nucleophilic attack by a hydroxyl ligand followed by oxygen transfer in either a singly bridged or chelated (as in Scheme I) intermediate.

Both of these mechanisms depend on the expansion of the As(III) coordination sphere with the fourth oxygen in the product As(V) deriving from $Ag(OH)_4^-$. While the possibility of the solvent being an oxygen source cannot be discounted, the transfer of a hydroxyl ligand to arsenic involving donation of its electron pair to silver(III) via the empty $d_{x^2-y^2}$ orbital (which is oriented in the equatorial plane of the complex) appears reasonable. The formation of a four-coordinate As(III) intermediate resulting from nucleophilic attack by H_2O has been postulated in the oxygen-exchange reaction of aqueous arsenite ion[27] and provides a convenient precursor to tetrahedral arsenate.

Support for the possibility that redox occurs through a five-coordinate intermediate as in Scheme I is provided by the results of other $Ag(OH)_4^-$ reactions. For example, the presence of third-order terms in the reaction with ethylenediamine[28] and HO_2^-[20] implies the formation of a five-coordinate transient.[29] Activation parameters for silver(III) complexation reactions have been interpreted in terms of an associative mechanism for ligand exchange.[3]

For simple redox systems, ΔS^* often correlates well with the charge type of the reactants. Thus, one might expect a progressively more negative ΔS_i^* for the silver(III)–arsenite reaction as the charge on arsenic(III) decreases. A recent compilation of activation parameters by Cannon, however, contains a number of examples that do not fit this generalization even for simple, one-electron transfers.[30] Our reaction is likely to proceed by (i) ion association, (ii) axial attack by negative arsenite on the positive Ag(III) center, (iii) changes in bond lengths of the reactants and restructuring of their solvation spheres, and (iv) an electron-transfer step involving the rupture of a silver–oxygen bond. In spite of the uncertainties resulting from a poorly determined value of ΔH_3, it is clear that the activation parameters for the k_3 path are significantly different from those for k_1 and k_2. Thus, it seems that the relative importance of these factors is changed by the final deprotonation of As(III).

It has been suggested that the reason for the proximity of the second and third deprotonations of arsenous acid is that there is an electronic stabilization associated with the dissociation of the third proton.[9] The Raman study of Loehr and Plane[8] of the arsenite system show that all three anions have the same pyramidal geometry in solution. This study also confirmed that there are no polymeric arsenite species in strongly basic media. It seems unlikely, then, that ions so similar should react by different mechanisms.

In the cases of the mono- and dianions the rate seems to be due to the formation of the oxygen-bridged precursor complex (A or A′), which is then followed by a fast redox process.[31] This is consistent with a large negative activation entropy as observed. In fact, at lower ionic strength, ΔS^* should be even more negative.[32] The difference in activation parameters for AsO_3^{3-} compared to those for $H_2AsO_3^-$ and $HAsO_3^{2-}$ probably arises from an increased barrier to redox (steps (iii) and/or (iv)) in the fully deprotonated species. The enthalpy of activation for the trianion reaction is more than twice that of the others, suggesting a large energy barrier to the transfer of two electrons. It is possible that this difference in reactivities has the same origin as the "anomalous" pK_{a3} of arsenous acid.

Acknowledgment. We thank Sigma Xi, The Scientific Research Society, for a Grant-in-Aid, and the URI Academic Computer Center for its technical support.

Registry No. $Ag(OH)_4^-$, 23172-26-1; $H_2AsO_3^-$, 14102-45-5; $HAsO_3^{2-}$, 21581-64-6; AsO_3^{3-}, 15502-74-6.

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[29] The first-order $[OH^-]$ dependence cannot be explained by deprotonation of these substrates, and indeed, the absence of an $[OH^-]^{-1}$ term or an $[OH^-]$-independent rate law rules out replacement of an equatorially bound hydroxyl group on Ag(III). Thus, the third-order rate law is best explained by axial attack of the reductant or OH^- on Ag(III) followed by further reaction of the resulting five-coordinate intermediate.

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Kinetics of the Reaction of Chromium(II) with (3-Cyano-2,4-pentanedionato-*N*)pentaamminecobalt(III): Intramolecular Electron Transfer between Cobalt(III) and Chromium(II)

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The complex $[(NH_3)_5CoNCacac]^{2+}$, where NCacac = 3-cyano-2,4-pentanedionate, reacts with chromium(II) by way of a binuclear intermediate $[(NH_3)_5CoNCacacCr]^{4+}$ followed by inner-sphere intramolecular electron transfer. The formation constant for the precursor complex is 58 L mol^{-1} at 25 °C and 1.00 mol L^{-1} ionic strength, with thermodynamic parameters $\Delta H = -7.1 \pm 0.5$ kcal mol^{-1} and $\Delta S = -14 \pm 3$ cal deg^{-1} mol^{-1}. The kinetic parameters for the intramolecular electron transfer in the precursor complex are $k_{is} = 7.3 \times 10^2$ s^{-1}, $\Delta H^* = +8.4 \pm 0.5$ kcal mol^{-1}, and $\Delta S^* = -17 \pm 2$ cal deg^{-1} mol^{-1}. This example of intramolecular electron transfer in Co(III)–Cr(II) systems will be discussed in relation to other systems.

Introduction

The study of electron-transfer reactions between metal ions involves analysis of several discrete steps along the reaction pathway.[1-3] For most of the reactions studied, separation of these steps is not possible; however, in a few cases the intramolecular electron-transfer step may be separated.[4-7] This

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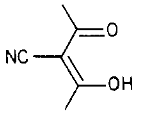
is of special interest since the factors involved in assembling the reactant species do not complicate the analysis.[8]

Outer-sphere intramolecular electron-transfer rates have been measured for a few systems,[9–12] e.g. the reaction of $Fe(CN)_6^{4-}$ with $(NH_3)_5CoOH_2^{3+}$.[11] Inner-sphere intramolecular electron-transfer rates have also been observed in some cases, especially when oxidant and reductant are both relatively inert to substitution.[4,10,13,14] For example, the preparation of Co(III)–Ru(III) binuclear complexes enables intramolecular rate constants to be determined after selective reduction of Ru(III) with Eu(II).[15] In general, if one of the reactants contains a ligand with an available site for strong complexation of the redox partner, separation of the rates for complexation and for intramolecular electron transfer can theoretically be achieved.[8]

We wish to report the determination of the intramolecular rate constant for electron transfer between chromium(II) and cobalt(III). In this system the bridging ligand, 3-cyano-2,4-pentanedione (A), was chosen with the above comments in mind. It was anticipated that, for a nitrile-bonded oxidant, chromium(II) would interact strongly with the free β-diketonate moiety.



A

Experimental Section

All reagent solutions were prepared in water that was deionized and distilled from alkaline permanganate in an all-glass apparatus. Perchloric acid solutions were prepared by dilution of 70% doubly distilled reagent grade perchloric acid (G. Frederick Smith Chemical Co.) in water and filtering through a 0.6-μm Millipore filter. Lithium perchlorate 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.

All metal salts, solvents, and organic starting materials were of reagent grade and were used without further purification. Organic materials were obtained from Aldrich Chemical Co. and metal salts obtained from G. Frederick Smith Chemical Co. and Fisher Scientific Co.

Chromium(II) perchlorate solutions were prepared prior to use by reduction of degassed solutions of chromium(III) perchlorate hexahydrate in aqueous perchloric acid using zinc amalgam and standardized as described previously.[16]

Vanadyl perchlorate solutions were prepared by adding a slight excess of barium perchlorate tetrahydrate to a solution of vanadyl sulfate pentahydrate. The precipitate of barium sulfate was filtered off with use of a 0.6-μm Millipore filter. Stock vanadyl concentrations were determined by oxidation of aliquots to vanadium(V) with permanganate, followed by titration with standard iron(II) solution. Vanadium(II) solutions used in kinetic studies were prepared by reduction of degassed vanadyl perchlorate solutions with zinc amalgam under argon. It was assumed that the VO^{2+} was quantitatively reduced to V(II).

Cobalt(III) sepulchrate trichloride was prepared by following the method of Sargeson.[17] Solutions of cobalt(II) sepulchrate for use in kinetic studies were prepared by dissolving a weighed amount of cobalt(III) sepulchrate trichloride in degassed water under argon and adding zinc dust. The solutions were freshly prepared before use. Addition of acid to the cobalt(II) solutions resulted in degradation of the complex and was avoided. Concentrations of reductant were determined by reaction of an aliquot with an excess of standard ferric ammonium sulfate solution and determination of the excess iron(III) by titration with standard sodium thiosulfate solution.

Instrumentation. All kinetic measurements were performed on a Durrum Model D-110 stopped-flow spectrophotometer with temperature controlled by a Colora constant-temperature bath in conjunction with a peristaltic pump. The stopped-flow system was modified with Teflon plungers for gastight operation. UV/visible measurements were obtained from a Beckman Acta CIII spectrophotometer. Infrared spectra were obtained from KBr pellets on a Beckman IR12 infrared spectrophotometer. The proton magnetic resonance spectra were obtained on a Varian A60 or Bruker WP60FT spectrometer. pH measurements were made by using a Radiometer Model PHM26 pH meter with a Radiometer G202C glass electrode and Orion 90-02-00 double-junction reference electrode.

Kinetic Measurements. All measurements were carried out under anaerobic conditions on solutions saturated with high-purity argon. Syringe techniques were used for dilution and transfer of reagent solutions. All reactions were carried out under pseudo-first-order conditions at 480 nm. Observed rate constants were obtained directly from the exponential decay traces displayed on a DASAR digital storage system by curve matching with a calibrated decay generator. Agreement between these values and values obtained from a plot of log $(A_t - A_\infty)$ vs. t was within 1%.

Equilibrium Measurements. The pK_a of $(NH_3)_5CoNCacacH^{3+}$ was determined by measurement of the absorbance of solutions of the complex at various concentrations of H^+.[18] The pK_a of NCacacH was determined by potentiometric titration with 0.01 mol L^{-1} KOH.[18]

Product Analyses. Reaction mixtures from kinetic runs were ion exchanged on SP Sephadex cation-exchange resin and eluted with gradually increasing concentrations of $NaClO_4/HClO_4$ solutions. The bands eluted were characterized by UV/visible spectroscopy. Chromium concentrations were determined by oxidation to CrO_4^{2-} and measuring the absorbance at 372 nm ($\epsilon = 4.82 \times 10^3$ L mol^{-1} cm^{-1}). Difficulties encountered in removing product bands from the ion-exchange column may have been due to interference from Co(II) or some reaction with the resin.

Syntheses. 3-Cyano-2,4-pentanedione, NCacacH.[19] An excess of cyanogen gas, $(CN)_2$ [generated by dropwise addition of an aqueous solution of sodium cyanide (65 g, 1.33 mol in 125 mL of water) to a stirred solution of copper(II) nitrate trihydrate (160 g, 0.662 mol in 350 mL of water)], was bubbled through a stirred solution of 2,4-pentanedione (20.0 g, 0.20 mol) and sodium methoxide (0.2 g, 0.004 mol) in 200 mL of absolute ethanol at 5 °C. Complete reaction took ~1$^1/_2$ h. The solution was stirred an additional 1 h at 5 °C, during which time the ligand precipitated. The light yellow precipitate was filtered off, dried, and dissolved in a minimum of 10% sodium hydroxide, yielding a red solution. This solution was treated with 3 mol L^{-1} HCl until the pH reached 5 and cooled to 0 °C, and the crystals of 3-cyano-2,4-pentanedione were filtered out, washed with a small amount of cold water, and air-dried. The product was stored in an airtight bottle in the freezer. (*Caution*! There is a grave danger of exposure to cyanide fumes and cyanogen gas at all times during the synthesis and workup.) ^{1}H NMR ($CDCl_3$): CH_3, τ 7.56; CH, τ 7.25 (relative to Me_4Si).

Anal. Calcd for $C_6O_2NH_7$: C, 57.6; H, 5.6; N, 11.2. Found: C, 56.6; H, 5.2; N, 10.9.

(3-Cyano-2,4-pentanedionato-*N*)pentaamminecobalt(III) Perchlorate, $[(NH_3)_5CoNCacac](ClO_4)_2$. A solution of $[(NH_3)_5Co(OSO_2CF_3)](SO_3CF_3)_2$[20] (3.0 g, 5.1 mmol) and 3-cyano-2,4-pentanedione (1.0 g, 8.0 mmol) in 25 mL of sulfolane was stirred at 40–50 °C for 2 h, during which time the color changed from red to orange. The solution was poured into 500 mL of rapidly stirred diethyl ether, and the orange solid that was deposited was filtered out, washed with ether,

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and air-dried. The complex was purified by ion-exchange chromatography on CM Sephadex cation exchange resin and was isolated as the perchlorate salt.

Anal. Calcd for $CoN_6C_6H_{21}O_{10}Cl_{21}$: C, 15.4; H, 4.5; N, 18.0. Found: C, 15.3; H, 5.0; N, 17.8.

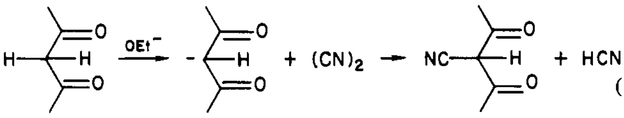
(3-Cyano-2,4-pentanedionato)bis(ethylenediamine)cobalt(III) Perchlorate, $[(en)_2Co(acacCN)](ClO_4)_2$. To a stirred solution of $[(en)_2Co(OSO_2CF_3)_2](CF_3SO_3)$[20] (1.5 g, 2.4 mmol) in 20 mL of sulfolane were added 3-cyano-2,4-pentanedione (0.3 g, 2.4 mmol) and *N*,*N*-dimethylbenzylamine (0.36 mL, 2.4 mmol). The solution was stirred at room temperature for 24 h and poured into 500 mL of diethyl ether. The orange oil that separated was treated with two 250-mL portions of diethyl ether, resulting in the formation of a light orange powder, which was filtered off and air-dried. The complex was purified by chromatography on CM Sephadex and isolated as the perchlorate salt.

Anal. Calcd for $CoN_5C_{10}O_{10}H_{22}Cl_2$: C, 23.9; H, 4.4; N, 13.9. Found: C, 23.5; H, 5.0; N, 13.6.

(3-Cyano-2,4-pentanedionato)tetraaquochromium(III), $[(OH_2)_4Cr(acacCN)]^{2+}$. A solution of chromium(III) perchlorate and 3-cyano-2,4-pentanedione was stirred for 2 h at room temperature and then charged onto a SP-Sephadex cation-exchange column. The desired complex was eluted as a pale green band that moved with the characteristics of a 2+ ion.

Results

Syntheses. The reaction to form the nitrile-substituted β-diketone ligand is basically an electrophilic attack of the cyanogen molecule $(CN)_2$ on the methine carbon of the deprotonated 2,4-pentanedione, with sodium methoxide functioning as the organic base to remove the proton (eq 1).[21]



(1)

Substitution by the electron-withdrawing nitrile function results in a considerable enhancement of the acidity of the remaining methine hydrogen, with the pK_a determined to be 3.64 ± 0.05 as compared to ~9.0 for 2,4-pentanedione.[22]

Coordination of the nitrile moiety of the ligand to pentaamminecobalt(III) was accomplished via reaction with $[(NH_3)_5Co(OSO_2CF_3)](CF_3SO_3)_2$ (pentaamminecobalt(III) "triflate") in a weakly coordinating solvent (sulfolane) (eq 2).

$$[(NH_3)_5Co(OSO_2CF_3)]^{2+} \xrightarrow{S} [(NH_3)_5CoS]^{3+} + CF_3SO_3^- \xrightarrow{NCacacH} [(NH_3)_5CoNCacac]^{2+} + H^+ \quad (2)$$

Complexation of the nitrile increases the acidity of the methine hydrogen even more (pK_a = 1.30 ± 0.01) due to the positive metal center. This effect is accompanied by a shift in the nitrile stretching frequency to 2265 cm^{-1} as compared to 2225 cm^{-1} for the free ligand. The ^1H NMR spectrum in Me_2SO-d_6 shows the expected peaks due to the amine hydrogens (cis NH_3, τ 6.1; trans NH_3, τ 6.4) and methyl groups (τ 7.91).

The UV/visible spectrum of the complex at pH 7 exhibits a peak at 490 nm (ϵ = 150 L mol^{-1} cm^{-1}) assigned to the $^1A_{2g} \leftarrow {}^1A_{1g}$ transition. Upon acidification this peak shifts to 478 nm (ϵ = 75 L mol^{-1} cm^{-1}) as the ligand becomes protonated.

Solutions of the complex in pure water were unstable, and decomposition was evident after about 1 h. Attempts to form the amide-coordinated complex via hydrolysis by attack of OH^- resulted in degradation to form the aquopentaamminecobalt(III) ion.[23]

Kinetics of the Chromium(II) Reduction. From the data in Table I, it is apparent that the rate constants are not directly proportional to chromium(II) concentration but start to level off and tend toward a less than first-order dependence on chromium(II) at higher concentrations. This nonlinear behavior is noticed over a wide range of chromium(II) concentrations at different temperatures and acid concentrations from 0.02 to 0.6 mol L^{-1} (Figure 1).

Table I. Kinetic Data for the Reduction of $[(NH_3)_5CoNCacac]^{2+}$ by Chromium(II)[a,b]

T, °C	$[H^+]$, mol L^{-1}	$[Cr^{2+}]$, mol L^{-1}	k_{obsd},[c] s^{-1}	k_{calcd}, s^{-1}
25.0	0.200	0.00675	54	53
	0.200	0.0135	99	99
	0.200	0.0270	166	175
	0.200	0.0405	244	234
	0.200	0.0540	279	282
	0.200	0.0810	346	355
	0.050	0.0135	224	206
	0.100	0.0135	155	152
	0.200	0.0135	101	99
	0.300	0.0135	74	74
	0.400	0.0135	58	58
	0.600	0.0135	40	42
15.2	0.200	0.0135	84	84
	0.200	0.0270	141	141
	0.200	0.0405	177	183
	0.200	0.0540	213	214
	0.200	0.0810	262	260
20.0	0.200	0.00675	48	49
	0.200	0.0135	91	91
	0.200	0.0270	156	157
	0.200	0.0405	209	207
	0.200	0.0540	252	247
	0.200	0.0810	299	305
30.0	0.200	0.00675	60	57
	0.200	0.0135	107	107
	0.200	0.0270	198	193
	0.200	0.0405	273	264
	0.200	0.0540	322	323
	0.200	0.0810	392	416

[a] All runs were carried out at ionic strength = 1.00 mol L^{-1} adjusted with $LiClO_4$. [b] $[[(NH_3)_5CoNCacac]^{2+}] = 4.5 \times 10^{-4}$ mol L^{-1}. [c] Values for k_{obsd} are averages from at least six runs.

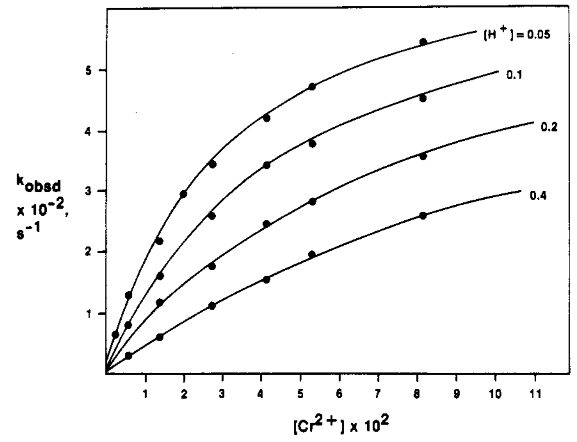


Figure 1. Cr(II) reduction of $[(NH_3)_5CoNCacac]^{2+}$ at ionic strength = 1.00 mol L^{-1} and T = 25 °C. The circles represent averages of at least six runs. The solid lines were drawn by using calculated values of k_{obsd} from eq 2 and constants from Table II.

These data are consistent with a rate law of the form

$$k_{obsd} = \frac{a[Cr^{2+}]}{1 + b[H^+] + c[Cr^{2+}]} \quad (3)$$

A mechanism consistent with this behavior is given in Scheme I. This mechanism gives the rate law (4) where $a = k_{is}K_p$, $b = K_a^{-1}$, and $c = K_p$.

$$k_{obsd} = \frac{k_{is}K_p[Cr^{2+}]}{1 + [H^+]K_a^{-1} + K_p[Cr^{2+}]} \quad (4)$$

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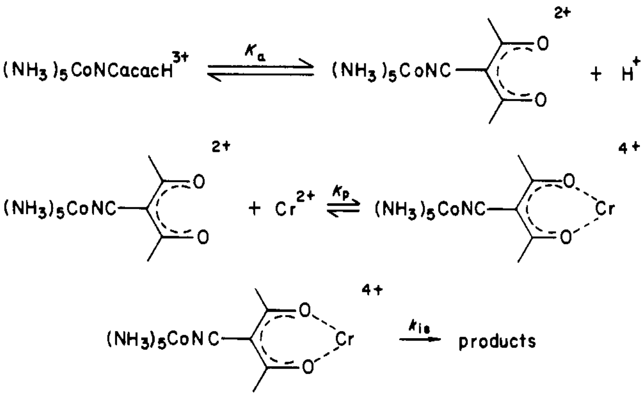
Scheme I



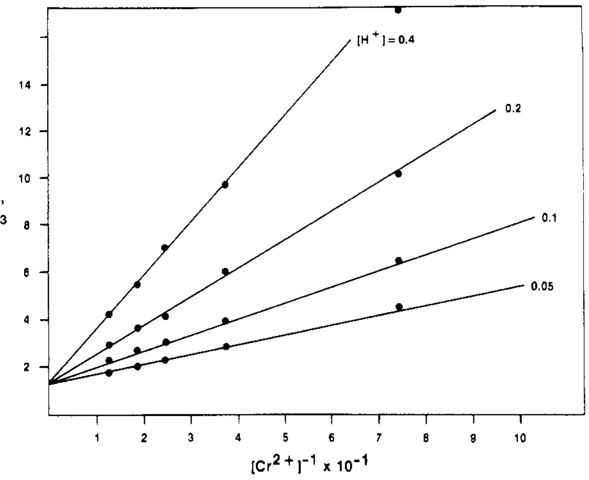


Figure 2. Plot of k_{obsd}^{-1} vs. $[Cr^{2+}]^{-1}$ for the chromium(II) reduction of $[(NH_3)_5CoNCacac]^{2+}$ (25 °C, ionic strength = 1.0 mol L^{-1}). Solid lines are from a linear regression of the data points (circles).

Table II. Rate Constants and Activation Parameters for the Reduction of $[(NH_3)_5CoNCacac]^{2+}$ by Chromium(II)

T, °C	K_a, mol L^{-1}	k_{is}, s^{-1}	K_p, L mol^{-1}	$10^{-4}k_{is}K_p$, L mol^{-1}
15.2	0.053	448 ± 8	82 ± 2	3.7
20.0	0.051	578 ± 8	68 ± 2	3.9
25.0	0.050	735 ± 10	58 ± 2	4.3
30.0	0.048	978 ± 20	47 ± 2	4.6
$\Delta H^\ddagger$, ΔH^a		+8.4 ± 0.5	−7.1 ± 0.5	+1.3 ± 0.5
$\Delta S^\ddagger$, ΔS^a		−17 ± 2	−14 ± 3	−31 ± 2

[a] $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for kinetic entries; ΔH and ΔS for equilibrium entries. ΔH values in kcal mol^{-1}; ΔS values in cal mol^{-1} deg^{-1}.

At a given [H+], eq 4 predicts a plot of k_{obsd}^{-1} vs. $[Cr^{2+}]^{-1}$ should yield a straight line with the slope equal to $(1 + [H^+]K_a^{-1})(k_{is}K_p)^{-1}$ and intercept k_{is}^{-1}. Such a plot is shown in Figure 2. From the measured K_a, the values for k_{is} and K_p can be obtained and are presented in Table II. Also given in Table II are the activation parameters determined for each constant. Equation 4 also predicts an inverse acid dependence for the reaction, and at constant chromium concentration a plot of k_{obsd}^{-1} vs. [H+] should be linear with the slope equal to $(k_{is}K_aK_p[Cr^{2+}])^{-1}$ and intercept equal to $(1 + K_p[Cr^{2+}])(k_{is}K_p[Cr^{2+}])^{-1}$. The acid dependence was studied for H^+ concentrations ranging from 0.02 to 0.60 mol L^{-1}. The data are plotted in Figure 3 for $[Cr^{2+}]$ = 0.0135 mol L^{-1}, giving the predicted dependence of k_{obsd}^{-1} on [H+]. The solid lines in Figure 1 were calculated by using the constants in Table II. The calculated rate constants are also given in Table I.

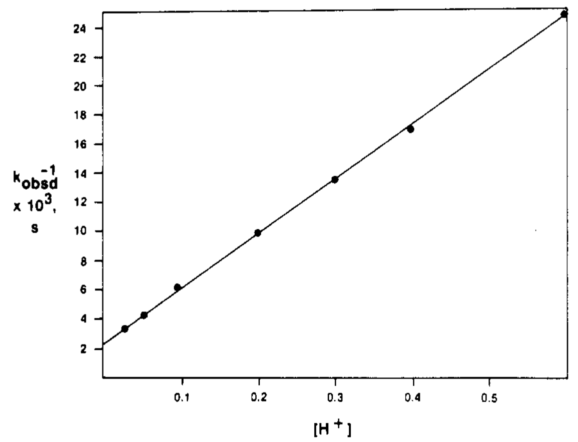


Figure 3. Acid dependence of the Cr(II) reduction of $[(NH_3)_5CoNCacac]^{2+}$ at 25 °C and $[Cr^{2+}]$ = 0.0135 mol L^{-1}. Data points are averages of six runs, and the solid line represents a linear regression of the data points.

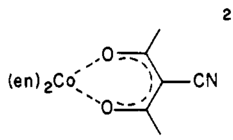
Table III. Position of the Electronic Spectral Bands for Chromium(III) β-Diketone Complexes in Aqueous Solution

complex	λ_{max} (ϵ_{max}), nm (L mol^{-1} cm^{-1}) $4T_2 \leftarrow 4A_2$	λ_{max} (ϵ_{max}), nm (L mol^{-1} cm^{-1}) $4T_1(^4F) \leftarrow 4A_2$
$[(OH_2)_4Cr(acac)]^{2+}$	553 (27)	
$[(OH_2)_4Cr(3\text{-formylacac})]^{2+}$	557 (30)	
$[(OH_2)_4Cr(NCacac)]^{2+}$	552 (38)	410 (60) (sh)

Plots of absorbance–time data were linear to better than 5 half-lives, indicating that there was no significant inhibition of the reaction due to competition for the β-diketone moiety between cobalt(II) produced in the reaction and chromium(II) at the concentrations used. Experiments with added Co(II) showed only a slight decrease in rate at high concentrations of Co(II). Stoichiometric experiments with varying ratios of Co:Cr indicated that 1 mol of Cr(II) was consumed for each mole of Co(III) complex (within 3%).

Reaction mixtures of Cr(II) and complex were submitted to cation-exchange chromatography to determine the products formed. No free ligand was detected in the initial eluants. Further elution gave a Cr(III) product that exhibited spectral characteristics similar to those of a genuine sample of $[(OH_2)_4Cr(acacCN)]^{2+}$. The spectral parameters were similar to those of other Cr(III)–β-diketone complexes (Table III).[24]

The reaction of $[(en)_2Co(acacCN)]^{2+}$ (B) with Cr(II) was



B

found to be first order in complex and in chromium(II), unlike the reduction of $[(NH_3)_5CoNCacac]^{2+}$. The second-order rate constant was determined to be 6.2 × 10^{-3} L mol^{-1} s^{-1} at 25 °C and ionic strength I = 1.00 mol L^{-1}. No acid dependence was observed.

Kinetics of the V(II) Reduction. The reaction of $[(NH_3)_5CoNCacac]^{2+}$ with vanadium(II) followed a simple rate law of the type

$$k_{obsd} = k[V^{2+}] \qquad (5)$$

A plot of k_{obsd} vs. $[V^{2+}]$ is given in Figure 4. The rate constants obtained from the slopes at 20.0, 25.0, and 30.0 °C are 6.72, 9.32, and 11.8 L mol^{-1} s^{-1}, respectively, leading to activation parameters $\Delta H^* = 9.4 \pm 0.5$ kcal mol^{-1} and $\Delta S^* = -23 \pm 2$ cal deg^{-1} mol^{-1}. No acid dependence was observed for concentrations of H^+ ranging from 0.10 to 0.40 mol L^{-1}.

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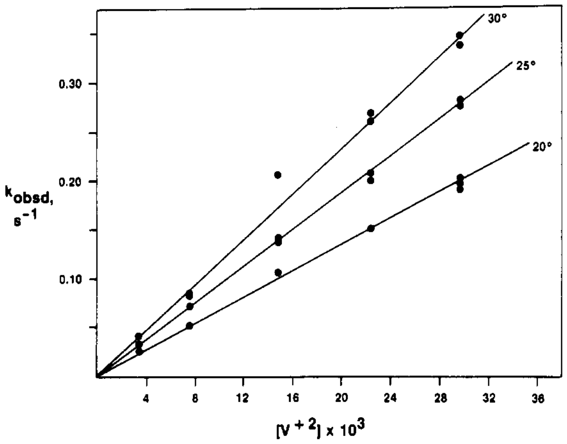


Figure 4. Vanadium(II) reduction of $[(NH_3)_5CoNCacac]^{2+}$ at $[H^+]$ = 0.2 mol L^{-1} for temperatures of 20, 25 and 30 °C.

Kinetics of the Cobalt(II) Sepulchrate Reduction. The reaction of $[(NH_3)_5CoNCacac]^{2+}$ with cobalt(II) sepulchrate was studied at $[H^+]$ = 0.05 mol L^{-1} and ionic strength I = 0.10 mol L^{-1} (NaCl). As expected for a necessarily outer-sphere reductant, the rate of reaction obeyed eq 6 with the second-order rate constant $k_2 = 73 \pm 3$ L mol^{-1} s^{-1} at 25.0 °C.

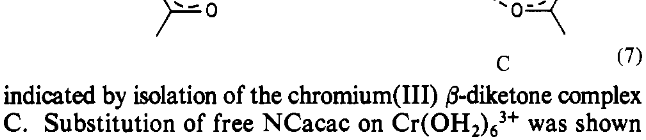
$$k_{obsd} = k_2[Co^{II}sep] \tag{6}$$

The reduction of $[(en)_2Co(acacCN)]^{2+}$ was studied under the same conditions. Simple first-order kinetics were obeyed, and k_2 was found to be 65 ± 10 L mol^{-1} s^{-1} at 25.0 °C.

Discussion

The large amount of data relating to inner-sphere electron transfer for chromium(II)–cobalt(III) amine redox systems has failed to separate the intramolecular electron-transfer rate from precursor complex formation,[25-27] due mainly to the extreme lability of chromium(II) in aqueous solution. The synthesis of $(NH_3)_5CoNCacac^{2+}$ afforded us an opportunity to investigate the possibility of "saturation" kinetics being observed for two reasons: an expected strong affinity of the chromium(II) for a "hard" bidentate oxygen chelate function[28] and an enhanced electrostatic attraction due to the delocalized negative charge on the β-diketonate moiety.

The rates obtained for the Cr(II) reduction of $(NH_3)_5CoNCacac^{2+}$ were too high for typical outer-sphere reactions between Cr(II) and Co(III) nitrile complexes,[29] e.g. for $(NH_3)_5CoNCCH_3{}^{3+}$ k_2 = 0.020 L mol^{-1} s^{-1} at 25 °C.[29] Furthermore, an inner-sphere reaction as outlined by eq 7 is indicated by isolation of the chromium(III) β-diketone complex C. Substitution of free NCacac on $Cr(OH_2)_6{}^{3+}$ was shown to be several orders of magnitude slower than the electron transfer under similar conditions. Since the only available site for an inner-sphere mechanism is the remote diketone function, the precursor complex must involve attack by Cr(II) on one or both of the oxygen atoms. The choice of mono- or bidentate chelation will not affect the rate law; however, the preferential formation of chelate rings in tetraaquochromium(III) β-diketone complexes has been shown.[24]



C (7)

As the chromium concentration is increased, saturation kinetics are observed (i.e., the decomposition via electron transfer of the precursor complex is the rate-limiting step), and a measurement of the electron transfer rate k_{is} is obtained. Presumably this results from a strong interaction of chromium(II) with the pendant β-diketone moiety.

For selected reductions, the ionic strength of the reaction mixture was lowered to 0.15 mol L^{-1}. A significant increase in the observed rate constant was noted, implying that oppositely charged species are reacting; i.e., the chromium(II) ion is "seeing" only the negatively delocalized β-diketonate moiety, and the overall 2+ charge on the complex is ignored. Although no detailed study was undertaken, it seems reasonable to assume that the increase in rate is mainly due to an increase in K_p in the detailed rate expression.

The magnitude of K_p measured in this work appears reasonable in light of the estimate of 10 L mol^{-1} made for monodentate carboxylate complexation with chromium(II).[28] For the NCacac complex, a larger value would be predicted on the basis of the chelate effect and/or electrostatic attraction.

Activation parameters for binuclear complex formation for this system and others are given in Table IV. It has been suggested that enthalpies of association should be an indication of intrinsic bond strength in the associated ions.[13] The ΔH obtained in this study (−7.0 kcal mol^{-1}) is reasonable when compared to those obtained for other systems and is in agreement with theoretical considerations.[27]

Table IV. Thermodynamic Parameters for Binuclear Complex Formation

complex	ΔH, kcal mol^{-1}	ΔS, cal deg^{-1} mol^{-1}	ref
$(NH_3)_5Ru^{III}$-4vpy-Cu^{I} [a]	−9.7	−18	13
$(NH_3)_5CoSCNHg$	−5.2	−17	32
$(NH_3)_5Co(fum)Cu^{I}$ [b]	−11.5	−22	12
$(NH_3)_5CoNTAFe^{II}$ [c]	+1.5	−23	5
$(NH_3)_5CoNCacacCr^{II}$	−7.1	−14	this work

[a] 4vpy = 4-vinylpyridine. [b] fum = fumarate. [c] NTA = nitrilotriacetate.

Entropy terms for ion association arise largely from displacement of coordinated water upon complex formation and reorganization of outer-sphere solvent molecules in the binuclear complex.[33] Values of ΔS in Table IV are largely in the range −14 to −23 cal deg^{-1} mol^{-1}, indicating a similar type of mechanism is operative in these reactions.

The rate of intramolecular electron transfer in $[(NH_3)_5CoNCacacCr]^{4+}$ was found to be 735 s^{-1} at 25 °C. This value is not unreasonable in light of the rate estimated for $[(NH_3)_5CoNCCH_2\cdot]^{2+}$ [36] (≤ 500 s^{-1}). In another study, involving a cobalt(III) radical cation generated by chromous reduction of (pyrazinecarboxylato)pentaamminecobalt(III), a value of 2.4 s^{-1} for intramolecular reduction of cobalt(III) was obtained.[7] This relatively low value can be attributed to formation of a stable radical species and a low electron permeability of the carboxylato group. Similar effects are observed for the radical species, $[(NH_3)_5CoO_2C\text{–}R\cdot]^+$, generated by pulse radiolysis techniques (e.g. for $[(NH_3)_5CoO_2CC_6H_4NO_2\cdot]^+$, k_{is} = 2600 s^{-1} [37]).

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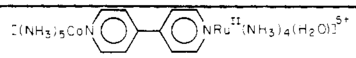
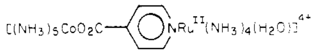
Table V. Rate Constants and Activation Parameters for Intramolecular Electron Transfer[a]

complex	k, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	ref
	~4 × 10^{-4}	20.0 ± 0.3	2.6 ± 1.2	10, 35
$[(NH_3)_5CoNH_2CH_2CH_2COOCr^{II}]^{4+}$	0.25			9
	7.4 × 10^{-3}	19.1 ± 0.2	−4.0 ± 0.7	35
$[(NH_3)_5Co(NTA)Fe^{II}]^{2+}$ [b]	0.115	18.7 ± 1.3	0 ± 4	5
$[(NH_3)_5Ru^{III}\text{–4vpy–}Cu^{I}]^{4+}$ [c]	0.24	15.1 ± 0.2	−10 ± 4	13
$[(Co(NH_3)_3)_2(OH)_2L]_2Fe^{II}$ [d]	3.7 × 10^{-3}	24.0 ± 0.2	11 ± 1	34
$[(acac)_2Ru^{III}\text{–fpd–}Ti^{III}(OH)]^{2+}$ [e]	21			14
$[(NH_3)_5Co(im)Fe^{II}(CN)_5]^{-}$ [f]	0.165	19.2 ± 0.2	2.4 ± 0.2	4
$[(NH_3)_5Co(pz)Cr^{II}]^{4+}$ [g]	263; 2.4[h]			7a
$[(NH_3)_5CoNCacacCr^{II}]^{4+}$	735	8.4 ± 0.5	−17 ± 2	this work

[a] At 25.0 °C unless noted. [b] NTA = nitrilotriacetate. [c] 4vpy = 4-vinylpyridine; 23 °C. [d] L = pyridine-2,4,6-tricarboxylate. [e] fpd = 3-formyl-2,4-pentanedionate. [f] im = imidazole. [g] pz = pyrazinecarboxylato. [h] The first rate relates to formation of a Cr(III)–Co(III) radical-cation complex; the second to reduction of Co(III) in this complex.

Most Co(III)–Cr(II) redox systems (remote attack) are believed to proceed via a radical-ion mechanism due to the symmetry mismatch between the metal orbitals and ligand orbitals.[38] However, in this work, the ligand, NCacac, is not reduced by chromium(II) and a chemical mechanism does not seem feasible. Thus, we favor a "resonance-transfer" mechanism.

Activation parameters for intramolecular electron transfer are listed in Table V. Except for $[(NH_3)_5CoNCacacCr]^{4+}$ and $[(NH_3)_5Ru\text{–4vpy–}Cu^I]^{4+}$, ΔS^* values are all close to zero. Small values are reasonable on the basis that entropy changes associated with stretching and compression of oxidant and reductant ligand bonds would be expected to cancel each other out, or at least be small. Also, solvent reorganization contributions to ΔS^* during redistribution of charge in the activated complex should be minimal.

A decrease in the entropy of activation may be observed when a low transition probability for electron transfer (nonadiabaticity) in the activated complex is encountered.[8] For reactions where $\Delta S^* \simeq 0$, it appears that adiabatic electron transfer is observed. A ΔS^* value of −10 cal deg^{-1} mol^{-1} for $(NH_3)_5Ru\text{–4vpy–}Cu^I$ may be due to nonadiabaticity or the fact that Cu(I) changes its coordination geometry upon oxidation.[13] No firm evidence of nonadiabaticity in binuclear systems has yet been found.[8] The value of −17 cal deg^{-1} mol^{-1} for ΔS^* in our system may however indicate nonadiabaticity. One can envisage a path for electron transfer via the delocalized bridging ligand, but further results in similar systems will have to be examined before conclusions can be drawn.

Overall activation parameters for electron transfer, i.e. for the reaction with rate constant $k_{is}K_p$ (L mol^{-1} s^{-1}) are $\Delta H^* = \Delta H_{K_p} + \Delta H^*_{k_{is}} = 2.0 \pm 0.5$ kcal mol^{-1} and $\Delta S^* = \Delta S_{K_p} + \Delta S^*_{k_{is}} = -31 \pm 3$ cal deg^{-1} mol^{-1}. These values are typical for inner-sphere electron-transfer reactions between Cr(II) and Co(III).[3,38]

In addition to the chromium(II) reduction described above, the reaction of V(II) with $[(NH_3)_5CoNCacac]^{2+}$ was investigated to determine whether saturation kinetics would also be observed. The observed rate was strictly first order in $[V^{2+}]$ with a rate constant at 25 °C of 9.2 L mol^{-1} s^{-1}. Although this rate is within the limit for substitution-controlled inner-sphere electron-transfer reactions of V(II), an outer-sphere mechanism is favored on the basis of the absence of a significant acid dependence for the reaction.

The rate of reduction of $[(NH_3)_5CoNCacac]^{2+}$ with cobalt(II) sepulchrate was found to be 73 ± 3 L mol^{-1} s^{-1} at 25 °C. This study was carried out in order to obtain a purely outer-sphere rate constant for comparative purposes.

The related compound $[(en)_2Co(acacCN)]^{2+}$ was also studied with the reductants chromium(II) and cobalt(II) sepulchrate in order to ascertain the effect on the electron-mediating ability of the NCacac ligand when the acac moiety is coordinated to the oxidant rather than free for attack. The only possible group for inner-sphere attack is the nitrile function, and the rate of Cr(II) reduction was found to be 6.2 × 10^{-3} L mol^{-1} s^{-1} at 25 °C. This rate is comparable to rates determined for other bis(ethylenediamine)cobalt(III) complexes of substituted β-diketones in which an inner-sphere mechanism is operative;[24] however, due to the extreme lability of $Cr^{III}\text{—N}\equiv\text{C–}$ linkages, no concrete evidence for an inner-sphere process could be obtained.

The outer-sphere rate for reduction by cobalt(II) sepulchrate was determined to be 65 ± 10 L mol^{-1} s^{-1}.

In summary, the reduction of $[(NH_3)_5CoNCacac]^{2+}$ by chromium(II) provides the first example of the separation of the rates and activation parameters for intramolecular electron transfer and precursor complex formation in Co(III)–Cr(II) systems. Before any detailed conclusions can be made, it will be necessary to obtain intramolecular electron-transfer rates for several systems. To this end, we are currently investigating a series of cobalt(III) complexes containing remote β-diketonate groups similar to the one used in this study.

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Registry No. $[(NH_3)_5CoNCacac]^{2+}$, 87145-53-7; $[(NH_3)_5CoNCacac](ClO_4)_2$, 87145-54-8; $[(en)_2Co(acacCN)](ClO_4)_2$, 87145-56-0; $[(OH_2)_4Cr(acacCN)]^{2+}$, 87145-57-1; Cr, 7440-47-3; V, 7440-62-2; cobalt(II) sepulchrate, 63218-22-4.

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