis of the following few general principles.

(i) The precursor complex has chromium(II) coordinated to a nitrile nitrogen. This explains why all the initial products have at least one $Cr{-}N{\equiv}C$- function, why a substantial amount of free succinonitrile is formed from free fumaronitrile (Scheme I), and why no species with two Cr—C bonds are formed.

(ii) The second chromium(II) reacts with the precursor complex at the available basic sites. These are the -C=C- system and the nitrile nitrogen in fumaronitrile. About 17% of reaction occurs at the nitrogen in free fumaronitrile (Scheme I). Since the chromium(III)–fumaronitrile complex has both nitrile nitrogens coordinated in the precursor complex, the second chromium(II) must react at the -C=C- center, and the products all have a Cr—C bond.

(iii) The composition of the reduction products have been assigned in large part by their reactivity. The kinetic results that are the basis of these assignments are summarized in Table VI. The aquation rate constants of the pentaaquachromium(III) complexes fall in the following order: conjugated nitriles, $k \sim 2 \times 10^{-2}$ s^{-1}; aliphatic nitriles, $k \sim 3 \times 10^{-4}$ s^{-1}; carboxamides, $k \sim 5 \times 10^{-5}$ s^{-1}.

Table VI. Aquation Rates of Pentaaquochromium(III) Complexes (25 °C)

complex[a]	rate constant, s^{-1}
Cr–$NCCH_3$	4.3×10^{-4} [b]
 $Cr—CHCN$, $CH_2CN—Cr^*$	3.6×10^{-4}
 $Cr—CHC(NH_2){=}O—Cr$, $CHCN—Cr^*$	2×10^{-4}
Cr–NCCH=CHCN	$1.19 \times 10^{-2} + 4.14 \times 10^{-4}[H^+]^{-1}$
Cr–NC–C_6H_4CN	1.7×10^{-2} [c]
 $Cr—CHC(NH_2){=}O—Cr^*$, CH_2CN	3.6×10^{-5}
	6.5×10^{-5} [d]
	5×10^{-5} [d]

[a] An asterisk indicates the site of aquation in cases of ambiguity. [b] Reference 7. [c] Balahura, R. J., private communication In 0.1 M $HClO_4$. [d] Taube, H.; Nordmeyer, F. *J. Am. Chem. Soc.* 1968, *90*, 1162.

(iv) It has been proposed that the nitrile group is activated toward carboxamide formation by the neighboring chromium(III) atoms in the $(H_2O)_5Cr—CH—C{\equiv}N—Cr(OH_2)_5$ system. This explains the formation of V in both systems studied here (Schemes I and II).

There have been varying observations on the rate law for chromium(II) reductions analogous to those studied here. Under conditions of [substrate] > [Cr(II)], it has been concluded that fumaric and maleic acids[4,5] are reduced with a rate law first order in each reactant. On the other hand, diethyl fumarate[18] has an overall third-order rate law when [Cr(II)] > [diethyl fumarate], analogous to that reported here (eq 5). The observations of Castro et al.[18] on the secondary reaction are also analogous to those reported here, indicating Cr(II)-catalyzed aquation of the initial organochromium(III) product. Preliminary results[19] with fumaric and maleic acids, with [Cr(II)] > [substrate], show a third-order rate law with rate constants of 2.6 M^{-2} s^{-1} and 79 M^{-2} s^{-1}, respectively. It is not clear at present if the rate law really changes with the relative reagent concentrations or if the original[4,5] evaluation of the rate law on the basis of the linearity of the appropriate plots is in error. If the general mechanism is

$$Cr^{2+} + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{CrL\}^{2+} \xrightarrow[H^+]{k_2[Cr^{2+}]} \text{products}$$

and a steady state is assumed for the intermediate, then rate $\propto k_1k_2[Cr^{2+}]^2[L](k_{-1} + k_2[Cr^{2+}])^{-1}$. This does not predict that the order with respect to $[Cr^{2+}]$ should change from first to second as $[Cr^{2+}]$ is increased.

The fact that free fumaronitrile is reduced about 10^3 times more slowly than its chromium(III) complex may be attributed to the affect of coordination on the reducibility of the ligand. However, this type of rate enhancement seems not to apply to fumarate[16] and maleate[17] coordinated to chromium(III) since previous studies on these systems in the presence of chromium(II) do not appear to be complicated by ligand reduction. Possibly the comparison is not justified, because a proton in the acid has been replaced by $(L)_5Cr^{3+}$ in the complex. The proton may enhance reducibility more than L_5Cr^{3+}. The fumaronitrile system is free from this ambiguity.

The rate constant for the chromium(II) reduction of the $(NH_3)_5Co^{3+}$ complex of fumaronitrile is $\sim 10^7$ times larger than that of succinonitrile.[1] This is a particularly dramatic example of the large effect of a simple change in ligand structure on the electron-transfer rate. Of course the mechanism has also changed from outer sphere with succinonitrile to inner sphere with fumaronitrile. Although the lead-in and remote groups are the same, the –C=C– bond in fumaronitrile greatly affects the ligand reducibility and facilitates electron transfer between the two metal centers.

It might be surprising that the rate constant for reduction of the $(NH_3)_5Co^{3+}$ complex of 1,4-dicyanobenzene (0.92 M^{-1} s^{-1})[2] is so much smaller than that of the fumaronitrile complex (1.9×10^5 M^{-1} s^{-1}). This may be due to the difference in ligand reducibility. The polarographic half-wave potentials (DMF vs. SCE) are −1.35 and −1.57 V for fumaronitrile[20] and 1,4-dicyanobenzene,[21] respectively. This observation implicates a chemical reduction mechanism at least for the fumaronitrile complex.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for support of this work.

Registry No. I, 97633-49-3; III, 97633-50-6; IV, 97633-51-7; VII, 97633-52-8; $[(NH_3)_5CoNCCH{=}CHCN](ClO_4)_3$, 80679-82-9; $(H_2O)_5CrNCCH{=}CHCN^{3+}$, 97633-48-2; Cr, 7440-47-3; (*E*)-NCCH=CHCN, 764-42-1.

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(18) Castro, C. E.; Stephens, R. D.; Mojé, S. *J. Am. Chem. Soc.* **1966**, *88*, 4964.

(19) Jordan, R. B., unpublished results. For fumaric acid the reaction was monitored at 580 nm in 0.90 M $HClO_4$ with [fumaric acid] = 7.0×10^{-4} M and $[Cr^{2+}]$ between 1.90×10^{-2} and 4.70×10^{-2} M. With maleic acid the reaction was monitored at 410 and 580 nm in 0.93 M $HClO_4$, with [maleic acid] = 5.5×10^{-4} M and $[Cr^{2+}]$ between 0.79 $\times 10^{-2}$ and 2.37×10^{-2} M.

(20) Petrovich, J. P.; Barzer, M. M.; Ort, M. R. *J. Electrochem. Soc.* **1969**, *116*, 743.

(21) Bartak, D. E.; Houser, K. J.; Rudy, B. C.; Hawley, M. D. *J. Am. Chem. Soc.* **1972**, *94*, 7526.

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Homoleptic Isocyanide Complexes of Ruthenium(II) and Osmium(II)

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The diruthenium(II,III) and diosmium(III) acetates $Ru_2(O_2CCH_3)_4Cl$ and $Os_2(O_2CCH_3)_4Cl_2$ react with alkyl isocyanides RNC (R = $CHMe_2$, CMe_3, or C_6H_{11}) to give the homoleptic metal(II) complexes $[M(CNR)_6](PF_6)_2$ (M = Ru or Os). This is the first general synthetic route to these complexes and is an important further illustration of the use that can be made of the cleavage of multiple metal-metal bonds by π-acceptor ligands such as isocyanides. The *tert*-butyl isocyanide complexes readily undergo a dealkylation reaction to give the cyano derivatives $[M(CNCMe_3)_5CN]PF_6$. The spectroscopic (IR and ^1H and ^{13}C NMR) and electrochemical properties of these complexes have been measured.

Introduction

Homoleptic isocyanide complexes of ruthenium and osmium are rare. Reduction of *trans*-$Ru(CNR)_4Cl_2$ (R = CMe_3 or $CHMe_2$) with sodium amalgam in the presence of excess isocyanide has been used to prepare $Ru(CNCMe_3)_5$ and $Ru_2(CNCHMe_2)_9$.[1,2] The only zerovalent osmium complex of this

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