has been obtained in 4% yield from the reaction of CF_3CN with $(NSCl)_3$ in SO_2 at 55 °C in a Teflon autoclave,[30] and **9** (R = ^{t}Bu) has been isolated in unspecified yield from the reaction of trimethylacetamidine and $(NSCl)_3$.[31]

Summary and Conclusions. The initial product of the reaction of organic nitriles with $(NSCl)_3$ in carbon tetrachloride is the six-membered ring **2**. This direct synthesis of **2** should expedite investigations of the corresponding eitht-π-electron systems, **4**. The rate of formation of **2** is much faster for R = R'_2N than for R = ^{t}Bu, Ph, and CCl_3. This difference is attributed to the stabilization of the intermediate **7** by electron donation from the R'_2N group to the electron-deficient carbon ($p\pi$–$p\pi$ bonding). The isolation of **7** (R = Me) offers the possibility of preparing polymers of the type $[(R)CNSN]_x$ via reduction. The thermal conversion of **2** into **1** upon thermolysis explains previous reports of the formation of **1** from the reaction of organic nitriles with $(NSCl)_3$ at elevated temperatures and provides a good synthesis of dialkylamino derivatives of the five-membered ring. The reaction of Me_2NCN with $(NSCl)_3$ in *nitromethane* is an improved route to the trithiatetrazocine ring system **9** (R = Me_2N) that will facilitate studies of this eight-membered ring.

Acknowledgment. Financial support from the NSERC (Canada) and postgraduate awards to A.A. from the Alberta Heritage Scholarship Fund and the Killam Foundation (The University of Calgary) are gratefully acknowledged. We thank Professor J. Passmore and Dr. M. J. Schriver (University of New Brunswick) for a preprint of ref 16.

Note Added in Proof. The synthesis of **1** (R = NMe_2) in 54% yield from the reaction of *N,N*-dimethylguanidinium hydrochloride with excess sulfur dichloride in acetonitrile has been reported recently.[32]

Supplementary Material Available: A table of kinetic data for the thermolysis of **2** (R = Me_2N) (1 page). Ordering information is given on any current masthead page.

---

(30) Höfs, H. V.; Hartman, G.; Mews, R.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 988.

(31) Boeré, R. T.; Oakley, R. T.; Cordes, A. W. *Acta Crystallogr., Sect. C* **1985**, *C41*, 1686.

(32) Cordes, A. W.; Goddard, J. D.; Oakley, R. T.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1989**, *111*, 6147.

Contribution from The Guelph-Waterloo Centre for Graduate Work in Chemistry,
Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada

Chromium(II) and Vanadium(II) Reduction of Pentacyanocobaltate(III) Complexes

Robert J. Balahura* and Michael D. Johnson

Received October 12, 1988

The chromium(II) and vanadium(II) reductions of the pentacyanocobaltate(III) complexes of pyrazine (pyz), isonicotinamide (isn), 4-cyanopyridine (4-CN-py), and pyridine (py) have been studied. For chromium(II), the reductions are first order in Cr(II) and cobalt(III) complex and independent of hydrogen ion concentration. At 25 °C, I = 1.0 M ($LiClO_4$), $k_{Cr} = 1.5 \times 10^3$, 19, 28, and 1.2 $M^{-1}\,s^{-1}$ for pyz, isn, 4-CN-py, and py, respectively. A radical-ion mechanism is proposed for the reduction of the first three complexes. For V(II), two reactions are observed with rate laws $k_{obs1} = k_1[V^{2+}] + k_{-1}$ and $k_{obs2} = k[V^{2+}]/(1 + K_1[V^{2+}])$. The first reaction is the formation of a binuclear intermediate precursor complex bridged by a cyanide from the oxidant. Values of k_1 ($M^{-1}\,s^{-1}$), k_{-1} (s^{-1}) for pyz, isn, 4-CN-py, py: 65, 1.1; 55, 1.0; 46, 1.2; 49, 1.0. The saturation type kinetics observed in the second reaction are consistent with formation of a precursor complex that is a "dead end" on the reduction pathway and a subsequent outer-sphere reduction between monomeric reactants.

Introduction

The chemistry of pentacyanocobaltate(III) complexes has provided a wealth of information concerning thermal and photochemical substitution reactions in octahedral systems.[1] Comparison of UV–vis and ^{13}C NMR spectra for these complexes with those for analogous pentacyanoferrate(II) systems has been important in the study of π-back-bonding interactions between the metal center and coordinated ligands.[2] Surprisingly, however, few investigations of the reduction of pentacyanocobaltate(III) complexes have been made.

Espenson and Davies[3] reported the first studies on the vanadium(II) reductions of $[(CN)_5Co^{III}L]$ complexes where L = Cl^-, Br^-, I^-, SCN^-, N_3^-, and H_2O. For the N_3^- and NCS^- complexes, an inner-sphere redox pathway was proposed. The reaction was postulated to proceed via ion-pair formation followed by a V(II) substitution-controlled electron transfer as illustrated for the azide complex.

$$[V(OH_2)_6]^{2+} + [Co(CN)_5N_3]^{3-} \rightleftarrows [V(OH_2)_6,Co(CN)_5N_3]^{-} \qquad K$$

$$[V(OH_2)_6,Co(CN)_5N_3]^{-} \rightarrow [Co(CN)_5]^{3-} + [V(OH_2)_5N_3]^{2+} \qquad k$$

In order to investigate the generality of the above mechanism and because of the paucity of data on the redox reactions of $(CN)_5Co^{III}$ complexes, we report here the kinetics of the chromium(II) and vanadium(II) redox reactions with pentacyanocobaltate(III) complexes possessing potential organic bridging ligands. We also report the results of a reinvestigation of the vanadium(II) reduction of $[Co(CN)_5N_3]^{3-}$ and $[Co(CN)_5SCN]^{3-}$.[3]

Experimental Section

All reagent solutions were prepared in water that had been passed through a Milli-Q Water purification system. Perchloric acid solutions were prepared by dilution of 70% doubly distilled perchloric acid (G. F. Smith Chemical Co.) and standardized with standard sodium hydroxide. Lithium perchlorate stock solutions were prepared from G. F. Smith anhydrous reagent grade $LiClO_4$ and filtered through a 0.5-μm Millipore filter. The solutions were standardized by charging aliquots on an ion-exchange column of Amberlite IR 120(H) resin and determining the acid released by titration with standard sodium hydroxide.

Chromium(II) perchlorate solutions were prepared by reduction of solutions of G. F. Smith chromium(III) perchlorate with zinc amalgam. Chromium(II) concentrations were determined as described previously.[4]

---

(1) Abou-El-Wafe, M. H.; Burnett, M. G. *J. Chem. Soc., Chem. Commun.* **1983**, 833. Borea, R.; Ellis, J.; Tsao, M.; Wilmarth, W. K. *Inorg. Chem.* **1967**, *6*, 243.

(2) Figard, J. E.; Paeekstelis, J. V.; Byrne, E. F.; Petersen, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 8417.

(3) Davies, K. M.; Espenson, J. H. *J. Chem. Soc. Chem. Commun.* **1969**, 111. Davies, K. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 3093.

Table I. Kinetics of the $Cr^{2+}/[(CN)_5CoL]^{2-}$ Reaction[a] and the Analogous $Cr^{2+}/[(NH_3)_5CoL]^{3+}$ Reduction

L	k_{Cr}, M^{-1} s^{-1}	k_{Cr}, M^{-1} s^{-1} [b]	k_{NH_3}/k_{CN} [c]
pyrazine	1.5×10^3	8.7×10^4 [d]	58
4-cyanopyridine[e]	28	124[f]	4.4
isonicotinamide[e]	19	17.4[g]	0.9
pyridine	1.2	4.0×10^{-3} [g]	3.3×10^{-3}

[a] Conditions: $I = 1.0$ M ($LiClO_4$), $[H^+] = 0.1$ M ($HClO_4$), [Co] ~ 0.1 mM, $T = 25.0$ °C. [b] $[(NH_3)_5CoL]^{3+}$ complexes, $I = 1.0$ M ($LiClO_4$), $T = 25$ °C, reductions independent of $[H^+]$. [c] Ratio of $[(NH_3)_5CoL]^{3+}$ rate constant to $[(CN)_5CoL]^{2-}$ rate constant. [d] Reference 7. [e] Bonded through the pyridine nitrogen. [f] Reference 8. [g] Reference 6a.

Table II. Rate Constants for the First Reaction in the $V^{2+}/[(CN)_5CoL]^{2-}$ System[a]

L	k_1, M^{-1} s^{-1}	k_{-1}, s^{-1}	$K_1(k_1/k_{-1})$
pyrazine	65	1.1	59
4-cyanopyridine	46	1.2	38
pyridine	49	1.0	49
isonicotinamide	55	1.0	55
N_3^{-} [c]	53	1.0	53
SCN^-	52	1.3	40

[a] Conditions: $I = 1.0$ M ($LiClO_4$), $[H^+] = 0.1$ M ($HClO_4$), [Co] ~ 10^{-4} M, $T = 25.0$ °C, $\lambda = 330$ nm. [b] k_1 values are good to ±3 M^{-1} s^{-1} and k_{-1} values to ±0.1 s^{-1}. [c] The value of K_1 reported in ref 3 is 31 M^{-1}.

Table III. Activation Parameters for k_1 in the $V^{2+}/[(CN)_5CoL]^{2-}$ Reaction[a]

L	ΔH^*, kcal mol^{-1}	ΔS^*, eu
pyrazine	10.6	−15
pyridine	10.4	−17
isonicotinamide	10.5	−25

[a] $I = 1.0$ M ($LiClO_4$); $[H^+] = 0.10$ M ($HClO_4$).

Vanadyl perchlorate was prepared by adding a stoichiometric amount of barium perchlorate to a solution of vanadyl sulfate and filtering the barium sulfate with a 0.6-μm Millipore filter. Standardization of stock vanadyl solutions was performed spectrophotometrically after oxidation to vanadium(V). It was assumed that the VO^{2+} was quantitatively reduced to V(II) by zinc amalgam.

The pentacyanocobaltate(III) complexes were prepared by literature methods.[5] The complexes were characterized by UV–vis spectrophotometry and proton NMR.

Instrumentation. All kinetic measurements were performed by using a Dionex D-110 stopped-flow spectrophotometer interfaced with a DASAR digital storage unit. Observed rate constants were obtained from the DASAR instrument by matching exponential traces with a calibrated curve generator. UV–vis measurements were obtained from a Beckman Acta CIII spectrophotometer. The rapid-scan stopped-flow apparatus used a Harrick rapid-scan monochromator and was designed by Dr. R. DeSa (OLIS, Jefferson, GA).

Kinetic Measurements. Solutions for kinetic studies were deoxygenated with argon. Syringe techniques were used for dilution and transfer of reagent solutions. All reactions were carried out under pseudo-first-order conditions with the reductant concentration in at least 10-fold excess over the cobalt(III) concentration. Measurements were made at 330 nm and at 1.0 M ionic strength unless otherwise indicated.

Results and Discussion

Chromium(II) Reductions. Reduction of the pentacyanocobaltate(III) complexes by chromium(II) was established by observing the bright blue $CoCl_4^{2-}$ ion upon addition of concentrated hydrochloric acid to the reaction mixtures. Several attempts at product analysis using standard chromatographic techniques proved unsuccessful. Elution with sodium perchlorate typically showed two or three poorly resolved bands. This behavior was attributed to the presence of relatively large amounts of HCN from the oxidant, which may coordinate to chromium either during or after the redox reaction. It was therefore not possible to conclude whether the reaction proceeds via an inner- or outer-sphere pathway from the product analysis. For an outer-sphere reduction, the products expected would be $[Co(CN)_5]^{3-}$ and $[Cr(OH_2)_6]^{3+}$ and the free organic ligand. Therefore, the visible spectra of each product mixture would be expected to be similar. On the other hand, in an inner-sphere process where the reductant attacks the heterocyclic ligand, the chromium(III) product would contain the organic ligand and the product spectra would vary depending on the cobalt complex reduced. Spectra were obtained for 1:1 ratios of Cr^{2+}–$[(CN)_5CoL]^{2-}$ immediately after reduction. For pyrazine, 4-cyanopyridine, and isonicotinamide, different spectra were observed, thereby supporting an inner-sphere process. An inner-sphere process is also observed for reduction studies on pentaamminecobalt(III) complexes with these ligands.[6a,7,8] Finally, if the reductant attacked at one of the cyanide groups, identical spectra should be obtained for all complexes (not observed). The fact that there is a substantial variation in the rate constants as a function of the organic ligand (Table I) also lends support to an inner-sphere process. Thus, it appears reasonable that reduction occurs by attack of chromium(II) at the organic ligand for pyrazine, 4-CN-pyridine, and isonicotinamide.

The kinetics of the reaction were found to be first-order in both chromium(II) and each pentacyanocobaltate(III) complex. No dependence on the hydrogen ion concentration was observed between 0.1 and 1.0 M perchloric acid. The data are consistent with a rate law of the form

$$-\frac{d[Co(III)]}{dt} = k_{obs}[Co(III)] \qquad (1)$$

where $k_{obs} = k_{Cr}[Cr^{2+}]$. A tabulation of k_{Cr} for the complexes studied is shown in Table I along with the reduction rate constants for the analogous pentaamminecobalt(III) complexes.

The relative rates of reduction of the pentaamminecobalt(III) versus the pentacyanocobaltate(III) complexes (column 3 in Table I) indicate that the inner-sphere reductions occur via a chemical or radical-ion mechanism. The basis for this premise comes from the work of Taube and Nordmeyer[6a] on the reduction of (isonicotinamide)pentaamminecobalt(III) by chromium(II). The mechanism requires a rate-determining step that involves transfer of an electron to the organic ligand coordinated to the oxidant. For such a rate-determining step, it is expected that the rate constants would be relatively insensitive to the nature of the oxidant and its nonbridging ligands. For the first three entries in Table I, the reduction rates for the pentacyano and pentaammine complexes are roughly comparable[6] for the same ligand. As pointed out by Diaz and Taube,[6b] the ratio of reduction rates need not be exactly 1, and in their study, a ratio of 80 was observed. Since the redox potentials for each pair of complexes should be very different, the data are consistent with the requirements for a radical-ion type mechanism. Note that for the pyridine complexes an outer-sphere mechanism is probably operable and the rate constants are not similar. However, it should be noted that this criterion for a radical-ion mechanism must be applied cautiously, especially when different metal ions are compared where the rate-determining step for one metal may be reduction by a rapidly formed radical and the rate-determining step for the other metal is formation of the radical.[9]

Vanadium(II) Reductions. The addition of excess vanadium(II) to a solution of a pentacyanocobaltate(III) complex results in the rapid formation of a brown intermediate, followed by its slow decay. As the vanadium(II) concentration is increased, the brown color intensifies, which is indicative of an equilibrium situation.

---

(4) Balahura, R. J.; Jordan, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 625.

(5) Wohlers, H. D.; Van Tassel, K. D.; Bowerman, B. A.; Petersen, J. D. *Inorg. Chem.* **1980**, *19*, 2837.

(6) (a) Nordmeyer, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1162. (b) Dias, H.; Taube, H. *Inorg. Chem.* **1970**, *9*, 1304.

(7) Wu, M.-Y.; Paton, S. J.; Fanchiang, Y.-T.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 326.

(8) Balahura, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 1487.

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

Table IV. Activation Parameters for V^{2+} Substitution Reactions

L	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	ref
NCS^{-a}	13.5	−7	11
$[(OH_2)_5CrSCN]^{2+b}$	13.0	−11	12
$[(NH_3)_5CoC_2O_4]^{-c}$	12.3	−10	13

[a] $I = 0.84$ M ($LiClO_4$); $[H^+] = 0.50$ M. [b] $I = 1.0$ M ($Mg(ClO_4)_2$); acid-independent step. [c] $I = 1.0$ M ($LiClO_4$); $[H^+] = 0.20$ M.

The kinetics of the intermediate formation were studied at 330 nm and yielded the rate law

$$\frac{d[\text{int}]}{dt} = k_{obs1}[\text{Co(III)}] \qquad (2)$$

where $k_{obs1} = k_1[\text{V(II)}] + k_{-1}$. The values of k_1 and k_{-1} were graphically determined from a plot of k_{obs1} vs [V(II)]. Values of these rate constants for each complex studied are given in Table II.

No hydrogen ion dependence was observed between 0.1 and 0.5 mol L^{-1} acid concentrations. The temperature dependence of k_1 was studied and activation parameters are reported in Table III as calculated by the method of Eyring.

The kinetic data are virtually identical for all six systems listed in Table II and indicate a complexation equilibrium for the first step. Values of other vanadium(II) complexation rate constants, along with activation parameters, are listed in Table IV. As may be seen, these agree reasonably well with the kinetic and thermodynamic data determined in this study. The slightly larger values of $\Delta H^{\ddagger}$ for the $[Co(CN)_5L]^{2-}$ complexes may be due to a larger association equilibrium constant as a result of favorable electrostatic interactions (see later).

Therefore, the overall first step in the reaction can be represented by

$$[V(OH_2)_6]^{2+} + [(CN)_5CoL]^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [V(OH_2)_5Co(CN)_5L] + H_2O \qquad (3)$$

The substitution site on the cobalt(III) complexes by vanadium(II) may be at one of three positions: the trans CN, the cis CN, or the organic ligand. For the chromium(II) reductions, the spectral data determined for product solutions as well as the relative rates obtained indicate attack at the organic ligand. For V(II), the spectra of the V(II)/Co(III) complexes with pyridine, pyrazine, isonicotinamide, and 4-cyanopyridine were obtained by using rapid-scan stopped-flow methods. In each system, the absorption maximum occurred at ~360 nm. Since the pyridine complex has no organic binding site and yet has an absorption spectrum identical with those of the other complexes studied, it is reasonable to conclude that binding occurs at a cyanide nitrogen for all complexes. Whether binding is at the cis or trans CN cannot be ascertained. This behavior is in contrast to the earlier work by Davies and Espenson[3] where binding was "observed" at the sixth ligand. As may be seen later, their assignment of the binding site may be in error.

The second reaction was found to have a more complicated vanadium(II) dependence than the first reaction. The data fit the rate law

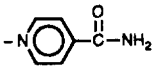
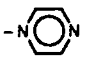
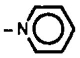
$$-\frac{d[\text{int}]}{dt} = k_{obs2}[\text{int}]$$

$$k_{obs2} = \frac{a[V^{2+}]}{1 + b[V^{2+}]} \qquad (4)$$

At low vanadium(II) concentrations a linear dependence of k_{obs2} on V(II) was observed. However, at high V(II) concentrations, the rates became independent of the V(II) concentration.

No hydrogen ion dependence was observed between 0.1 and 0.5 M acid. The terms a and b may be evaluated from the slope and intercept of a plot of k_{obs2}^{-1} vs $[V^{2+}]^{-1}$. At the low V^{2+} concentrations, the absorbance changes are small and reproducible data difficult to obtain. Table V lists the values of a and b for the isonicotinamide, pyrazine, and pyridine complexes.

Table V. Kinetics of the Redox Step in the $V^{2+}/[(CN)_5CoL]^{2-}$ System[a]

L	a,[b] $M^{-1}\ s^{-1}$	b,[b] M^{-1}
	14 ± 1	128 ± 10
	13 ± 1	98 ± 10
	2.3 ± 0.2	19 ± 2

[a] $T = 25.0$ °C, $I = 1.0$ M ($LiClO_4$), and $[H^+] = 0.10$ M. [b] $a = k$ and $b = K_1$ in Scheme I.

Before any mechanistic conclusions can be made, it is necessary to unambiguously establish which step corresponds to electron transfer. Several qualitative experiments were performed by adding concentrated HCl to reaction mixtures (typically, 10 mL of concentrated HCl to 5 mL of a solution containing 10^{-3} M complex and 10^{-2} M vanadium(II)) at various times and observing the production of or lack of a bright blue color due to Co(II). Addition of HCl within 1–2 s after addition of V^{2+} (at the end of the first reaction) gave no discernible color. Addition of HCl 30–60 s after addition of V^{2+} (at the end of the second reaction) produced a bright blue color, indicating that the reduction step corresponds to the second of the observed reactions. A more quantitative approach was also used. Since reduction produces the $[Co(CN)_5]^{3-}$ species, itself a good reductant, the disappearance of an appropriate redox scavenger may be used to determine the redox step. The redox scavenger chosen was $[(NH_3)_5CoNCS]^{2+}$, as first suggested by Espenson.[3]

A solution of $[(CN)_5CoL]^{2-}$ and $[(NH_3)_5CoNCS]^{2+}$ was mixed with vanadium(II) in a stopped-flow apparatus and the decrease in the $[(NH_3)_5CoNCS]^{2+}$ absorbance monitored. Since the redox reaction between V^{2+} and $[(NH_3)_5CoNCS]^{2+}$ is slow but that between $[Co(CN)_5]^{3-}$ and $[(NH_3)_5CoNCS]^{2+}$ is very fast, any absorbance changes observed must be due to reduction of $[(NH_3)_5CoNCS]^{2+}$ by $[Co(CN)_5]^{3-}$ produced in the $V^{2+}/[(CN)_5CoL]^{2-}$ reaction. The reactions involved are

$$V^{2+} + [Co(NH_3)_5NCS]^{2+} \rightarrow \text{products} \qquad k \sim 0.3\ M^{-1}\ s^{-1}$$

$$[Co(CN)_5]^{3-} + [Co(NH_3)_5NCS]^{2+} \rightarrow \text{products}$$
$$k \sim 10^6\ M^{-1}\ s^{-1}$$

The results of the experiment for $[(CN)_5Co[isn)]^{2-}$ (isn = isonicotinamide) are shown in Figure 1. Under the conditions used, the first reaction between V^{2+} and $[(CN)_5Co(isn)]^{2-}$ is essentially complete after 2 s and the second reaction between V^{2+} and $[(CN)_5Co(isn)]^{2-}$ is complete after 20 s (Figure 1A, 330 nm). Figure 1B shows that at 500 nm and under exactly the same conditions there is no detectable absorbance change for the $V^{2+}/[(CN)_5Co(isn)]^{2-}$ reaction on exactly the same time scale. For reduction of $[(NH_3)_5CoNCS]^{2+}$, an absorbance decrease is expected at 500 nm; however, since the reduction of $[(NH_3)_5CoNCS]^{2+}$ by V^{2+} is slow, no absorbance change is observed as shown in Figure 1C. When a solution of $[(NH_3)_5CoNCS]^{2+}$ and $[(CN)_5Co(isn)]^{2-}$ is mixed with V^{2+} the absorbance change observed at 500 nm is shown in Figure 1D. The decrease in absorbance takes place over the full 20-s time period. If reduction of $[(CN)_5Co(isn)]^{2-}$ was occurring in the first step, the decrease in absorbance should be complete after approximately 2 s. Clearly, the $V^{2+}/[(CN)_5Co(isn)]^{2-}$ electron transfer reaction occurs in the second step. The same results were obtained for concentrations of $[(NH_3)_5CoNCS]^{2+}$ of (1–3) × 10^{-3} M. This is in contrast to the earlier report by Espenson and Davies[3] where reduction was postulated to occur in the first step. To resolve this discrepency, we repeated the scavenging experiments with the complexes $[Co(CN)_5N_3]^{3-}$ and $[Co(CN)_5SCN]^{3-}$ investigated in the earlier study. Both complexes gave results identical to those obtained with $[(CN)_5Co(isn)]^{2-}$; i.e., the absorbance changes indicated that reduction occurs in the second step.

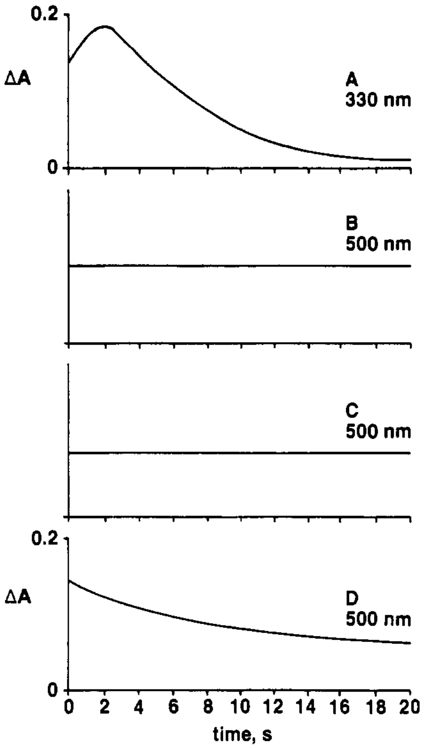


Figure 1. Absorbance changes for the reaction of V^{2+} with $[(CN)_5Co(isn)]^{2-}$ and $[(NH_3)_5CoNCS]^{2+}$: (A) $[V^{2+}] = 0.010$ M, $[[(CN)_5Co(isn)]^{2-}] = 1 \times 10^{-3}$ M, $[H^+] = 0.10$ M; (B) $[V^{2+}] = 0.010$ M, $[[(CN)_5Co(isn)]^{2-}] = 1 \times 10^{-3}$ M, $[H^+] = 0.10$ M; (C) $[V^{2+}] = 0.010$ M, $[[(NH_3)_5CoNCS]^{2+}] = 1 \times 10^{-3}$ M, $[H^+] = 0.10$ M; (D) $[V^{2+}] = 0.010$ M, $[[(CN)_5Co(isn)]^{2-}] = 1 \times 10^{-3}$ M, $[[(NH_3)_5CoNCS]^{2+}] = 1 \times 10^{-3}$ M, $[H^+] = 0.10$ M.

The kinetics of the reaction of V^{2+} with $[(CN)_5CoNCS]^{3-}$ and $[(CN)_5CoN_3]^{3-}$ were also reinvestigated at several wavelengths. At 330 nm, the absorbance changes were virtually identical with those observed in the heterocyclic systems (increase followed by a decrease). When the same reactions were monitored at the wavelengths reported in the earlier work, monophasic absorbance changes were observed for low vanadium(II) concentrations (<0.01 M). However, at high vanadium(II) concentrations (>0.01 M), the reaction was biphasic. The change was difficult to observe and could account for the data reported by Espenson. The rate constants for the first reaction (increase in absorbance) are given in Table II and are identical with those found for the heterocyclic systems.

A mechanism consistent with the observations is given in Scheme I. In this mechanism, step one represents the formation of an inner-sphere "dead-end" complex[10] where V(II) has complexed with one of the cyanide nitrogens on the oxidant. The redox reaction then occurs by an outer-sphere pathway in step 2. For this mechanism, *a* and *b* in eq 4 correspond to K_1 and *k*, respectively. Adequate agreement is obtained between K_1 measured in the first step and K_1 determined from saturation kinetics in the second (Tables II and V).

Scheme I

$$[Co(CN)_5L]^{2-} + [V(OH_2)_6]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [L(CN)_4CoCNV(OH_2)_5]^0 \quad K_1$$

$$[Co(CN)_5L]^{2-} + [V(OH_2)_6]^{2+} \xrightarrow{k} [Co(CN)_5]^{3-} + V^{3+}(aq) + L$$

Reaction of the binuclear complex with V^{2+} does not appear to be involved since the redox step has the expected dependence on ionic strength for a 2 +/2− interaction.

A somewhat similar situation pertains in the reactions of $[CoEDTA]^{2-}$ with $[Fe(CN)_5L]^{2-}$ complexes.[14-16] In the latter case, however, a cyano-bridged binuclear complex is formed that contains Co(III) and Fe(II). This dead-end complex undergoes back-electron-transfer and the products $[CoEDTA]^-$ and $[Fe(CN)_5L]^{3-}$ result from a parallel outer-sphere pathway. In this study, the dead-end complex can be characterized unambiguously by making use of the charge-transfer properties of the $(CN)_5Fe^{II}$ unit and the general inertness of cobalt(III). In the present study, due to the lability of both V(II) and V(III),[17] the existence of the binuclear complex was inferred from the kinetic data. The data collected in Tables II and III are consistent with the formation of a binuclear complex where the bridging ligand is cyanide in all six cases reported. The binuclear complex is formed via the ion-pair $[Co(CN)_5L^{2-},V(OH_2)_6^{2+}]$, followed by slow interchange of a bound water molecule for a cyanide nitrogen. The rate constant for the interchange reaction can be estimated from the experimental values of k_1 and the calculated[18] value of K_{IP}, the outer-sphere association constant. For $K_{IP} = 3$ M^{-1},[19] the interchange rate constant is approximately 17 s^{-1} ($k_1 \sim 50$ M^{-1} s^{-1} for all complexes). Nichols, Ducommun, and Merbach have obtained a value for the interchange rate constant of 20 s^{-1} for the $[V(OH_2)_6]^{2+}/SCN^-$ system.[20] It is likely that the substitution reaction described herein corresponds to an I_a mechanism.

Furthermore, the assignment of the oxidation states in the binuclear complex as V(II) and Co(III) is confirmed by the scavenging experiments described earlier. Thus, electron transfer takes place in a second subsequent step, and the data suggest an outer-sphere pathway. It is not clear why the inner-sphere binuclear complex is unreactive to reduction by V(II).

Conclusions. The chromium(II) reductions of pentacyanocobaltate(III) complexes with pyrazine, 4-cyanopyridine, and isonicotinamide proceed via attack at the organic ligand in an inner-sphere process. A radical-ion mechanism is postulated for these reactions on the basis of rate comparisons.

In the vanadium(II) reductions of these complexes, a binuclear inner-sphere complex between $V^{2+}(aq)$ and $[(CN)_5CoL]^{2-}$ is produced that is redox inactive. Reduction of the cobalt(III) center proceeds by an outer-sphere pathway between the two monomeric reactants.

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

Registry No. Cr^{2+}, 22541-79-3; V^{2+}, 15121-26-3; $[(CN)_5Co(pyz)]^{2-}$, 64915-93-1; $[(CN)_5Co(4\text{-}CN\text{-}py)]^{2-}$, 64915-94-2; $[(CN)_5Co(py)]^{2-}$, 38684-03-6; $[(CN)_5Co(isn)]^{2-}$, 64915-91-9; $[(CN)_5Co(N_3)]^{3-}$, 19400-45-4; $[(CN)_5Co(NCS)]^{3-}$, 19584-48-6.

Supplementary Material Available: Tables SI–SIV, giving kinetic data for the Cr(II) and V(II) reductions (5 pages). Ordering information is given on any current masthead page.

---

(10) Wilkins, R. G. *The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes*; Allyn and Bacon, Inc.: Boston, MA, 1974; p 28.

(11) Malin, J. M.; Swinehart, J. H. *Inorg. Chem.* **1968**, *7*, 250.

(12) Orhanovic, M.; Po, H. N.; Sutin, N. *J. Am. Chem. Soc.* **1968**, *90*, 7224.

(13) Hwang, C.; Haim, A. *Inorg. Chem.* **1970**, *9*, 500.

(14) Rosenheim, L.; Speiser, D.; Haim, A. *Inorg. Chem.* **1974**, *13*, 1571.

(15) Huchital, D. H.; Lepore, J. *Inorg. Chem.* **1978**, *17*, 1134.

(16) Phillips, J.; Haim, A. *Inorg. Chem.* **1980**, *19*, 1616.

(17) It is expected that V(III) complexed to a cyanide nitrogen would be much more labile than either $V^{2+}(aq)$ or $V^{3+}(aq)$: Bennett, L.; Taube, H. *Inorg. Chem.* **1968**, *7*, 254.

(18) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.

(19) Value calculated by using the Fuoss equation[18] and a collision diameter of 7.8×10^{-8} cm. In ref 11, a value of 0.2 M^{-1} is estimated for the ion-pair $V(OH_2)_6^{2+},NCS^-$. In ref 20, the value calculated from the Fuoss equation is 1.2 M^{-1} for the latter system.

(20) Nichols, P. J.; Ducommun, Y.; Merbach, A. E. *Inorg. Chem.* **1983**, *22*, 3993.