for these matters, Raman spectroscopy in the M–M stretching region can be a useful structure-sensitive tool. In the case of [DMTED][$Fe_2(CO)_8$] we would not have been able to elucidate the tautomeric equilibrium by infrared spectroscopy owing to absorption by the solvent, DMF, in the bridging CO stretching region. No such interference exists in the Raman spectral region characteristic of the Fe–Fe stretch.

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Registry No. $Co_2(CO)_8$ (bridged), 10210-68-1; $Co_2(CO)_8$ (nonbridged), 15226-74-1; [(π-Cp)Ru$(CO)_2$]$_2$ (bridged), 12132-87-5; [(π-Cp)Ru$(CO)_2$]$_2$ (nonbridged), 12132-88-6; (Et_4N)[$HFe_2(CO)_8$], 26062-33-9; $(Et_4N)_2$[$Fe_2(CO)_8$], 26024-88-4; $(Bu_4N)_2$[$Fe_2(CO)_8$], 58341-98-3; (DMTED)[$Fe_2(CO)_8$] (bridged), 58281-29-1; (DMTED)[$Fe_2(CO)_8$] (nonbridged), 58341-97-2; $Co_4(CO)_{12}$, 17786-31-1.

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Mechanism and Steric Course of Octahedral Aquation. XVIII.[1] Spontaneous, Base Catalyzed and Mercuric Ion Catalyzed Aquation of *cis*-Chlorocyanobis(ethylenediamine)cobalt(III) Cations. The Trans Effect of Cyanide

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The kinetics of aquation of *cis*-[Co(en)$_2$(CN)Cl]Cl (en = 1,2-diaminoethane) have been studied over a range of temperature and pH. In acid solution, the rate is independent of pH and the product is exclusively *cis*-[Co(en)$_2$(CN)H$_2$O]$^{2+}$; $k = 6.2 \times 10^{-6}$ s^{-1} at 25 °C, $\Delta H^{*} = 24.6$ kcal mol^{-1}, and $\Delta S^{*} = -5$ cal deg^{-1} mol^{-1}. Base hydrolysis gives 90 ± 3% *cis*-[Co(en)$_2$(CN)OH]$^{+}$ product, the rest being the trans isomer; $k_{OH} = 8.9 \times 10^{-3}$ M^{-1} s^{-1} at 0.0 °C, $\Delta H^{*} = 23.2$ kcal mol^{-1}, $\Delta S^{*} = +18$ cal deg^{-1} mol^{-1}. The mercuric ion catalyzed aquation obeys the rate law $-d \ln [\text{complex}]/dt = kK[Hg^{2+}]/(1 + K[Hg^{2+}])$; $k = 1.30 \times 10^{-2}$ s^{-1}, and $K = 85$ M^{-1} at 50.8°, $\mu = 0.500$. Adduct formation is confirmed spectroscopically. A trans specific labilizing effect, opposed by a positionally nonspecific retarding effect, is proposed to account for the effect of the cyanide on the reactivity of the complex.

Introduction

A major interest in the study of substitution reactions of octahedral complexes has been in the way in which the rate and the stereochemistry of an act of substitution depend upon the nature and the position of the other ligands in the complex. The extensive range of examples to be found among the complexes of the type [Co(en)$_2$(A)X]$^{n+}$, where both cis and trans isomers are known and fully characterized, has enabled the effect of varying the nature and position of one ligand, A, upon the rates, activation parameters, and stereochemistry of displacement of ligand X to be studied in great detail, especially in the solvolytic aquation reaction.[2] In most cases it has been shown that, whereas the rate can be very sensitive to the nature of A, it is far less dependent upon its position with respect to the leaving group and so it is not realistic to talk about cis and trans effects in the way that can be applied most successfully to substitution of square-planar complexes[3] (and even of other octahedral centers, e.g., rhodium(III)[4]). Nevertheless, there is a group of ligands whose labilizing effect is greatest when they are cis to the leaving group, culminating in $-NH_2^-$ and $-NHR^-$, where it has been suggested that the exceptionally strong labilizing effect is cis specific.[5] This proposal, which rests on an interpretation of stereochemical data, has recently been challenged.[6] The ligands of this group are all characterized by the presence of a lone pair of electrons which can, in principle, be shared with the metal in the five-coordinate intermediate in the dissociative act of substitution. Such reactions are often accompanied by stereochemical change, especially when A is trans to X. The study of complexes containing ligands, A, that do not fall into this category is less systematically advanced, generally because one of the isomers either is missing or else reacts in an unwanted fashion. All substitution reactions take place with complete retention of configuration. Data are available for A = NH_3,[7] N_3,[8] and NO_2[9] for X = Cl and Br, and, in the first two cases, the labilities of the two isomers are similar. In the case of the chloro–nitro complexes, the trans isomer is more labile than the cis and, in order to see whether this is an indication of the development of a trans-labilizing effect which is strongly established when A = SO_3,[10] we have sought other complexes in this category. The *cis*-[Co(en)$_2$(CN)Cl]$^{+}$ cation was characterized some time ago[11] and this paper reports the kinetic and stereochemical data relating to the spontaneous aquation and the base and mercuric ion catalyzed hydrolysis in order to make comparison with the trans isomer[12] and also to compare the labilizing power of the cyanide and nitro groups.

Experimental Section

Preparations. *cis*-[Co(en)$_2$(CN)Cl]Cl·H$_2$O was made by the method of Shimura[11] except that the reaction between Na$_3$[Co(C-

$N)_2(SO_3)_2(NH_3)_2]$ and ethylenediamine was carried out almost at the boiling point of the reaction mixture which was allowed to evaporate almost to dryness. Under milder conditions, the entry of ethylenediamine is only partially achieved and products which could not be purified or well characterized but which had spectra not greatly dissimilar from that of the required product were obtained. The sample was characterized by chemical analysis. The material, stored over $CaCl_2$, is anhydrous. Anal. Calcd for $C_5H_{16}N_5Cl_2Co$: C, 21.8; H, 5.84; N, 25.4; Cl, 25.7. Found: C,21.6; H, 5.89; N, 25.5; Cl, 25.6.

The visible–ultraviolet spectrum agrees closely with that reported in the literature: λ_{max} 507 nm (ϵ_{max} 67.0 M^{-1} cm^{-1}), 343 nm (ϵ_{max} 94.2 M^{-1} cm^{-1}) and a shoulder at 438 nm. The corresponding literature values[11] are 507 (66.1), 342 (89.1), and 434. The infrared spectrum of a Nujol mull contains a characteristic sharp band at 2132 cm^{-1} assigned to ν_{C-N}, and a pair of peaks at 900 and 893 cm^{-1}, usually assigned to rocking modes of the ring methylene groups, are typical of a *cis*-$[Co(en)_2(X)Y]^{n+}$ species.[13] (The trans isomer has a single peak at 898 cm^{-1}.)

Mercuric perchlorate solutions were prepared by dissolving mercuric oxide in a known excess of perchloric acid and the mercuric ion concentration was determined by standard titrimetric means.

Kinetics. The reactions were generally followed spectrophotometrically in the thermostated cell compartment of a Unicam SP 800 recording spectrophotometer. In the aquation studies, the perchloric acid solvent was brought to the required temperature in the spectrophotometer cell and the solid complex was added to start the reaction. Dissolution took place within a couple of seconds and the mixture was stirred briefly with a thin glass rod. The concentration could be determined from the absorbance values at the end of the reaction. The spectrum was scanned at appropriate times and the rate constant was obtained from the slope of the ln $(A_t - A_\infty)$ vs. time plot. (A_t and A_∞ are the absorbances at time t and after 10 half-lives, respectively.) The rate constant was independent of the wavelength chosen, provided that there was an adequate change in absorbance. The rate constants quoted were obtained from data at 315 and 530 nm. The temperature of the reaction was held constant by a Unicam SP 875 electrical control unit (temperatures above 60 °C) and by water circulation at lower temperatures and determined by a copper–constantan thermocouple placed in the block. Preliminary experiments showed that the block temperature and the solution temperature were within 0.02 °C of one another. The thermocouple potential was measured with a Solartron LM 1604 digital voltmeter and generally remained constant to within ±0.004 mV (±0.1 °C). The thermocouple was calibrated against a standard thermometer during the time that the reaction was being followed. The base hydrolysis was followed by bringing the solution (generally 10.0 ml) containing the appropriate amounts of sodium hydroxide and lithium perchlorate to the reaction temperature in the thermostated cell holder, adding 0.10 ml of a solution of the complex to start the reaction, and then recording the change in absorbance at constant wavelength with the recorder bed moving at a fixed rate. For the slower reactions the absorbance was determined from time to time by depressing the pen for 2 s while the spectrophotometer was in the fixed-wavelength mode. The mercuric ion catalyzed reaction was followed in a similar way and started by adding 0.10 ml of the solution of the complex to a thermally equilibrated solution containing the appropiate amount of mercuric and lithium perchlorate in dilute perchloric acid. The aquation was also studied titrimetrically by measuring the change in anionic chloride concentration. Aliquots of 1.00 ml were withdrawn from a thermostated solution at the appropriate times, delivered into cold acetone, acidified with dilute nitric acid, and titrated with standard silver nitrate solution using a Radiometer PHM 26, TTT 11, ABU 11, TTA 3, SBR 2 automatic titration assembly with a silver billet and $Hg-Hg_2SO_4$ reference electrode.

Results

(1) The Aquation of *cis*-$[Co(en)_2(CN)Cl]^+$ Cations. The spectrum of a solution of *cis*-$[Co(en)_2(CN)Cl]Cl$ in dilute aqueous $HClO_4$ solution changes slowly into one very similar to that of an authentic sample of *cis*-$[Co(en)_2(CN)H_2O]^{2+}$.[14] The absorbance is somewhat higher at the lower wavelengths where the chloro complex absorbs much more strongly than the aquo product indicating that the reaction does not go to completion. At the concentrations used, the amount of chloro complex at equilibrium is less than 3% of the total. Well-defined isosbestic points are maintained at 477 and 393 nm, precisely where the spectra of the *cis*-chlorocyano and *cis*-aquocyano complexes cross. The change in absorbance follows a first-order rate law and the rate constants are independent of the wavelength at which the measurements are made. The rate constants are collected in Table I where it will be seen that the rate is independent of the concentration of acid used and indeed is unchanged when no acid is added. However, in the last case, the spectral change is more complicated and suggests that two consecutive reactions are occurring, the first of which is the stereoretentive aquation of the chloro complex which is unaffected by the pH and the second of which is the cis to trans isomerization of the aquocyano product. This isomerization is very much slower in the presence of acid but can be observed at very long reaction times at 90 °C. There is some resemblance to the isomerization of the aquoamminebis(ethylenediamine)cobalt(III) cation, which takes place much more rapidly through its hydroxoammine conjugate base.[15]

Table I. First-Order Rate Constants for the Aquation of *cis*-$[Co(en)_2(CN)Cl]Cl$ in Dilute Perchloric Acid[a]

Temp/°C	$[HClO_4]$/M	[Complex]/mM	$k_1/10^{-4}$ s^{-1}
90.2	0.010	6.3	12.8
90.2	0.010	10.3	12.5
90.2	0.010	15.4	12.8
90.2	0.000	6.5	12.6
80.1	0.100	7.4	4.63
80.1	0.100	10.6	4.50
80.1	0.010	8.5	4.83
80.1	0.010	10.6	4.57
70.7	0.100	20.0	1.77
67.6	0.100	13.0	1.27

[a] Rate constants determined from absorbance data at 315 and 530 nm.

(2) Base-Catalyzed Hydrolysis of *cis*-$[Co(en)_2(CN)Cl]^+$. Provided the concentration of hydroxide is not too high, the coordinated chloride is replaced relatively slowly at room temperature and the spectrum changes slowly to one that is similar to, but not identical with, that of *cis*-$[Co(en)_2(CN)OH]^+$.[14] The change is consistent with a single-stage reaction and isosbestic points are maintained throughout at 491 and 326 nm. The acidified reaction product has a spectrum that is identical with one containing 90 ± 3% *cis*-$[Co(en)_2(CN)H_2O)^{2+}$ and 10 ± 3% of the trans isomer. The kinetics of base hydrolysis were conveniently followed at 280 nm where the change in absorbance is very large and concentrations of complex as low as 3×10^{-4} M were sufficient for a change in absorbance of 1.2 units when a 40-mm cell was used. Such low concentrations of complex made it possible to study the kinetics under pseudo-first-order conditions without requiring a high concentration of base. Good straight lines were obtained in the semilogarithmic plots for more than 4 half-lives and the observed first-order rate constants are collected in Table II. Plots of k_{obsd} vs $[OH^-]$ are linear and pass through the origin. The derived second-order rate constants are also collected in Table II. The reactions were carried out at constant ionic strength and over a temperature range. The plot of ln (k_B/T) is linear over a temperature range of 30 °C.

(3) Mercuric Ion Catalyzed Aquation of *cis*-$[Co(en)_2(CN)Cl]^+$. In the presence of an excess of mercuric perchlorate, the spectrum of a solution initially containing *cis*-$[Co(en)_2(CN)Cl]Cl$ changes to that of the *cis*-$[Co(en)_2(CN)H_2O]^{2+}$ species. Two well-defined isosbestic points are maintained throughout, indicating a single-stage process, but the wavelength of the first isosbestic point is significantly dependent upon the concentration of the mercuric ion present (e.g., 464 nm at 0.080 M Hg^{2+}; 467, 0.010; 473, 0.0050; 477, no mercuric ion present). The effect is due to a relatively

Table II. Pseudo First-Order Rate Constants and Derived Second-Order Rate Constants for the Base Hydrolysis of *cis*-[Co(en)$_2$(CN)Cl]$^+$ [a]

Temp/°C	[OH$^-$]/M	k_1/10^{-2} s^{-1}	k_2/M^{-1} s^{-1}
40.6	0.0050	1.24	2.73 ± 0.17
40.6	0.0100	2.72	
40.6	0.0200	5.45	
40.6	0.0300	8.48	
40.6	0.0400	11.6	
31.0	0.0100	0.773	0.828 ± 0.047
31.0	0.0250	1.98	
31.0	0.0500	4.29	
31.0	0.0750	6.24	
31.0	0.1000	8.87	
20.9	0.0100	0.186	0.203 ± 0.014
20.9	0.0250	0.486	
20.9	0.0500	1.03	
20.9	0.0750	1.55	
20.9	0.1000	2.22	
11.7	0.0200	0.104	0.0538 ± 0.0018
11.7	0.0400	0.207	
11.7	0.0600	0.333	
11.7	0.0800	0.429	
11.7	0.1000	0.557	

[a] [Complex] = 2.0 × 10^{-4} M, μ = 0.10 M (LiClO$_4$).

Table III. Pseudo-First-Order Rate Constants for the Mercuric Ion Catalyzed Aquation of *cis*-[Co(en)$_2$(CN)Cl]$^+$ at 50.8 ± 0.1 °C[a]

[Hg^{2+}]/M	k_{obsd}/10^{-3} s^{-1}	[Hg^{2+}]/M	k_{obsd}/10^{-3} s^{-1}
0.00350	3.0	0.0280	9.6
0.00700	4.7	0.0420	10.1
0.0140	7.2	0.0700	11.0

[a] [Complex] = 2.86 × 10^{-4} M; [H$^+$] = 0.10 M; μ = 0.500 M (LiClO$_4$).

small, mercury-dependent change in the spectrum of the starting material which appears as a shift of the long-wavelength absorption peak to shorter wavelengths (507 to 497 nm on increasing the concentration of Hg^{2+} to 0.080 M). The rest of the spectrum is far less strongly affected. The kinetics were followed in much more dilute solutions of complex by measuring the change in absorbance at 285 nm where the chloro complex absorbs very much more strongly that the aquo product. The first-order rate constants are collected in Table III. The reactions were carried out at constant ionic strength (μ = 0.50 M, LiClO$_4$) and at constant hydrogen ion concentration (0.10 M, HClO$_4$).

Discussion

The rate constants, together with the activation parameters and stereochemistries, where known, of the aquation and base hydrolysis of compounds of the type *cis*- and *trans*-[Co(en)$_2$(A)Cl]$^{n+}$ (A = NH$_3$, n = 2; A = N$_3$, NO$_2$, CN; n = 1) are collected in Table IV. It can be seen that, for the aquation reaction, the ratio of the rate constants for the two isomeric forms, k_{trans}/k_{cis}, increases quite dramatically along the sequence A = NH$_3$ < N$_3$ < NO$_2$ < CN. The absolute reactivities, however, do not follow the same sequence and both cyano–chloro isomers are less labile than the corresponding nitro–chloro species, the cis isomer responding more to the change than the trans. If a trans-labilizing effect was the dominant reactivity controlling influence, it would be necessary for the absolute reactivities and the ratio of the rate constants for the trans and cis isomers to follow the same sequence, and, indeed, variation of A when it is cis to the leaving group, provided that other factors such as charge and steric hindrance are held constant, should have little effect upon reactivity. The observed behavior indicates a much more complicated relationship between the nature and the position of ligand A and the reactivity of these complexes but it may be premature to enter into a full-scale discussion of specific labilizing and retarding effects while the number of systems fully examined is less than the number of variables to be taken into account. Nevertheless, it has been recognized for a long time that the rate constants for the aquation of cis complexes of the type *cis*-[Co(en)$_2$(A)Cl]$^+$ are not normally very sensitive to the nature of A. For example, 10^6k/s^{-1}(at 25 °C) = 122 (after correction for the statistical factor), 140, and 11 for A = Cl,[19] Br,[20] and –NCS,[21] respectively, which, coupled with the relevant data in Table IV, might suggest that the main labilizing influence in these cis complexes, when A = N$_3$, NO$_2$, Cl, Br, and NCS, comes from the ligand trans to the leaving group which, in every case, is ethylenediamine. The greater lability of the hydroxo complex and the conjugate base in base hydrolysis (A = NH$_2$, NHR, or NR$_2$) is thought to arise from their special π-donor properties. The rate constants for the dipositive cations when A is a neutral ligand, e.g., H$_2$O or NH$_3$, are some 10^2 times smaller,[22] probably because of the higher cationic charge on the complex and its effect upon the departure of the anionic leaving group.[18] It would therefore seem that the reactivity of the *cis*-chlorocyano complex toward aquation is unusually low, and, taken with the previously reported reactivity of the trans isomer,[12] this suggests that, in addition to a trans-specific labilizing effect, cyanide can also exert a rate reducing effect that is not particularly dependent upon its position with respect to the leaving group. Such behavior is consistent with the ability of cyanide to act as a strong σ donor and a potential π acceptor. There is now considerable evidence that strong covalent σ donors, of which cyanide is a typical example,[25] specifically lengthen and presumably weaken the bond trans to themselves in octahedral and square-planar complexes. Furthermore, in square-

Table IV. Rate Constants, Activation Parameters, and Products of the Aquation and Base Catalyzed Hydrolysis of *cis*- and *trans*-[Co(en)$_2$(A)Cl]$^{n+}$

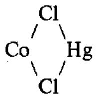
	Rate constant			$\Delta H^‡$/kcal mol^{-1}		$\Delta S^‡$/cal K^{-1} mol^{-1}		
A	Cis	Trans	k_t/k_c	Cis	Trans	Cis	Trans	Ref
			(1) Aquation[a,b]					
NH$_3$	0.50	0.34	0.68	24.5	23.2	−6	−11	7
N$_3$	200	260	1.3	21.3	20.7	−4	−6	8
NO$_2$	110	980	8.9	21.8	20.9	−3	−2	9
CN	0.62	82	132	24.6	22.5	−5	−2	12, this work
			(2) Base Hydrolysis[c]					
NH$_3$	0.50 (78)[d]	1.25 (36)[d]	2.5					7, 16
N$_3$	0.17 (45)	0.41 (90)	2.4					8
NO$_2$	0.032 (67)	0.080 (94)	2.5	22.5	23.9	+17	+24	9, 17
CN	0.0089 (90)	0.13 (100)	14.6	23.2	23.5	+18	+22	12, this work

[a] 10^6k/s^{-1} at 25 °C. [b] All aquations occur with complete retention of configuration except when A = cis N$_3$ which appears to produce 15% of the *trans*-aquoazido product. [c] k/M^{-1} s^{-1} at 0 °C. [d] Values in parentheses are the percentage of the product with the same geometric configuration as the starting material. In the case of the cis complexes there can be a considerable amount of D ↔ L change. See ref 18.

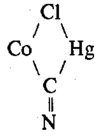
pyramidal five-coordinate species, the strong σ donor prefers the apical position.[28] The trans effect of this type of ligand is therefore a combination of a ground-state weakening (often called the trans influence) with a transition state stabilization when the mechanism is dissociative. The π-acceptor properties of cyanide, which contribute to its very strong trans effect in the bimolecular substitution reactions of platinum(II) by assisting bond formation in the five-coordinate transition state,[3] will act in the opposite sense when the reaction mechanism is dissociative and the electron withdrawl will reduce the reactivity by strengthening all of the σ bonding to the metal, including that with the leaving group. The overall effect of the cyanide ligand is the general reduction of reactivity arising from its π-acceptor properties overlaid by a specific labilization when it is trans to the leaving group.

The rate constant for the base hydrolysis of the *cis*-chlorocyano complex is unusually low, although the reduction in reactivity when compared to the other complexes in Table IV is somewhat less marked than in the case of aquation. The electron displacement requirements for the formation of the conjugate base (i.e., the removal of an amine proton) are opposite to those of its subsequent dissociation and so it is not surprising that the rate of base hydrolysis is less sensitive to the position and the nature of ligand A than is the rate of aquation;[18] nevertheless, a litle of the trans-labilizing but overall rate-depressing properties of the cyanide ligand appear to remain. The absence of any cis product in the base hydrolysis of *trans*-$[Co(en)_2(CN)Cl]^+$ suggests that the five-coordinate intermediate in the aquation of the amido conjugate base is either square pyramidal with the cyanide apical and the amido group basal or else trigonal bipyramidal with the cyanide and the amido groups in equatorial positions. In the latter case it is also necessary for the water to join the cobalt at the side remote from the cyanide ligand. Since the cis isomer gives some trans product (albeit only 10%) a square-pyramidal intermediate with the cyanide in a basal position cannot be the only form present, although it might account for the cis part of the product. The trigonal-bipyramidal intermediate is more likely in this case and two forms (more if the location of the amido group is taken into account) are possible. That with cyanide in the trigonal plane will be identical with the one obtained from the trans isomer (although it must hold the same enantiomeric configuration as the original cis complex) and must therefore give only trans product. The other, with cyanide in an axial position, can only give cis product, which should be racemic unless the amido group in the trigonal plane exerts a very strong influence on the entering water.[29] The observed stereochemistry of the product suggests that the intermediate with an axial cyanide is favored in this case. The extent of optical activity in the product of base hydrolysis of a resolved sample of the *cis*-chlorocyano complex will help to resolve this problem.

The mercuric ion catalyzed aquation provides a further example of a departure from a simple first-order dependence upon the concentration of Hg^{2+} which is the normal type of behavior for this type of reaction.[30] Analysis of the data in Table III (the plot of $1/k_{obsd}$ against $1/[Hg^{2+}]$ is linear with a finite positive intercept) indicates that the mercuric ion dependence can be summarized by $k_{obsd} = kK[Hg^{2+}]/(1 + K[Hg^{2+}])$, where $k = 1.30 \times 10^{-2}$ s^{-1} and $K = 85$ M^{-1} at 50.8 °C, $\mu = 0.500$ M, and $[H^+] = 0.10$ M. Preliminary studies at lower ionic strengths indicate that k does not vary significantly with ionic strength whereas K decreases markedly with decreasing ionic strength. K also decreases slightly with decreasing temperature. The kinetics can be explained in terms of the formation of an adduct between the mercury and the substrate such that $[\text{adduct}]/([\text{substrate}][Hg^{2+}]) = K$, and this is mirrored in the immediate change in the spectrum of *cis*-$[Co(en)_2(CN)Cl]^+$ when mercuric perchlorate solution is added. Adduct formation has already been proposed to account for the departure from first-order kinetics in the Hg^{2+}-catalyzed aquation of *cis*-$[Co(en)_2Cl_2]^+$ [30] and α-*cis*-$[Co(eee)Cl_2]^+$ [31] (eee = 1,8-diamino-3,6-dithiaoctane) and similar spectral changes have been observed. However, while the formation of a



ring is a very reasonable explanation for the high stability of the adduct,[30] a similar ring involving the cyanide ligand would seem to be rather unusual. If the linearity of the Co—C≡N system is maintained, ring formation would be most unlikely; on the other hand, if there is interaction between the mercury and the carbon to form a



ring, one might expect to find a significant change in the ligand field strength of the cyanide. As it is, the change in the spectrum is rather small and since it only affects the longest wavelength band and shifts it to higher frequencies, it would seem to arise more from a perturbation of the chloride–cobalt interaction rather than that between the cyanide and the cobalt. We are currently examining the factors that cause departures from the simple first-order dependence on $[Hg^{2+}]$ in catalyzed aquations of this sort and will report our results and discuss the problem in more detail elsewhere.

Registry No. *cis*-$[Co(en)_2(CN)Cl]Cl$, 14322-28-2; Hg^{2+}, 14302-87-5.

References and Notes

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Studies of Ammineaquocobalt(III) Chemistry. Kinetics and Mechanism of Some Electron-Transfer Reactions of *cis*-Diammineaquocobalt(III) in Acid Perchlorate Solution

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The stoichiometry and kinetics of reduction of *cis*-$Co(NH_3)_2{}^{3+}{}_{aq}$ species by iodide, hydroquinone, tris(*o*-phenanthroline)iron(II), vanadium(II), iron(II), and chromium(II) have been investigated in acidic, 2 M perchlorate media ($HClO_4$, $NaClO_4$). The stoichiometries were measured by standard techniques and the kinetics were measured by conventional and stopped-flow spectrophotometry over a range of concentrations and temperatures. The rate law for the reactions with $Cr^{2+}{}_{aq}$ and $Fe^{2+}{}_{aq}$ is given by $-d[Co^{III}]/dt = d[\text{product}]/dt = (A + B/[H^+])[Co^{III}][\text{reductant}]$ whereas the rate law for the other reductants is given by $-(1/S)d[Co^{III}]/dt = d[\text{product}]/dt = A[Co^{III}][\text{reductant}]$, where S is the appropriate stoichiometric factor. The values of A for the reactions with $I^-{}_{aq}$, H_2Q, $Fe^{2+}{}_{aq}$, $Fe(o\text{-phen})_3{}^{2+}{}_{aq}$, $V^{2+}{}_{aq}$, and $Cr^{2+}{}_{aq}$ are 0.38, 0.028, 11.0, 2.42, 3350, and 151 M^{-1} s^{-1}, respectively, at 25 °C. For reduction by $Cr^{2+}{}_{aq}$ and $Fe^{2+}{}_{aq}$, the values of B are 497 and 1.99 s^{-1}, respectively, at 25°. Comparison of the kinetic data with those for reduction of analogous cobalt(III) systems suggests that the reactions of $Co(NH_3)_2{}^{3+}{}_{aq}$ and $Co(NH_3)_2OH^{2+}{}_{aq}$ with $I^-{}_{aq}$, $V^{2+}{}_{aq}$, $Fe(o\text{-phen})_3{}^{2+}{}_{aq}$, and H_2Q are outer sphere, while that of $Co(NH_3)_2OH^{2+}{}_{aq}$ with $Cr^{2+}{}_{aq}$ may be limited by substitution at the chromium(II) center. A value of $\mathcal{E}° \geq 0.91$ V for the standard potential of the $Co(NH_3)_2{}^{3+}{}_{aq}/Co(NH_3)_2{}^{2+}{}_{aq}$ couple is consistent with the experimental data.

Introduction

Recent studies of the reduction of $Co(NH_3)_2OH^{2+}{}_{aq}$ by Br^- [1] and H_2O_{2aq}[2] have revealed the existence of a base-catalyzed substitution-controlled mechanism like that found for the corresponding reactions of $CoOH^{2+}{}_{aq}$,[3,4] although great differences exist in the substitutional labilities of these two cobalt(III) species. An examination of the available data for reduction of $CoOH^{2+}{}_{aq}$ by a wide variety of reducing agents (including those of this study) has suggested that reactions of this complex may be grouped on the basis of their rate constants and activation parameters:[4] thus, substitution-controlled reduction reactions of $CoOH^{2+}{}_{aq}$ consistently exhibit higher observed enthalpies and entropies of activation, $\Delta H^{\ddagger}{}_{obsd}$, and $\Delta S^{\ddagger}{}_{obsd}$, respectively, than do outer-sphere reactions involving the same reactant charge product. In addition, the dependence of the observed free energy of activation, $\Delta G^{\ddagger}{}_{obsd}$, on the overall free energy change, ΔG_0, for the outer-sphere reactions of $Co^{3+}{}_{aq}$ and $CoOH^{2+}{}_{aq}$ deviates markedly from theoretical predictions and this has prompted speculation concerning the mechanistic involvement of a high-spin cobalt(III) species.[4]

The existence of substitution-controlled mechanisms for reduction of $CoOH^{2+}{}_{aq}$ and $Co(NH_3)_2OH^{2+}{}_{aq}$ suggests that similar, but energetically different, reactivity barriers exist in the series $Co(NH_3)_n(H_2O)_{6-n}{}^{3+}{}_{aq}$ as n increases from 0 to 6. With a view toward understanding the thermodynamic and kinetic factors which determine the reactivity of these centers, we have investigated the stoichiometry and kinetics of some of the faster reactions of *cis*-diammineaquocobalt(III). In this paper we report on the reduction of *cis*-diammineaquocobalt(III) by iodide, hydroquinone, iron(II), tris(*o*-phenanthroline)iron(II), vanadium(II) and chromium(II) at ionic strength 2.0 M ($HClO_4$, $NaClO_4$). The reactions have been studied over a range of temperatures so that the respective activation parameters may be compared with those for the corresponding reactions of aquocobalt(III) complexes.

Experimental Section

Materials. The water used throughout this work was doubly distilled from an all-glass apparatus and deoxygenated before use with a stream of purified nitrogen. Sodium perchlorate stock solutions were prepared by neutralization of perchloric acid with sodium carbonate and contained no detectable chloride ion impurities. The preparation and purification of anhydrous *cis*-diammineaquocobalt(III) perchlorate have been described previously.[1] All air-sensitive chemicals were prepared and stored under a purified nitrogen atmosphere. Stock solutions of iron(II) perchlorate in perchloric acid were prepared by reaction of iron(II) sulfate with the stoichiometric amount of barium perchlorate. The iron(III) content of these solutions was reduced to less than 0.5% by reduction at a platinum electrode for ca. 3 h. Solutions of vanadyl perchlorate in perchloric acid were prepared by addition of a slight excess of barium perchlorate to vanadyl sulfate (Ventron Corp.). Chromium(III) perchlorate solutions in perchloric acid were made from the solid hexahydrate (G. F. Smith Chemical Co.). Vanadium(II) and chromium(II) solutions were prepared from stock $VO^{2+}{}_{aq}$ and $Cr^{III}{}_{aq}$ solutions by reduction with freshly prepared zinc amalgam. Hydroquinone (Will Corp.) was recrystallized from absolute methanol and then sublimed. Fresh solutions were prepared daily in 0.001 M $HClO_4$ and stored in darkened containers. Stock solutions of sodium iodide were also protected from light and were used within a few days of preparation. Tris(*o*-phenanthroline)iron(II) sulfate solutions were made by dilution of a stock 0.025 M solution (G. F. Smith Chemical Co.). The complex $[Co(NH_3)_5Cl]Cl_2$ was prepared and purified according to a literature method.[5] Zinc perchlorate solutions were made by dissolving purified zinc metal in perchloric acid. All other chemicals used were of reagent grade.

Analytical Procedures. *cis*-Diammineaquocobalt(III) (hereafter referred to as cobalt(III)) and cobalt(II) concentrations were determined spectrophotometrically (ϵ_{537} 48 M^{-1} cm^{-1} [1] and ϵ_{509} 4.84 M^{-1} cm^{-1},[6] respectively). The concentration of cobalt(III) was also checked by adding an aliquot to an excess of standardized iron(II) solution and determining the excess iron(II) by titration with standard chromium(VI) using barium diphenylaminesulfonate as indicator. Concentrations of iron(III) were measured spectrophotometrically