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Kinetics and Mechanism of Base-Catalyzed Axial Substitution Reactions of Some Organocobalt(III) Complexes Containing Equatorial Chelating Ligands

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The kinetics of axial ligation by ammonia of a series of *trans*-organoaquocobalt(III) complexes containing an equatorial chelating ring have been measured in aqueous solution as a function of the hydroxide ion concentration. (Throughout, equatorial refers to the (near-) macrocyclic chelate ligand and axial to the fifth and sixth coordination sites.) The hydrolysis of the corresponding organoammine complexes has also been studied under the same experimental conditions. The kinetic data indicate that a conjugate base mechanism operates for both the replacement of ammine by water ligand and vice versa. The conjugate base is identified as the species formed by deprotonation of the equatorial ligand system in both cases. The equilibria of the axial ligation and acidic properties of the complexes are studied; the effect of the trans organo groups on the rate and equilibrium constants is discussed, and a comparison is made with the kinetics of the structurally similar organocobaloxime complexes.

Introduction

Some kinetic studies on the substitution of the water ligand by various groups in complexes of the type $\{RCo[(DO)(DOH)pn]H_2O\}^+$ (Figure 1) have been reported by us[2] (R = alkyl and (DO)(DOH)pn = diacetyl monoxime diacetyl monoximato propane-1,3-diyldiimino). There it was observed that the rate law is first order in complex and first order in ligand for various inorganic and organic incoming groups (viz., SCN^-, N_3^-, NH_3, piperidine, morpholine). However, ligands containing an aromatic group, e.g., pyridine, imidazole and aniline, were exceptional, kinetic data revealing evidence for intermediates of the type $\{RCo[(DO)(DOH)pn]H_2O\}^+\cdot L$. In those cases the low acidity of the H_2O ligand permitted the study of weak bases as incoming ligands without appreciable formation of the hydroxo complexes $\{RCo[(DO)(DOH)pn]OH\}$. However in more basic solutions the kinetics might be complicated by acid–base equilibria involving not only the ligand water as above but also the equatorial hydrogen-bonded proton of the (DO)(DOH) unit.

In the present work we examine the effect of hydroxide ion concentration upon the rate and mechanism of the substitution reactions of various cobalt(III) complexes containing planar chelating rings. Similar studies have been previously reported for other cobalt(III) complexes containing planar chelating rings. Randall and Alberty have observed that the rate of substitution reactions of aquocobalamin show a significant decrease in alkaline solution.[3,4] They attribute this to the formation of unreactive hydroxocobalamin. Similar conclusions were reported by Tsiang and Wilmarth[5] for the displacement of water by SCN^- in *trans*-(sulfito)aquobis(dimethylglyoximato)cobalt(III), reaction 1. (Bis(dimethylglyoximate) is abbreviated to D_2H_2 and hereafter referred to as cobaloxime.)

$$[SO_3Co(D_2H_2)H_2O]^- + SCN^- \rightarrow [SO_3Co(D_2H_2)SCN]^{2-} + H_2O \quad (1)$$

The rate is independent of pH in acid solution but decreases in alkaline solution because of formation of the hydroxo complex which does not react at an appreciable rate with SCN^-.

Aquation and base hydrolysis of some halogenoamminecobaloximes have also been studied.[6,7] The latter involves the formation of the conjugate base of the complex by rapid reversible removal of the proton from the equatorial ligand as in (2) and (3), where X = Cl^- or Br^- and A = pyridine, γ-picoline,[6] or NH_3.[7]

$$[ACo(D_2H_2)X] + OH^- \rightleftarrows [ACo(D_2H)X]^- + H_2O \quad (2)$$

$$[ACo(D_2H)X]^- + H_2O \rightarrow [ACo(D_2H_2)OH] + X^- \quad (3)$$

An identical mechanism has been proposed for the hydrolysis of the organocobaloximes[8,9] of the type $[RCo(D_2H_2)L]$, where L represents a series of substituted pyridines or ammines. Comparison of the results reported for the organometallic and nonorganometallic compounds indicates that the former exhibit a less pronounced tendency to undergo deprotonation, as indicated by smaller values for the preequilibrium constants. The rate constant of the aquation of the conjugate base is about 10 times greater than that of the parent complex.

In the present work we show that, in the case of RCo[(DO)(DOH)pn] complexes, evidence for the conjugate base mechanism involving deprotonation of the equatorial system can be obtained not only for the base hydrolysis but also in the substitution of the axial water ligand.

For these reactions a pH-dependent mechanistic pathway, which satisfactorily accounts for all the kinetic and thermodynamic results, is proposed (Scheme I).

Experimental Section

Materials. Samples of the complexes $\{RCo[(DO)(DOH)pn]H_2O\}^+ClO_4^-$ and $\{RCo[(DO)(DOH)pn]NH_3\}^+ClO_4^-$, where R = C_6H_5, CH_3, or C_2H_5, were prepared according to previously reported methods.[10] $\{C_2H_5Co[(DO)(DOBF_2)pn]H_2O\}^+ClO_4^-\cdot 2H_2O$ was prepared by adding 1.5–2 equiv of $(C_2H_5)_2O\cdot BF_3$ to a suspension of $\{C_2H_5Co[(DO)(DOH)pn]H_2O\}^+ClO_4^-$ (2 mM in 100 mL of diethyl ether) and stirring for 24 h. The ether was evaporated and the solid dissolved in water and reprecipitated with $NaClO_4$. Anal. Calcd for $C_{13}H_{29}BClCoF_2N_4O_9$: C, 29.5; H, 5.5; N, 10.6. Found: C, 29.4; H, 5.5; N, 10.6.

All other chemicals were analytical grade unless otherwise stated. Ammonia solutions were standardized by potentiometric titrations against 0.1 M HCl.

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[1] (a) University of Trieste. (b) University of York.

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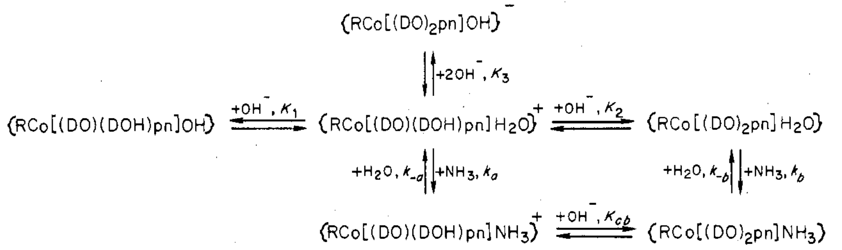
Scheme I



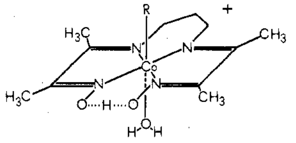


Figure 1.

General Experimental Conditions. Both the equilibrium and kinetic measurements were carried out at 25.0 ± 0.1 °C. The ionic strength was maintained at 1 M with $NaNO_3$. The ammonia concentrations used in the calculation for equilibria and kinetics were corrected for the ionization of NH_4^+ by using a pK_a of 9.43 obtained by means of a potentiometric titration of ammonia solution in 1 M $NaNO_3$ at 25 °C with standard HCl and application of the usual relation

$$\log \frac{[NH_3]}{[NH_4^+]} = pH - pK_a$$

Equilibrium Studies. These were performed by spectrophotometric titrations. With use of a microsyringe, concentrated solutions of reactant (NH_3 or NaOH) were added to the solution of complex (generally $(0.2–2) \times 10^{-4}$ M) so that the volume of the solution was increased by no more than 0.05%. After the addition the solution was magnetically stirred for about 5 min.

Kinetic Runs. The reaction was monitored by following changes in absorbance. First-order and pseudo-first-order rate constants were obtained from the linear plot of $\log (A - A_\infty)$ vs. time. Generally, $(2–4) \times 10^{-4}$ M solutions of complex were used.

Instruments. For pH measurement a Radiometer pH-meter, Type pH M4, equipped with a glass and calomel electrode, was used. The equilibrium studies and slower kinetic runs were performed with a Perkin-Elmer Model 356 double beam–double wavelength spectrophotometer. The faster reactions were followed with use of a Durrum-Gibson stopped-flow spectrophotometer.

Results

Equilibrium Studies. The acidic properties of complexes $\{RCo[(DO)(DOH)pn]H_2O\}^+$ ($R = C_6H_5, CH_3, C_2H_5$) were examined by means of spectrophotometric titrations with NaOH. Good isosbestic points were observed. The pH dependence of the spectra is more pronounced in the visible region (Figure 2) and is consistent with a proton loss from the molecule. We assign this process (eq 4) to the formation of

$$\{RCo[(DO)(DOH)pn]H_2O\}^+ \overset{K_a}{\rightleftharpoons} \{RCo[(DO)(DOH)pn]OH\} + H^+ \quad (4)$$

$$R = C_6H_5, CH_3, C_2H_5$$

hydroxo complexes (see the Discussion). The pK_a for the ionization process was calculated by using relation 5, where

$$\log [(A_{AH} - A)/(A - A_{A^-})] = pH - pK_a \quad (5)$$

A is the measured absorbance of the solution in the presence of OH^-, A_{AH} is the absorbance of the aquo complex, and A_{A^-} is the absorbance of the hydroxo complex. Values of the pK_a are given in Table I. In strongly alkaline medium (1 M NaOH) for $R = C_6H_5$, a second acid–base equilibrium (eq 6) is observed which is well separated from the first process.

$$\{RCo[(DO)(DOH)pn]OH\} \rightleftharpoons \{RCo[(DO)_2pn]OH\}^- + H^+ \quad (6)$$

$$R = C_6H_5$$

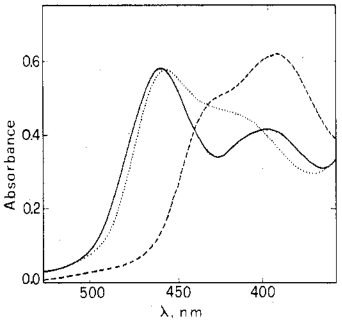


Figure 2. Spectra of $\{CH_3Co[(DO)(DOH)pn]H_2O\}^+$ (I) (—) at 25 °C, pH 3, and $\mu = 1$ M ($NaNO_3$), of $\{CH_3Co[(DO)(DOH)pn]OH\}$ (···), obtained from I at pH 13, and of $\{CH_3Co[(DO)(DOH)pn]NH_3\}^+$ (- - -), obtained from I at $[NH_3]_{free} = 0.5$ M. In these conditions the product formation is almost complete.

Table I. Summary of Equilibrium Data[a]

R	pK_a[b]	K_1,[c] M^{-1}	K_f,[d] M^{-1}
C_6H_5	11.4 ± 0.01	363 ± 8	3502 ± 226
CH_3	12.31 ± 0.02	48.9 ± 2.2	1862 ± 73
C_2H_5	12.65 ± 0.01	22.4 ± 0.3	902 ± 47

[a] Values at 25.0 ± 0.1 °C, $\mu = 1$ M ($NaNO_3$). Errors are standard deviations. [b] The pK_a values refer to the reaction $\{RCo[(DO)(DOH)pn]H_2O\}^+ \rightleftharpoons \{RCo[(DO)(DOH)pn]OH\} + H^+$. [c] The K_1 values refer to the reaction $\{RCo[(DO)(DOH)pn]H_2O\}^+ + OH^- \rightleftharpoons \{RCo[(DO)(DOH)pn]OH\} + H_2O$ and are related to K_a by the expression $K_1 = K_a/K_W$. [d] K_f are equilibrium constants for for the reaction $\{RCo[(DO)(DOH)pn]H_2O\}^+ + NH_3 \rightleftharpoons \{RCo[(DO)(DOH)pn]NH_3\}^+ + H_2O$.

Later this will be identified with deprotonation of the equatorial ligand.

The equilibrium constants for the ammonia ligation (eq 7)

$$\{RCo[(DO)(DOH)pn]H_2O\}^+ + NH_3 \overset{K_f}{\rightleftharpoons} \{RCo[(DO)(DOH)pn]NH_3\}^+ + H_2O \quad (7)$$

were also determined spectrophotometrically. These spectra reveal well-defined isosbestic points for an extended range of ammonia concentrations (Figure 2). However deviations occur at high ligand concentrations, pointing to a further reaction, which prevent the direct determination of the absorbance coefficient of the ammine complex. Therefore eq 8 was used

$$A = A_{NH_3} - (A - A_{H_2O})/K_f[NH_3] \quad (8)$$

to calculate the equilibrium constants K_f where A is the measured absorbance of the solution in NH_3, $[NH_3]$ is the actual concentration of ammonia allowing for formation of NH_4^+, and A_{H_2O} is the absorbance of the aquo complex. The values of $-K_f^{-1}$ and A_{NH_3}, the absorbance of the ammine complex, have been obtained as the slope and the intercept of the plot of A vs. $(A - A_{H_2O})/[NH_3]$. Values for K_f are given in Table I. The further reaction observed at high $[NH_3]$ suggests that in this case the deprotonation of the hydrogen bridge occurs to some extent in alkaline solutions as in reaction 9. For $R = C_6H_5$, equilibrium 9 was studied in excess am-

$$\{RCo[(DO)(DOH)pn]NH_3\}^+ + OH^- \rightleftharpoons \{RCo[(DO)_2pn]NH_3\} + H_2O \quad (9)$$

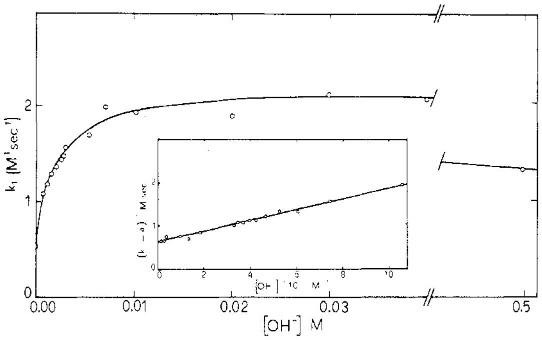


Figure 3. Dependence of second-order rate constant on hydroxide ion concentration at 25 °C and μ = 1 M ($NaNO_3$), for the ammonia binding on the phenyl derivative. The intercept ($a = k_a$) represents the hydroxide ion independent path. The insert shows the same data plotted as $(k_1 - a)^{-1}$ vs. $[OH^-]^{-1}$.

monia (0.2 M). An equilibrium constant of 15.1 M^{-1} was obtained by using eq 10, where A_{LH} and A_{L^-} refer to absorbance of the ammine and the deprotonated ammine complexes, respectively.

$$A = A_{LH} + K_{cb}(A_{L^-} - A)[NH_3] \qquad (10)$$

bance of the ammine and the deprotonated ammine complexes, respectively. K_{cb} and A_{LH} are the slope and the intercept of the graph of A vs. $(A_{L^-} - A)[NH_3]$. The equilibrium constants for R = CH_3 and C_2H_5 have not been calculated, because base hydrolysis (eq 11) cannot be totally repressed by excess ammonia and overlaps the ionization process.

$$\{RCo[(DO)(DOH)pn]NH_3\}^+ + OH^- \rightleftarrows \{RCo[(DO)(DOH)pn]OH\} + NH_3 \qquad (11)$$

Kinetic Measurements. (a) Ammonia Ligation. The effect of the hydroxide ions on the rate of substitution of the axial aquo group by ammonia for the complexes $\{RCo[(DO)(DOH)pn]H_2O\}^+$ (where R = C_6H_5, CH_3, C_2H_5) and $\{RCo[(DO)(DOBF_2)pn]H_2O\}^+$ (R = C_2H_5) was studied under the conditions reported in the Experimental Section. $Co[(DO)(DOBF_2)pn]$ is the derivative of $Co[(DO)(DOH)pn]$ formed by replacing the equatorial H by BF_2, the B being bonded to both O atoms. The hydroxide ion concentrations were varied by addition of appropriate amounts of standard NaOH or by use of buffered solutions. Incidentally ammonia is a useful incoming ligand because of the high equilibrium constant values for ammine complexes relative to those for other ligands.[11] It was used in constant excess (0.5 M). The consequent minimization of the back-reaction allows some simplification in the calculations. Linearity in log plots indicates reactions which are first order in cobalt concentration (see Experimental Section). First-order rate constants so obtained, viz., k_{obsd} (where $-d[\text{Co complex}]/dt = k_{obsd}[\text{Co complex}]$), were used to calculate the second-order rate constant: $k_1 = k_{obsd}/[NH_3]$. Values of k_1 are dependent upon hydroxide ion concentration in a nonlinear way.

The k_1 dependence on $[OH^-]$ for R = C_6H_5 is shown in Figure 3. The rate constant increases markedly over the range of moderately alkaline solutions; it reaches a maximum near $[OH^-] = 1 \times 10^{-2}$ M and then slowly decreases at higher $[OH^-]$. For R = CH_3 the curve is essentially linear (Figure 4). For R = C_2H_5 (Figure 5), after the initial rise k_1 assumes a constant value. In all three compounds there is a nonzero intercept $k_1 = a$. Good values of a were obtained by carrying out the reaction in buffered medium (NH_4Cl, NH_4OH) at pH 9.3 (see also Discussion) where the reaction rate becomes independent of hydroxide ion concentrations. Over the range of moderately alkaline solutions the kinetic data for R = C_6H_5 are consistent with a rate law for which the rate constant, k_1, can be expressed as in (12), which can be rewritten as (13).

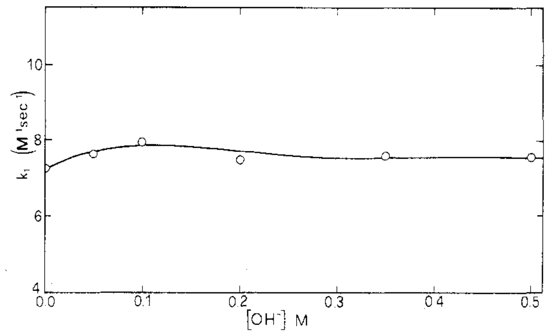


Figure 4. Dependence of second-order rate constant on hydroxide ion concentration at 25 °C and μ = 1 M ($NaNO_3$), for the ammonia ligation of the methyl derivative.

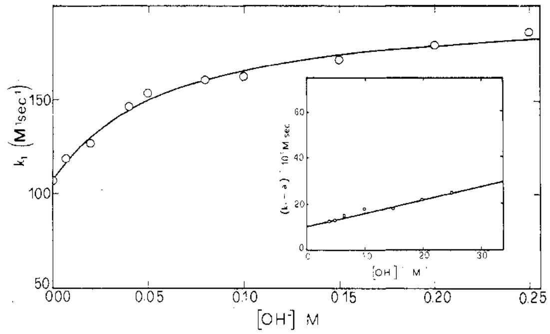


Figure 5. Dependence of the second-order rate constant on hydroxide ion concentration at 25 °C and μ = 1 M ($NaNO_3$), for the ammonia ligation of the ethyl derivative. The intercept ($a = k_a$) represents the hydroxide ion independent path. The insert shows the same data plotted as $(k_1 - a)^{-1}$ vs. $[OH^-]^{-1}$.

$$k_1 = (a + b[OH^-])/(1 + c[OH^-]) \qquad (12)$$

$$\frac{1}{k_1 - a} = \frac{1}{(b - ac)[OH^-]} + \frac{c}{b - ac} \qquad (13)$$

Plots of $1/(k_1 - a)$ against $1/[OH^-]$ were linear and allow the calculation of b and c (see insert of Figure 3). Later it will be shown that $a = k_a$, $b = k_bK_2$, and $c = K_1 + K_2$ (see Scheme III). Expression 12 describes completely the kinetics for R = C_2H_5 over the whole range of $[OH^-]$ studied. c and b follow as above (see insert of Figure 5). For R = CH_3, k_1 seems to be unaffected by the hydroxide ion concentration, so that for this complex

$$k_1 = a \qquad (14)$$

When the complex $\{C_2H_5Co[(DO)(DOBF_2)pn]H_2O\}^+$ is studied, an inverse dependence of k_1 on $[OH^-]$ is observed (Figure 6), which is consistent with expression 15. The values of a–c are reported in Table II.

$$k_1 = \frac{a}{1 + c[OH^-]} \qquad (15)$$

(b) Hydrolysis of the Ammine Complexes. Hydrolysis reactions of the complexes $\{RCo[(DO)(DOH)pn]NH_3\}^+$, where R = C_6H_5, CH_3, or C_2H_5, were studied by using the same experimental conditions and instrumental techniques as above. The reactions in the presence of excess $[OH^-]$ conform to the first-order rate law $-d[\text{Co complex}]/dt = k_{obsd}[\text{Co complex}]$.

The dependence of this k_{obsd} (indicated below as k_{-1}) on hydroxide ion concentration is shown in Figure 7 for the phenyl

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[11] For some other ligands (N_3^-, SCN^-, Py, piperidine, morpholine) the equilibrium constant values range from 40 to 300 M^{-1} (unpublished data).

Table II. Summary of Kinetic Data for the NH_3 Ligation Reactions[a]

	$a = k_a$, $M^{-1}\ s^{-1}$	$b = k_bK_2$, $M^{-2}\ s^{-1}$	$c = K_1 + K_2$, M^{-1}	$[OH^-]$ range, M
$\{C_6H_5Co[(DO)(DOH)pn]H_2O\}^+$	5.60×10^{-1} [b]	$(1.06 \pm 0.03) \times 10^3$ 0.95×10^3 [d]	484 ± 20.9	1×10^{-3}–5×10^{-2}
$\{CH_3Co[(DO)(DOH)pn]H_2O\}^+$	7.02[b] 7.05 ± 0.08[c]	4.29×10^2 [d]		
$\{C_2H_5Co[(DO)(DOH)pn]H_2O\}^+$	1.07×10^2 [b]	$(3.65 \pm 0.30) \times 10^3$ 3.90×10^3 [d]	18.11 ± 1.77	5×10^{-2}–2.5×10^{-1}
$\{C_2H_5Co[(DO)(DOBF_2)pn]H_2O\}^+$	$(5.98 \pm 0.68) \times 10$		118.5 ± 13.6[e]	5×10^{-3}–1×10^{-1}

[a] Data at 25.0 ± 0.1 °C, $\mu = 1$ M ($NaNO_3$). [b] Measured at pH 9.3. [c] From ref 2. [d] Calculated from relation 22 and data of Table III. [e] $c = K_1$ for this complex.

Table III. Summary of the Kinetic Data for the Aquation and Base Hydrolysis of the Complexes $\{RCo[(DO)(DOH)pn]NH_3\}^+$ [a]

R	$a' = k_{-a}$,[b] s^{-1}	$b' = k_{-b}K_{cb}$, $M^{-1}\ s^{-1}$	$c' = K_{cb}$, M^{-1}	$b'/c' = k_{-b}$, s^{-1}	$[OH^-]$ range, M
C_6H_5	2.00×10^{-4}	$(3.40 \pm 0.11) \times 10^{-1}$	25.5 ± 3.7	$(1.33 \pm 0.19) \times 10^{-2}$	4×10^{-3}–5×10^{-1}
CH_3	3.60×10^{-3}	$(2.19 \pm 0.16) \times 10^{-1}$	0.72 ± 0.16	$(3.04 \pm 0.71) \times 10^{-1}$	4×10^{-3}–5×10^{-1}
C_2H_5	1.06×10^{-1}	3.90 ± 0.06	0.24 ± 0.12	$(1.62 \pm 0.81) \times 10$	5×10^{-2}–5×10^{-1}

[a] Data at 25.0 ± 0.1 °C, $\mu = 1$ M ($NaNO_3$). [b] Constants for aquation kinetics in 0.1 M HCl.

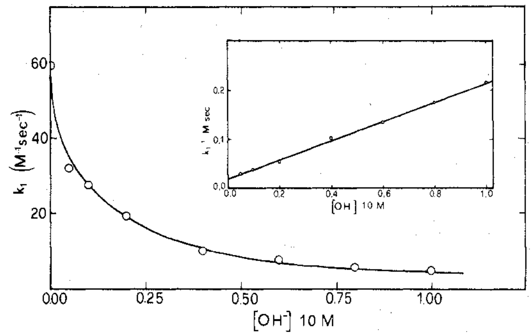


Figure 6. Dependence of the second-order rate constant on hydroxide ion concentration at 25 °C and $\mu = 1$ M ($NaNO_3$), for the ammonia ligation of $\{C_2H_5Co[(DO)(DOBF_2)pn]H_2O\}^+$. The insert shows the same data plotted as k_1^{-1} vs. $[OH^-]$.

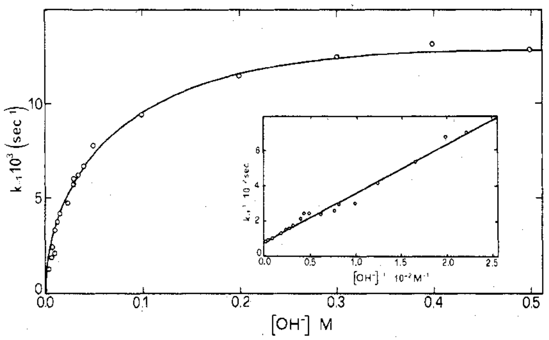


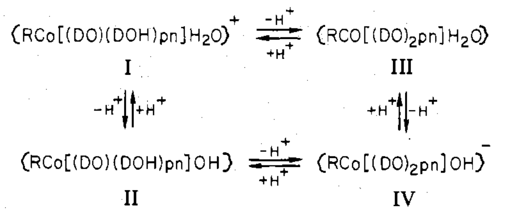
Figure 7. Rate of release of NH_3 from $\{C_6H_5Co[(DO)(DOH)pn]NH_3\}^+$ as a function of $[OH^-]$ at 25 °C and $\mu = 1$ M ($NaNO_3$). The insert shows the same data plotted as k_{-1}^{-1} vs. $[OH]^{-1}$.

derivative. Similar plots were found for the other complexes. The data are consistent with the expression for k_{-1} for all three complexes examined (eq 16).

$$k_{-1} = \frac{a' + b'[OH^-]}{1 + c'[OH^-]} \qquad (16)$$

Plots of $1/(k_{-1} - a')$ vs. $1/[OH^-]$ were found to be linear and allow the calculation of b' and c' (see insert of Figure 7). These require the knowledge of the values of a', which were obtained by studying the reactions in acidic medium. HCl was used for this purpose (no catalytic effect being observed over the whole range of the examined proton concentration 0.05–0.5 M HCl). Later it will be shown that $a' = k_{-a}$, $b' = k_{-b}K_{cb}$, $c' = K_{cb}$ (see Scheme IV). The values of a'–c' are reported in Table III.

Scheme II



Discussion

The spectrophotometric analysis (see Results) reveals that the CH_3 and C_2H_5 complexes behave as monoprotic acids and the C_6H_5 complex behaves as a biprotic acid. The identification of the two acid–base processes with reactions 4 and 6 has been made on the basis of criteria adopted for the cobaloximes. The spectral changes accompanying the loss of the first proton are manifested mainly in the visible region and are similar to those observed on binding an axial ligand to the complex. Therefore these spectral changes are assigned to the formation of the hydroxo complexes. The second proton loss is associated with spectral changes in the ultraviolet region as observed for the equatorial proton dissociation in other [(DO)(DOH)pn] complexes previously studied by means pH titrations, UV spectrophotometry, and NMR measurements,[12] hence the assignment to reaction 6. By applying to these complexes the general scheme for the ionization of a diprotic acid (Scheme II), one notices that there is good spectroscopic evidence for the presence of species II for R = C_6H_5, CH_3, or C_2H_5 and of IV for R = C_6H_5, but in no case is species III observed.

In the light of these facts, the positive catalysis by the hydroxide ions on the ammonia ligation reactions (see Figures 3–5) is rather surprising, since the pK_a values given in Table I for the aquo complexes indicate that a perceptible amount of hydroxo complex II is present in basic medium and since a retardation of the reaction would be expected as a consequence of the usual inertness of the hydroxo groups (see Introduction and cf. the behavior of $\{C_2H_5Co[(DO)(DOBF_2)pn]H_2O\}^+$). The most plausible explanation is that small amounts of complex III are actually produced in alkaline solution at concentrations undetectable by spectrophotometry and that this species is highly reactive. This hypothesis is supported by the fact that also in the base hydrolysis reactions the deprotonated species are more reactive than the protonated ones.[6-9]

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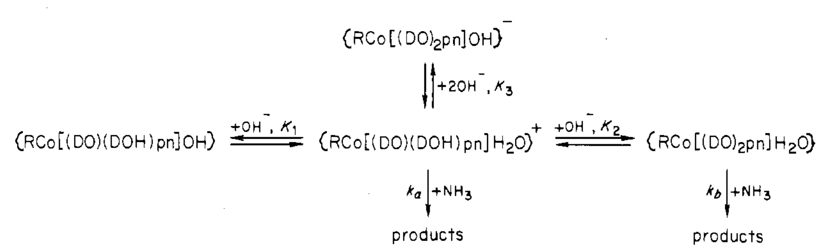
(12) G. Pellizer, G. R. Tauszik, G. Tauzher, and G. Costa, *Inorg. Chim. Acta*, 7, 60 (1973).

Scheme III



This interpretation is confirmed by the behavior of $\{C_2H_5Co[(DO)(DOBF_2)pn]H_2O\}^+$, which cannot form a species analogous to III. Equation 15 is consistent with reactions 17 and 18.

$$\{C_2H_5Co[(DO)(DOBF_2)pn]H_2O\}^+ + OH^- \overset{K_1}{\rightleftharpoons} \{C_2H_5Co[(DO)(DOBF_2)pn]OH\} + H_2O \tag{17}$$

$$\{C_2H_5Co[(DO)(DOBF_2)pn]H_2O\}^+ + NH_3 \xrightarrow{k_a} \{C_2H_5Co[(DO)(DOBF_2)pn]NH_3\}^+ + H_2O \tag{18}$$

K_1 and k_a corresponding to c and a, respectively, in expression 15. The decrease in the rate in basic solution is due to the formation of the more inert hydroxo complex in (17).

On the basis of the argument so far, we propose Scheme III. The corresponding kinetic expression is

$$k_1 = \frac{k_a + k_bK_2[OH^-]}{1 + (K_1 + K_2)[OH^-] + K_3[OH^-]^2} \tag{19}$$

When $[OH^-]^2$ is small in moderately alkaline solution, (19) can be simplified to (20). This agrees completely with (12),

$$k_1 = \frac{k_a + k_bK_2[OH^-]}{1 + (K_1 + K_2)[OH^-]} \tag{20}$$

the experimentally observed equation for R = C_2H_5, R = C_6H_5, $a = k_a$, $b = k_bK_2$, and $c = K_1 + K_2$. The $[OH^-]^2$ term is associated with the species $\{RCo[(DO)_2pn]OH\}^-$ and contributes to the decrease in rate in strong alkali. This retardation is most pronounced for the C_6H_5 derivative (see Figure 3), the species for which there was also good spectrophotometric evidence for the anionic $\{C_6H_5Co[(DO)_2pn]OH\}^-$ complex. Likely Scheme III applies also to the reactions of the methyl derivative; thus the independence of k_1 from $[OH^-]$ for this complex requires $k_1 = k_a$, viz.

$$\frac{k_a + k_bK_2[OH^-]}{1 + (K_1 + K_2)[OH^-]} = k_a$$

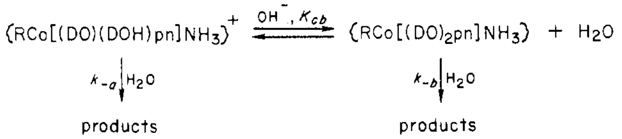
In this instance $k_bK_2 = k_a(K_1 + K_2)$; that is, the rate acceleration due to the formation of the conjugate base III is balanced by the retardation due to the formation of the unreactive hydroxo complex II. The fact that the linear dependence of k_{obsd} is observed even at highest concentration (2 M NH_3), when the substitution reaction of the CH_3 derivative is studied in unbuffered medium,[2] can thus be rationalized.

The hydrolysis reaction kinetic data suggest reaction Scheme IV in which there are contributions from both direct aquation and conjugate base pathways, viz., k_{-a} and k_{-b}. When R = C_6H_5, there was spectrophotometric evidence for the formation of the complex deprotonated in the equatorial position (see Results). The rate law for Scheme IV is eq 21 which is in

$$k_{-1} = \frac{k_{-a} + k_{-b}K_{cb}[OH^-]}{1 + K_{cb}[OH^-]} \tag{21}$$

complete agreement with the empirical rate expression 16: $a' = k_{-a}$, $b' = k_{-b}K_{cb}$, and $c' = K_{cb}$. The ratios k_{-b}/k_{-a} are 66 (R = C_6H_5), 85 (R = CH_3), and 150 (R = C_2H_5); then for these complexes the cis effect is much larger than for the cobaloximes, for which this ratio is about 10.[6-9] Therefore a relatively large cis effect is to be expected also in the substitution reactions of the $\{RCo[(DO)(DOH)pn]H_2O\}^+$ complexes.

Scheme IV



It follows as a consequence of microscopic reversibility principle (MRP) that the above results can be collected into the comprehensive reaction Scheme I. The consistency in Scheme I can be verified by the satisfactory agreement between calculated and measured kinetic and thermodynamic constants of the cycle reactions. An example is given in Table II where measured values for k_bK_2 are listed with those calculated by applying relation 22. Inspection of Scheme I

$$k_bK_2 = \frac{k_a}{k_{-a}}k_{-b}K_{cb} \tag{22}$$

suggests that the existence of the $\{RCo[(DO)_2pn]H_2O\}$ type complexes can be predicted on the basis of the MPR, once it has been established that base hydrolysis includes a conjugate base pathway. Furthermore, the hydrolysis reaction kinetics are not consistent with a bimolecular process, so that the MRP requires no formation of ammine complex by reaction 23.

$$\{RCo[(DO)(DOH)pn]OH\} + NH_3 \rightarrow \{RCo[(DO)(DOH)pn]NH_3\}^+ + OH^- \tag{23}$$

Similarly, it can also be shown that the $\{RCo[(DO)_2pn]OH\}^-$ species is unreactive toward NH_3 as in (24)

$$\{RCo[(DO)_2pn]OH\}^- + NH_3 \rightarrow \{RCo[(DO)_2pn]NH_3\} + OH^- \tag{24}$$

since the introduction of the reverse of such a path in the hydrolysis scheme would lead to a kinetic expression of the type

$$k_{-1} = \frac{a' + b'[OH^-] + c'[OH^-]^2}{1 + d'[OH^-]} \tag{25}$$

containing a quadratic term in $[OH^-]$ which is not consistent with experimental data. Reaction 24 is ruled out on the MRP.

The kinetic trans effect shown by k_a, k_{-a}, and k_{-b} rises in the sequence R = C_6H_5 < CH_3 < C_2H_5, which can be attributed to increasing donor character of R group. This sequence suggests a dissociative type of activation. The thermodynamic trans influence also follows the same sequence and is reflected by the equilibrium constants for ammonia ligand binding and by the pK_a values of the aquo complexes (both in Table I). On the other hand, the K_{cb} values can be regarded as an estimation of the cis influence of the R group. Table III illustrates that this cis influence rises with the donor character of R group in the same way as observed for the trans influence.

It would be of some interest to examine if Scheme I can be extended to other aquo complexes with planar chelating rings containing a potentially acidic function. Some of our preliminary data on rate of reaction of methyl cobaloxime with NH_3

as a function of pH show that water ligand deprotonation is the only acid–base preequilibrium. In other words, if expression 20 is generally valid, then in the case of the alkyl cobaloximes it must be $k_bK_2 \ll k_a(K_1 + K_2)$.

Registry No. $\{C_6H_5Co[(DO)(DOH)pn]H_2O\}^+$, 26334-77-0; $\{CH_3Co[(DO)(DOH)pn]H_2O\}^+$, 26334-78-1; $\{C_2H_5Co[(DO)(DOH)pn]H_2O\}^+$, 26317-25-9; $\{C_6H_5Co[(DO)(DOH)pn]NH_3\}^+$, 74779-51-4; $\{CH_3Co[(DO)(DOH)pn]NH_3\}^+$, 47021-87-4; $\{C_2H_5Co[(DO)(DOH)pn]NH_3\}^+$, 74764-00-4; $\{C_2H_5Co[(DO)(DOBF_2)pn]H_2O\}^+ClO_4^-$, 74764-02-6; $CH_3Co[(DO)(DOH)pn]OH$, 41975-58-0; NH_3, 7664-41-7.

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Synthesis of (Alkyl sulfito)dicarbonyl(η^5-cyclopentadienyl)iron(II) Complexes and Reactions of Ligated Alkyl Sulfite[1]

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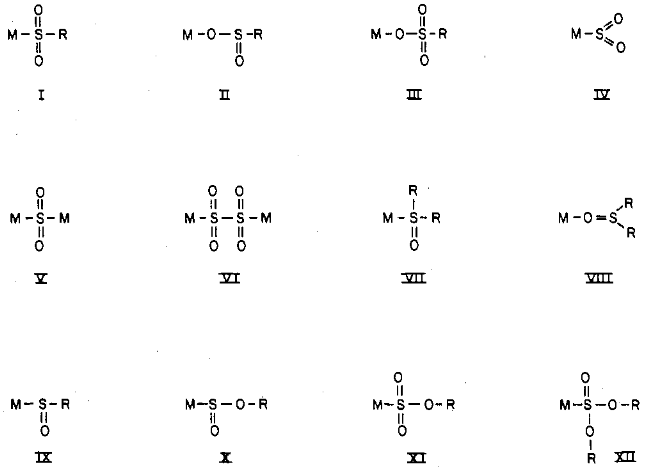
A series of alkyl sulfito complexes, $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$, have been prepared by substitution reactions of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H_2O]BF_4$ with $Na[S(O)_2OR]$ in ROH (R = CH_3, C_2H_5), $Na[S(O)_2OR']$ (R' = C_2H_5) in ROH (R = 1-C_3H_7, 2-C_3H_7), and Na_2SO_3 in ROH (R = C_2H_5), as well as by treatment of $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2]\cdot 0.5SO_2$ with $ROSO_2F$ or R_3OPF_6 (R = CH_3). However, attempts at similar substitution reactions of various other organometallic complexes were largely unsuccessful and furnished only $Mn(CO)_3(bpy)[S(O)_2OCH_3]$. The alkyl sulfito ligand in $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ undergoes transesterification with the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR']$ on heating in R'OH at reflux or on storage in R'OH in the presence of HBF_4 at room temperature. By use of $(+)_{589}$-2-octanol, it was shown that this exchange proceeds with cleavage of the S–OR bond. Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ with R_2NH (R = CH_3, C_2H_5) leads to the formation of $R_2NH_2[(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_3]$, whereas hydrolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ affords the hydrogen sulfito complex, $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OH]$, which is a strong acid. The hydrolysis is reversible, and the regeneration of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ occurs at ambient temperature via scission of the S–OH bond. Treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ with $(C_2H_5)_3OPF_6$ affords the dialkyl sulfite complexes, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)(OC_2H_5)OR]]PF_6$, whereas reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2[S(O)_2OR]$ with the acids HCl and CF_3CO_2H furnish $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2[OC(O)CF_3]$, respectively. Where possible, these reactions are compared with the corresponding reactions of the organic sulfonic esters, $RS(O)_2OR'$.

Introduction

Organometallic complexes containing diverse sulfur–oxygen ligands have been reported in recent years. Some of them, viz., metal sulfinates-*S* (I) and -*O* (II) and metal sulfonates (III), are accessible by insertion of SO_2[2,3] and SO_3,[4] respectively, into metal–carbon σ bonds. Other types of compounds have been obtained by a variety of methods to provide derivatives with terminal and bridging SO_2[5,6] (IV, V), dithionito[7] (VI), sulfoxide[8,9] (VII, VIII), sulfenato[10] (IX), alkoxysulfenato[10] (X), alkyl sulfito[11,12] (XI), and dialkyl sulfite[8] (XII) ligands (η^2-bonded ligands are not included).

In the course of an investigation of comparative chemistry of organometallic compounds containing sulfur–oxygen ligands, our attention was directed to alkyl sulfito complexes (XI). Such complexes are of considerable interest in that the $S(O)_2OR$ ligand may be viewed as the product of reaction of coordinated SO_2 with alkoxide. This presumed behavior finds a striking analogy in the observed formation of carboalkoxy ligands, C(O)OR, by nucleophilic attack of alkoxide on ligated CO.[13] Treatment of coordinated C(O)OR with acid regenerates the carbonyl ligand. From the foregoing comparison, neutral complexes XI represent possible precursors of cationic metal–SO_2 species, which may exhibit interesting and novel reactions with nucleophiles.



Although examples of alkyl sulfito complexes are known for nickel,[14] palladium,[15–17] platinum,[16–18] cobalt,[14] and rutheni-

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