the fact that 2,3-butanedione bis(2-diphenylarsinoethylimine) forms ligand-bridged square-pyramidal nickel(II) complexes rather than monomeric, square-pyramidal nickel(II) complexes as does 2,3-butanedione bis(2-diphenylphosphinoethylimine).

Registry No. $C_{32}H_{34}N_2As_2$, 37862-12-7; Ph_2AsK, 21498-51-1; $(CH_2)_2NH$, 151-56-4; $[Ni(C_{32}H_{34}N_2As_2)](ClO_4)_2$, 37862-13-8; $[Ni(C_{32}H_{34}N_2As_2)Cl]_n(ClO_4)_n$, 37862-14-9; $[Ni(C_{32}H_{34}N_2As_2)Br]_n(ClO_4)_n$, 37862-15-0; $[Ni(C_{32}H_{34}N_2As_2)I]_n(ClO_4)_n$, 38050-89-4; $CH_3C(O)C(O)CH_3$, 431-03-8; $Ph_2AsCH_2CH_2NH_2$, 31699-82-8.

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Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139; Contribution No. 4571 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109; and Contribution from the Division of Natural Science, University of California at Santa Cruz, Santa Cruz, California 95060

Photochemical Reactivity of *trans*-Diacidotetracyanocobaltate(III) Complexes

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The photochemistry of *trans*-$Co(CN)_4(SO_3)(X)^{n-}$ ($X = SO_3^{2-}$, OH^-, or OH_2) is reported. The principal photoreactions involve substitution of the sulfito group yielding aquation products. Photoreduction to yield Co(II) is a minor reaction. Disappearance quantum yields are in the range 0.1–0.6 and are modestly affected by variation in the wavelength of the exciting light.

Excited-state decay processes of a number of cyanometalate complexes have been reported.[2] Luminescence has been observed in a few cases at low temperature and in rigid media,[3] while chemical decay paths dominate in fluid solutions for many cyanometalate complexes.[2] Both redox and ligand substitution processes are observed upon irradiation of such complexes.

Population of ligand field excited states of cyanocobaltate(III) complexes leads to facile ligand substitution processes. The octahedral complex $Co(CN)_6^{3-}$ undergoes photoaquation[4] with a quantum yield of 0.31 which is independent of the exciting wavelength[4b] (254, 313, or 366 nm) and the acidity of the solution[4b] (in the range pH 2.0–7.5). The photoaquation is thought to occur *via* an interchange mechanism,[5] and the wavelength-independent quantum yields and triplet-sensitized aquation yields[6] support the notion that decay proceeds *via* the ${}^3T_{1g}(t_{2g}{}^5e_g{}^1)$ excited state.[2]

Cyanocobaltate(III) complexes of C_{4v} symmetry, $Co(CN)_5(X)^{n-}$ ($X = Cl^-$, Br^-, I^-, or OH_2), also give $Co(CN)_5(OH_2)^{2-}$ in high yield[4a,7] upon population of low-lying ligand field excited states. The photoaquation of $Co(CN)_5(X)^{n-}$ species apparently occurs *via* a dissociative type mechanism[5,7] and like $Co(CN)_6{}^{3-}$ preliminary results[6b] suggest that decay proceeds through the lowest ligand field triplet excited state. Thermal substitution of $Co(CN)_5(X)^{n-}$ also yields $Co(CN)_5(OH_2)^{2-}$ by a dissociative mechanism.[8] In marked contrast to $Co(NH_3)_5(X)^{n+}$ systems[2] the cyanocobaltate(III) complexes do not yield Co(II) upon direct irradiation.

We have extended the study of the photochemical behavior of cyanocobaltate(III) complexes to species of the type *trans*-$Co(CN)_4(SO_3)(X)^{n-}$ ($X = SO_3^{2-}$, OH^-, or OH_2). These complexes are of considerable interest because as reported herein their excited-state reactivity patterns show important differences from their ground-state behavior.

Experimental Section

Materials. The previously published preparation of *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ was used to obtain samples of both the sodium and potassium salts.[9,10] Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory for $K_5Co(CN)_4(SO_3)_2$. *Anal.* Calcd: C, 9.26; N, 1080; S, 12.36. Found: C, 9.30; N, 10.78; S, 10.64. Solutions of the *trans*-$Co(CN)_4(SO_3)(H_2O)^{3-}$ were prepared by dissolving appropriate amounts of $K_5Co(CN)_4(SO_3)_2$ in 0.01 *M* $HClO_4$. Formation of *trans*-$Co(CN)_4(SO_3)(H_2O)^{3-}$ is rapid and quantitative under these conditions.[10] Preparation of *trans*-$Co(CN)_4(SO_3)(OH)^{4-}$ was achieved by making solutions of *trans*-$Co(CN)_4(SO_3)(OH_2)^{3-}$ 0.1 *M* in NaOH.

Irradiation Procedures. Samples were irradiated using merry-go-rounds.[11] In various experiments different filter systems were used to isolate the group of lines near 254, 313, 366, or 436 nm in the spectrum of a mercury lamp. Light intensities were measured using ferrioxalate actinometry.[12] Three-milliliter samples were used and the light intensities were of the order of 10^{-7} einstein min^{-1}. Thermal aquation of *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ was sufficiently rapid to compete with photolysis. Correction was made by measuring rates in parallel control experiments. Both *trans*-$Co(CN)_4(SO_3)(OH)^{4-}$ and *trans*-$Co(CN)_4(SO_3)(H_2O)^{3-}$ are thermally inert under the reaction conditions.

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Disappearance of *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ was monitored by following the decrease in absorption at 317 nm; *trans*-$Co(CN)_4(SO_3)(OH_2)^{3-}$ was monitored at 263 nm; and *trans*-$Co(CN)_4(SO_3)(OH)^{4-}$ was followed at 260 nm. All analyses and sample preparations were carried out in darkened rooms.

The formation of Co(II) was detected by addition of aliquots of water-acetone solutions of ~6 *M* NH_4SCN to irradiated mixtures. The formation of the blue $Co(SCN)_4{}^{2-}$ (absorption maximum 623 nm) was determined spectrophotometrically. Calibration of the system was achieved using known concentrations of $CoCl_2$ using the same solvents.

Quenching of the aquation of *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ was studied by observing the effect of added sulfite on photoaquation rates using the continuous monitoring technique reported earlier.[5] Varying amounts of sodium sulfite were added to the solutions and the consequent repression of the initial rate of disappearance of *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ was measured.

Instruments. Spectrophotometric analysis were done with a Beckman DU spectrometer. Ultraviolet-visible absorption spectra were recorded with a Cary 17 spectrometer and ir spectra with a Perkin-Elmer 225 grating spectrometer.

Results

Electronic Spectra. The uv-vis spectra of *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$, *trans*-$Co(CN)_4(SO_3)(OH_2)^{3-}$, and *trans*-$Co(CN)_4(SO_3)(OH)^{4-}$ are shown in Figures 1 and 2. The spectra are dominated by low-energy charge-transfer (CT) bands attributable to excitation between Co(III) and coordinated $SO_3{}^{2-}$. The Co(III)-$SO_3{}^{2-}$ CT bands are assigned as ligand to metal. Higher energy Co(III) → π^*CN^- CT bands are also observed for the three complexes.

The relatively weak absorption maximum near 380 nm in each of the three complexes is logically a spin-allowed d-d transition. Following a recent interpretation[13] of the d-d spectra of $Co(CN)_5(X)^{3-}$ complexes, we assign the 380-nm band to the spin-allowed transition $d_{xz}, d_{yz} \rightarrow d_{z^2}$ (${}^1A_1 \rightarrow {}^1E$ for the C_{4v} complexes and ${}^1A_{1g} \rightarrow {}^1E_g$ for D_{4h}). The orbitally forbidden ${}^1A_{1\,(g)} \rightarrow A_{2\,(g)}$ ($xy \rightarrow x^2 - y^2$) transition, which should fall at slightly higher energy, either is obscured by the CT absorption or is too weak to be observed. Other high-energy transitions involving population of the $d_{x^2-y^2}$ orbital are not observed in the sulfito complexes.

Photochemistry. Reactions 1-4 have been observed upon irradiation of aqueous solutions of the sulfito complexes. Figure 3 shows a typical plot of the decay of the CT absorption of *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ upon 366-nm irradiation in alkaline media. The disappearance quantum yields for the three sulfito complexes are summarized in Table I for several

$$trans\text{-}Co(CN)_4(SO_3)_2{}^{5-} \xrightarrow[OH^-]{h\nu} trans\text{-}Co(CN)_4(SO_3)(OH)^{4-} + SO_3{}^{2-} \quad (1)$$

$$trans\text{-}Co(CN)_4(SO_3)(OH)^{4-} \xrightarrow[OH^-]{h\nu} Co(CN)_4(OH)_2{}^{3-} + SO_3{}^{2-} \quad (2)$$

$$trans\text{-}Co(CN)_4(SO_3)(OH_2)^{3-} \xrightarrow[H_2O]{h\nu} Co(CN)_4(OH_2)_2{}^{-} + SO_3{}^{2-} \quad (3)$$

$$trans\text{-}Co(CN)_4(SO_3)(OH_2)^{3-} \xrightarrow{254\ nm} \text{decomposition to Co(II)} \quad (4)$$

irradiation wavelengths. Reactions 1 and 2 were studied at pH 13, thereby precluding the possibility of protonated complexes. Reactions 3 and 4 were carried out in 0.01 *M* $HClO_4$, giving a significant fraction of protonated sulfito-aquo complex as starting material.[14]

The principal photoproduct from the disulfito complex is *trans*-$Co(CN)_4(OH)(SO_3)^{4-}$, as evidenced by the appearance of the characteristic CT band at 260 nm. The loss of sulfite from the monosulfito complexes is established by the disappearance of all low-energy $SO_3{}^{2-}$ → Co(III) CT absorption. The diaquo or dihydroxo complex thus formed shows low-energy d-d transitions (Figure 4). Addition of 0.5 *M* Na_2SO_3 to neutral solutions of the diaquo complex results

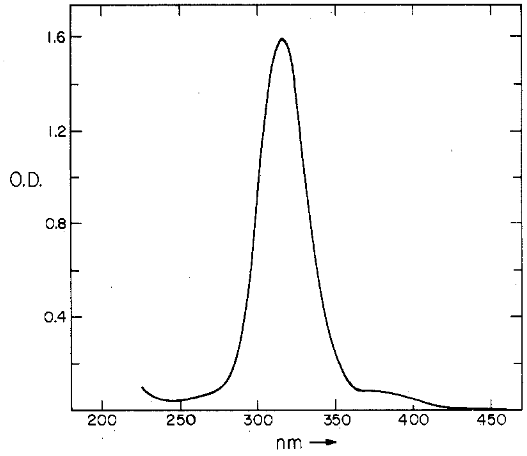

Figure 1. Absorption spectrum of 5.01 × 10^{-4} *M* *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ in 0.1 *M* NaOH, 1.00-cm path length. Bands are at 317 nm (ϵ 31,900) and 380 nm (ϵ 1350).

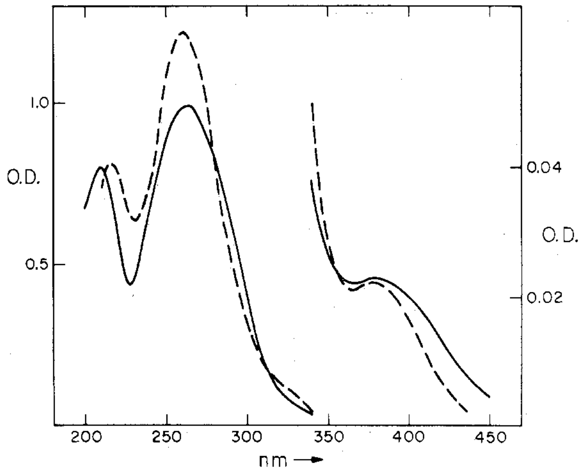

Figure 2. Absorption spectrum of 9.67 × 10^{-4} *M* *trans*-$Co(CN)_4(SO_3)(OH_2)^{3-}$ (——) and *trans*-$Co(CN)_4(SO_3)(OH)^{4-}$ (– – –), 1.00-cm path length. For the aquo complex bands are at 263 nm (ϵ 10,300) and 380 nm (ϵ 240); bands for the hydroxo complex are at 260 nm (ϵ 12,500) and 374 nm (ϵ 240).

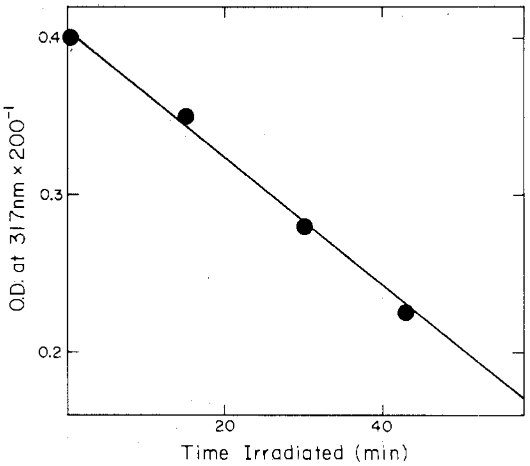

Figure 3. Decay of 317-nm absorption maximum upon 366-nm irradiation of *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ in 0.1 *M* NaOH. Light intensity is 1.28 × 10^{-7} einstein/min.

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Table I. Disappearance Quantum Yields[a] for $K_nCo(CN)_4(SO_3)(X)$ Complexes.

Compound	pH	$\Phi_{254\text{ nm}}$	$\Phi_{313\text{ nm}}$	$\Phi_{366\text{ nm}}$	$\Phi_{436\text{ nm}}$
$K_5Co(CN)_4(SO_3)_2$	>13		0.36	0.57	0.57
$K_3Co(CN)_4(SO_3)(OH_2)$	~2	0.15	0.11	0.14	
$K_4Co(CN)_4(SO_3)(OH)$	>13	0.13	0.09	0.19	

[a] Quantum yields are ±10%.

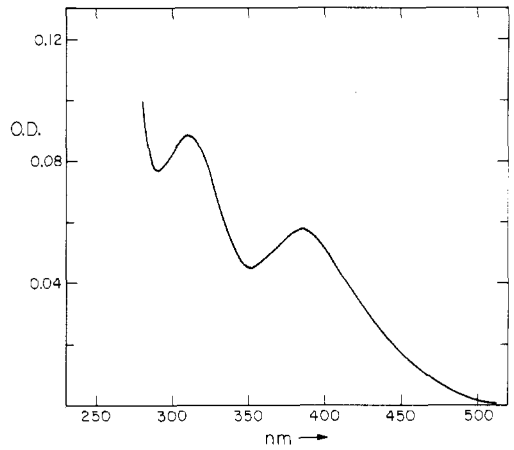

Figure 4. Absorption spectrum of photolysis product of *trans*-$Co(CN)_4(SO_3)(OH)^{4-}$ in 0.1 *M* NaOH. Bands are at 308 nm (ϵ 403) and 380 nm (ϵ 262).

in nearly quantitative regeneration of the starting *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$. This experiment strongly supports the assignment of the product as $Co(CN)_4(OH_2)_2{}^-$ in neutral or acidic media or the dihydroxo complex in basic media. While disappearance of the CT band could occur upon linkage isomerization of $SO_3{}^{2-}$, rapid regeneration of the -S bound isomer would be expected. Loss of the CT absorption occurs in the monosulfito complex when nitric acid is used to oxidize the sulfito groups to produce a diaquo complex.[15] All attempts to isolate salts of the diaquo complex have been unsuccessful thus far. Yellow, insoluble materials are obtained using standard isolation techniques.[15] Since the sulfito-aquo complexes are thought to undergo trans → cis isomerization upon standing,[14] it is likely that the diaquo or dihydroxo complexes are not pure trans in solution. It is very clear, however, that complete loss of sulfito ligands occurs.

The formation of Co(II) has been established as a primary product from *trans*-$Co(CN)_4(SO_3)(OH_2)^{3-}$ (reaction 4). Figure 5 shows the buildup of Co(II) and the disappearance of *trans*-$Co(CN)_4(SO_3)(OH_2)^{3-}$ upon 254-nm irradiation. The quantum yield for Co(II) production is 0.01 compared to the quantum yield of 0.15 for the disappearance of the parent complex. Even though reduction occurs, substitution is still the principal chemical decay pathway. The modest yields of Co(II), along with possible polymerization of the diaquo complex, account for the observation that *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ cannot be totally regenerated upon addition of $SO_3{}^{2-}$ to completely reacted mixtures.

In Table II we report the effect of added $SO_3{}^{2-}$ on the disappearance rates of the *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ complex. Addition of 1.4 *M* $NaClO_4$ had no effect on the rate of photodisappearance.

Discussion

Mechanistic discussion for the observed photoreactions must account for the wavelength-dependent quantum yields, the specific loss of the sulfito group, the photoreduction to yield Co(II), and the repression of the initial rate of photodisappearance of $Co(CN)_4(SO_3)_2{}^{5-}$ upon addition of Na_2SO_3. It is attractive to assume that Co(II) is only formed by population of CT excited states. The reduction of Co(III) → Co(II) is consistent with the $SO_3{}^{2-} \rightarrow$ Co(III) CT band assignment. The CT states could also lead to photosubstitution by a mechanism similar to that proposed for $Co(NH_3)_5(X)^{n+}$ complexes.[2] Substitution *via* a CT excited state should yield preferential loss of the sulfito group since the primary step would be homolytic cleavage of the $Co-SO_3$ bond. Invoking the CT excited state adequately accounts for the increase in quantum efficiency upon 254-nm excitation relative to 313-nm irradiation for the aquo and hydroxo complexes.

In contrast to the CT excited states, ligand field excited states are thought to yield only substitution chemistry.[2] Upon irradiation at 366 or 436 nm the sulfito complexes undergo the $d_{xz}, d_{yz} \rightarrow d_{z^2}$ ($^1A_1 \rightarrow {}^1E$) transition. According to a recently developed model,[16] this excitation should selectively labilize ligands on the *z* axis of the molecule when the d_{z^2} and $d_{x^2-y^2}$ levels are separated enough to ensure a "localized" d_{z^2} σ^* excitation. The one-electron population of the d_{z^2} orbital substantially weakens the metal-ligand bonds on the *z* axis. Further, the depopulation of the d_{xz}, d_{yz} orbitals affects the axial π bonding: for π-acceptor ligands depopulation of d_{xz}, d_{yz} leads to greater lability while some relative kinetic stability is gained for π-donor ligands. The H_2O ligand is recognized as a σ donor only, whereas OH^- is characterized as a π-donor ligand. The sulfur donor $-SO_3{}^{2-}$ is classed as a π-acceptor ligand based on

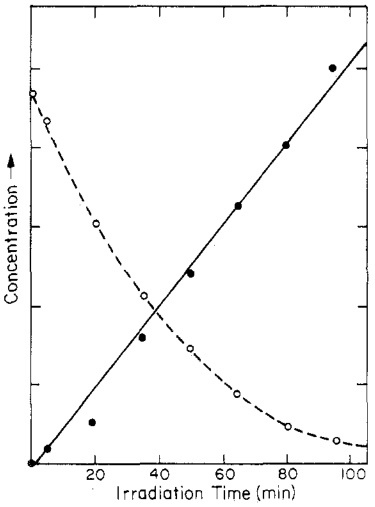

Figure 5. Disappearance of *trans*-$Co(CN)_4(SO_3)(OH_2)^{3-}$ (○) and appearance of Co(II) (●) upon 254-nm photolysis in 0.01 *M* $HClO_4$. The initial *trans*-$Co(CN)_4(SO_3)(OH_2)^{3-}$ concentration is 8.21×10^{-4} *M* and the Co(II) concentration is 9.38×10^{-5} *M* at 80 min.

Table II. Quenching of Photosubstitution of *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ with $SO_3{}^{2-}$ [a]

Added reagent	Concn, *M*	Rel rate
None		1.00
$SO_3{}^{2-}$	0.2	0.61
$SO_3{}^{2-}$	0.4	0.36
$SO_3{}^{2-}$	1.0	0.25
$NaClO_4$	1.4	1.0

[a] Irradiation source was a 75-W Pyrex-filtered Hg lamp.

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Table III. Summary of Excited-State Reactivity of *trans*-$Co(CN)_4(SO_3)(X)^{n-}$

Excitation (type)	Irradiation wavelength, nm[a]	Comment
$d_{xz}, d_{yz} \rightarrow d_{z^2}$ (ligand field)	436, 366	Labilizes z axis. Affects π-donor ligands least, σ donors have intermediate lability, and π acceptors are much more reactive than in the ground state. Found: dramatic increase in lability of the π acceptor $-SO_3^{2-}$ on the z axis
$d_{xy} \rightarrow d_{x^2-y^2}$ (ligand field) and $SO_3^{2-} \rightarrow$ Co(III) (L → M CT)	313[b]	For ligand field excitation: equatorially localized. Found: lower quantum yields for disappearance implicating facile decay directly to ground state without reaction For L → M CT: Precursor to either redox chemistry or substitution
$SO_3^{2-} \rightarrow$ Co(III) (L → M CT)	254	Precursor to either redox chemistry or substitution. Found: modest yields of Co(II) and higher substitution yields than in 313-nm photolysis

[a] Both irradiation and absorption bandwidths are too broad to yield pure excitations. [b] For X = SO_3^{2-} this irradiation wavelength corresponds closely to the L → M CT absorption maximum while for X = OH^- or OH_2 this excitation is mixed d–d and L → M CT absorption.

its position in the spectrochemical series[17] and its strong trans-labilizing power in cyanocobaltate(III) complexes.[10,14] The most significant reaction associated with ligand field excitation is the loss of sulfite, consistent with the prediction of a greatly weakened Co(III) $-SO_3$ bond upon *depopulation* of π-bonding orbitals (d_{xz}, d_{yz}) *and population* of d_{z^2} σ^*. In the ground-state loss of sulfite from either the aquo or hydroxo complex does not occur except under vigorous conditions.

The general decrease in reaction quantum yields upon 313-nm irradiation implicates a third excited state which gives less efficient reaction and/or incomplete internal conversion to the lower lying excited states. Nonradiative decay from this state must occur directly to the ground state. These observations could be accommodated satisfactorily by involving the lowest excited state arising from the $d_{xy} \rightarrow d_{x^2-y^2}$ excitation.

A summary of the key points above appears in Table III. The two ligand field states and the L → M CT state account for all of the results. As with the $Co(CN)_5(X)^{n-}$ complexes,[5] the ligand field excited-state substitution reaction apparently proceeds primarily *via* a dissociative mechanism since added SO_3^{2-} suppresses the rate of sulfite substitution. The five-coordinate species produced *via* photolysis of *trans*-$Co(CN)_4(SO_3)_2^{5-}$ may be the same as that produced in the thermal dissociation.[10] The fact that the photosubstitution is very efficient in strongly alkaline media even though the thermal reaction is apparently acid catalyzed[10] evidences the important changes in binding interactions upon ligand field excitation.

The $Co(CN)_4(OH_2)_2^-$ photoproduct is extremely thermally reactive as addition of Na_2SO_3 results in very rapid formation of *trans*-$Co(CN)_4(SO_3)_2^{5-}$. Spectral changes also occur upon addition of other nucleophiles and characterization of the products is in progress.

Registry No. *trans*-$K_5Co(CN)_4(SO_3)_2$, 37954-25-9; *trans*-$K_3Co(CN)_4(SO_3)(H_2O)$, 37954-26-0; *trans*-$K_4Co(CN)_4(SO_3)(OH)$, 37954-27-1.

Acknowledgments. This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research (Contract No. AF49(638)-1470), the Army Research Office (Durham), and the National Science Foundation.

[17] The first ligand band for $Co(CN)_5(SO_3)^{4-}$ is at 332 nm as compared with 312 nm for $Co(CN)_6^{3-}$ and 345 nm for $Co(CN)_5(NCCH_3)^{2-}$.

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Acid-Catalyzed Aquations of *cis*- and *trans*-Dicarboxylatoaminecobalt(III) Complexes[1a]

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The loss of one carboxylate ligand from *cis*-$Co(en)_2(RCO_2)_2^+$ (R = H, CH_3, C_2H_5, C_3H_7), *cis*-$Co(NH_3)_4(CH_3CO_2)_2^+$, *cis*-$Co(dipy)_2(CH_3CO_2)_2^+$, and *trans*-$Co(en)_2(RCO_2)_2^+$ (R = H, CH_3) is catalyzed by H^+ in aqueous solutions. For all the complexes studied, except *trans*-$Co(en)_2(HCO_2)_2^+$, the observed rate constant $k_{obsd} = -d(\ln [complex])/dt$ has a functional dependence with respect to $[H^+]$ (at ionic strength 1.00 M maintained with $LiClO_4$) given by $k_{obsd} = k_2Q[H^+]/(1 + Q[H^+])$. For *trans*-$Co(en)_2(HCO_2)_2^+$, k_{obsd} varies linearly with $[H^+]$. The kinetic results are interpreted on the basis of rapid preequilibrium protonation of the carboxylate complexes followed by slow aquation of the protonated complexes. The reactions of the cis complexes proceed with retention of configuration, whereas the trans complexes produce both *cis*- and *trans*-aquocarboxylatoamine products. An oxygen-18 tracer study of the acid-catalyzed aquation of *cis*-$Co(en)_2(CH_3CO_2)_2^+$ demonstrates that quantitative Co–O bond breaking obtains in this reaction. The reactivity trends observed and the mechanism of these reactions are discussed.

Introduction

In connection with our studies of the reductions of *cis*- and *trans*-diformatobis(ethylenediamine)cobalt(III) by chromium(II)[2] and vanadium(II),[3] it became necessary to obtain fairly detailed information about the hydrolytic stability of the two cobalt complexes. The trans isomer proved to be relatively stable toward loss of one formate group, whereas the cis isomer underwent rapid aquation in acid solution. The reaction is acid catalyzed, and detailed kinetic studies[1c] showed a first-order dependence on $[H^+]$