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Structure and Reactivity in Octahedral Complexes. X.
The Stepwise Hydrolysis of the *cis*-Diacetatobis(α,α′-dipyridyl)cobalt(III) Ion[1a]

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The hydrolysis of the *cis*-diacetatobis(α,α′-dipyridyl)cobalt(III) ion has been investigated over the pH range of 2–12. First-order kinetics were obtained throughout, with the exception of the lower end of the range where the contribution of an acid-catalysis term becomes important for the reaction of the first acetato ligand of the diacetato complex. In contrast, there is found no evidence of hydroxide ion catalysis. Essential rate data were also obtained for the intermediate product of the reaction, the *cis*-aquoacetato complex. The reactions are believed to result from a dissociation mechanism of aquation of the diacetato, aquoacetato, or hydroxoacetato species and, in the case of more acidic conditions, of the protonated species of the diacetato complex. With reference to the more basic conditions, the results are taken as a test for the validity of the SN1 CB mechanism for the base hydrolysis of N–H-containing Co(III) octahedral complexes.

Introduction

The base hydrolysis in aqueous media of many octahedral complexes of the type $M(NH_3)_5X^{n+}$ or $M(en)_2AX^{n+}$ is assumed to occur by a two-stage mechanism *via* a reactive conjugate base[2] (SN1 CB)

$$M(NH_3)_5X^{n+} + OH^- \rightleftharpoons \text{conjugate base} + H_2O \qquad (1)$$

$$\text{conjugate base} \xrightarrow{H_2O} M(NH_3)_5(OH)^{n+} + X^- \qquad (2)$$

The likelihood of such a mechanism has been supported by several approaches.[3–8] There are indications that the same mechanism also applies in the case of cobalt(III) complexes in which the leaving ligand is a carboxylato group,[9–13] such as acetato, AcO^-, or benzoato, $C_6H_5CO_2^-$, under conditions favoring metal–oxygen rather than carbon–oxygen bond breaking.[12]

However, one of the characteristic features of the SN1 CB mechanism, *i.e.*, the essential role of acidic protons present in the amino ligands, as shown by preequilibrium 1, has not been given much attention as yet in mechanistic studies. Work done in this direction with Ru(II) octahedral complexes[14] and with Pd(II) "pseudo-octahedral" complexes[15] does give support to this mechanism. If acidic protons are present in the nondisplaced ligands, the reaction rate depends on the hydroxide ion concentration; if they are absent, no such kinetic effect is observed. Similar indications in support of the above mechanism have also been reported by Basolo, Pearson, and their coworkers[16] with some pyridyl and α,α′-dipyridyl complexes.

In continuation of our work on cobalt(III) carboxylato complexes, we have taken up this problem by replacing en chelating ligands with α,α′-dipyridyl (dipy). We now report a kinetic study of the hydrolysis of *cis*-$Co(dipy)_2(OAc)_2^+$ and *cis*-$Co(dipy)_2(OH_2)(OAc)^{2+}$ in the pH range of 2–12.

Results and Discussion

Course of Reaction.—The *cis*-diacetatobis(α,α′-dipyridyl)cobalt(III) ion undergoes over-all hydrolysis to yield the diaquo complex $Co(dipy)_2(OH_2)_2^{3+}$ or any of the possible hydroxo species, depending on pH, as shown in

$$Co(dipy)_2(OH_2)_2^{3+} + B \rightleftharpoons Co(dipy)_2(OH_2)(OH)^{2+} + HB^+ \qquad (3)$$

$$Co(dipy)_2(OH_2)(OH)^{2+} + B \rightleftharpoons Co(dipy)_2(OH)_2^+ + HB^+ \qquad (4)$$

where B can be either H_2O or OH^-. The reaction is stepwise, as shown by the fact that in acid solution the aquoacetato complex, $Co(dipy)_2(OH_2)(OAc)^{2+}$, was isolated[17] under time-controlled hydrolysis of the diacetato complex and that such an intermediate can in turn be hydrolyzed at varying pH conditions to give the same products of the over-all hydrolysis of the diacetato complex. The actual species involved in the starting material of the latter reaction also depends on the pH of the medium according to

$$Co(dipy)_2(OH_2)(OAc)^{2+} + B \rightleftharpoons Co(dipy)_2(OH)(OAc)^+ + HB^+ \qquad (5)$$

The isolation of the intermediate in the hydrolysis of the diacetato complex depends on the rate of hydrolysis

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of the second acetato ligand relative to the first one (see subsequent sections); while this is possible in sufficiently acidic solutions where the aquo species of eq 5 is predominant, in basic solution it is made difficult by the relatively high rate of the corresponding hydroxo species.

The substrates herein investigated are only *cis* isomers. Since the existence of some previously described *trans*-bis(dipyridyl) complexes of Co(III) has been disproved[18] and *cis*-to-*trans* isomerization reactions do not seem to occur,[17] the products of hydrolysis shown in eq 3–5 are all assumed to be *cis* isomers.

The Aquoacetato Complex.—As the intermediate product of the stepwise hydrolysis, this complex was investigated to the extent of obtaining some essential information related to the main objects of the present paper (see following sections). The pK_a of $Co(dipy)_2(OAc)(OH_2)^{2+}$ was found to be about 6 by a potentiometric determination; in view of the similarity of the OR ligands (R = H, Ac), this result is in accord with the pK_a value of 5.7 for $Co(dipy)_2(OH)(OH_2)^{2+}$ [17] at the same ionic strength. Thus, we can assume this complex to be predominantly in the hydroxo form at pH values above 8 and in the aquo form at pH values below 4. The hydrolysis of either form appeared to be a first-order process; the corresponding rate constants are reported in Table I. In the admittedly narrow pH ranges investigated the rate constants were not found to be significantly sensitive to pH in each region. However, the kinetic form of the reaction with the aquoacetato complex was not studied in any further detail.

TABLE I

KINETIC DATA FOR THE HYDROLYSIS OF THE COMPLEXES $Co(dipy)_2(OAc)(OH_2)^{2+}$ AND $Co(dipy)_2(OAc)(OH)^+$ ([COMPLEX] = 0.001 M, μ = 0.006 M)

Temp, °C	pH (at zero time)	10^6k, sec^{-1}
55	2.5	5.1
55	3.0	5.2
35	11.3	830
35	11.8	790[a]

[a] At $\mu = 7.3 \times 10^{-3}$ M.

At intermediate pH values, under the nonbuffered conditions used in this work, the kinetics are complicated by the acid–base equilibria present in the medium. The pH of the system is not constant throughout the reaction and the proportions of the reactive species (aquo and hydroxo) change accordingly.

The Diacetato Complex.—Table II reports the rate data relative to the hydrolysis of the first functional group of the complex $Co(dipy)_2(OAc)_2^+$ at varying pH values. For the pH range 8–12, first-order kinetics were observed and the rate constants were evaluated on the assumption that the only reaction product is the dihydroxo complex, so the adopted integrated equation was $kt = \ln [a/(a - z)]$, where a is the concentration of the diacetato and z the concentration of the dihydroxo complex, *i.e.*, the product of the overall reaction. The assumption is made valid by the fact that the hydroxo form of the intermediate species hydrolyzes faster than the diacetato complex by a factor of about 10^2. It becomes less and less justified as the initial pH is moved toward the lower end of the above range (9–8); in this case the pH of the system tends to decrease during the reaction, to the extent that the proportion of the aquo form of the intermediate complex increases at the expense of the more reactive hydroxo form. This may explain why in the less basic conditions somewhat lower values for the rate constants are obtained. A typical plot for the more basic conditions (pH 12) is shown in Figure 1.

TABLE II

KINETIC DATA RELATIVE TO THE HYDROLYSIS OF THE FIRST FUNCTIONAL GROUP OF $Co(dipy)_2(OAc)_2^+$ IN BASIC AND ACID SOLUTIONS AT 35°

10^3 [complex], M	pH (at zero time)	$10^3\mu$, M	10^6k, sec^{-1}
1	12.0	11	2.3
1	12.0	11	2.5
1	11.7	6	2.7
1	11.7	6	2.7
2	11.7	10	2.9
1	11.3	5	2.5
1	11.0	2	2.3
1	11.0	2	2.7
1	10.0	10	2.15
1	9.0	10	1.5
1	8.0	10	1.5
1	6.0	50	3.0
1	6.0	6	2.0
1	5.2	6	3.0
1	4.1	6	6.0
1	3.85	50	25
1	3.0	6	58
3	2.53	6	240
3	2.0	13	810

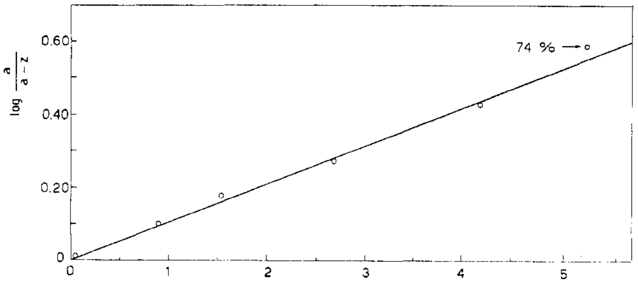

Figure 1.—Hydrolysis in basic solution (pH 12), where a is the initial concentration of the diacetato complex and z is the concentration of the dihydroxo complex.

The reaction appears to be subject to acid catalysis at pH values lower than 6. For a comparison with the first-order rate constants observed in basic solution, apparent first-order rate constants were calculated from the initial slopes of first-order plots, as obtained on the assumption that the only reaction product was the aquoacetato complex. On plotting log k_{obsd} over the whole range investigated (Figure 2), acid catalysis is quite evident at pH values between 2 and 6; the phenomenon has already been reported by other authors[19] for carboxylato cobalt(III) and other complexes[20,21] and is attributed to a protonation preequi-

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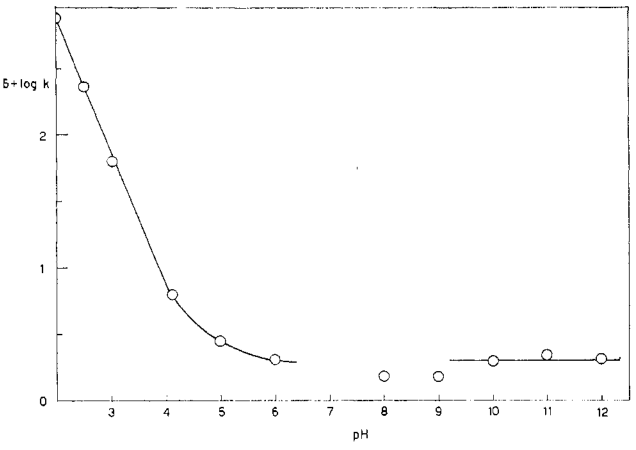

Figure 2.—Dependence of the first-order rate constant k_{obsd} on pH at 35° and μ = 0.006 *M* (acidic range) and 0.010 *M* (basic range).

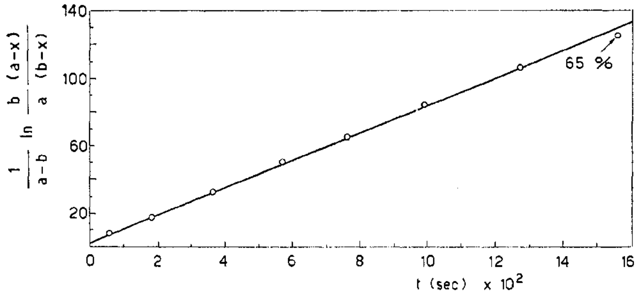

Figure 3.—Hydrolysis in acidic solution (pH 2), where *a* is the initial concentration of the diacetato complex, *b* is the initial concentration of H^+, and *x* is the concentration of the aquoacetato complex.

librium of the participating ligand, according to

$$Co(dipy)_2(OAc)_2^+ + H^+ \rightleftharpoons Co(dipy)_2(OHAc)(OAc)^{2+} \quad (6)$$

$$Co(dipy)_2(OHAc)(OAc)^{2+} + H_2O \xrightarrow{slow} Co(dipy)_2(OAc)(OH_2)^{2+} + AcOH \quad (7)$$

The rate law expected for the over-all process is given by

$$k_{obsd} = k + k_a[H^+] \quad (8)$$

where k and k_a are the specific rate constants for the uncatalyzed and the acid-catalyzed aquations, respectively. Accordingly, the slope of the "acid" branch of the curve reported in Figure 2 is unity. Also, in sufficiently acidic solution (pH 2–3), when $k_a[H^+] >> k$, the reaction was found to be first order in complex and first order in hydrogen ion throughout the reaction. A typical plot is shown in Figure 3 (pH 2). It should be noted that under such conditions there is a net consumption of a proton as the liberated acetato ligand is all in its nondissociated form.

The second-order rate constant obtained at pH values 2.0 and 2.5, 8.3 × 10^{-2} M^{-1} sec^{-1}, turned out to be equal, within experimental error, to the ratio $k_{obsd}/[H^+]$, k_{obsd} being the apparent first-order rate constant observed at the same pH.

The ionic strength was varied in the range of 6 × 10^{-3} to 50 × 10^{-3} *M*. As shown in Table II, the influence on the reaction rate is small.

At intermediate pH values, kinetic complications arise for reasons similar to the case of the aquoacetato complex (see preceding section). Thus, the pH of the system is not constant throughout the reaction and, consequently, the relative contribution of the two terms of eq 8 also changes.

Reaction Mechanisms.—We are now able to discuss the implications of the data illustrated in the preceding sections. Both the aquoacetato and the diacetato complexes seem to undergo an aquation reaction in the range of pH 2–12, corresponding to a first-order process. In the case of the diacetato complex the reactive species is the unipositive ion itself, except in the lower pH end where an acid-catalyzed process sets in, presumably involving the protonated dipositive ion $Co(dipy)_2(AcOH)(AcO)^{2+}$ as the more reactive species. As to the aquoacetato complex, the reaction involves predominantly either the aquo or the hydroxo species, as long as the pH of the medium is below 4 and above 8, respectively. The main result is the lack of hydroxide ion catalysis up to pH 12 under conditions whereby diacetatobis(ethylenediamino)cobalt complexes[11] and, more generally, acidic-proton-containing cobalt complexes display first-order dependence on hydroxide ion.[3] This result parallels that found by Bosnich[14] for octahedral bis(dipyridyl)ruthenium(II) complexes and is in accord with the view that the hydroxide ion has relatively little tendency to promote bimolecular attack in this type of reaction.

On dividing the first-order rate constant by the molarity of water we obtain a rate constant value of 4.5 × 10^{-8} in second-order units. It is of interest to note that this value is much lower than that found[11a] for the *cis*-bis(ethylenediamine)diacetato complex, 2.41 × 10^{-2}. Were the latter complex subject to some kind of bimolecular attack by the hydroxide ion, the rate for the corresponding reaction of the bis(dipyridyl)-diacetato complex should be distinctly lower than 4.5 × 10^{-8}. This dramatic rate-depressing effect could hardly be accounted for by the structure effect of the *intact* chelating ligands. Thus bimolecular mechanisms appear to be mutually inconsistent in the above comparison, and while the reaction of $Co(en)_2(OAc)_2^+$ is speeded up by the formation of the reactive conjugate base, that of $Co(dipy)_2(OAc)_2^+$ is likely to occur by a dissociative mechanism, in accord with other findings in octahedral complexes.[22–24]

Replacement of an acetato ligand with a hydroxo group gives rise to a large increase in the rate of hydrolysis of the remaining carboxylato group, while the kinetic form remains unchanged. This structural effect can be attributed to π bonding of the hydroxo group with the central metal atom and is also strongly suggestive of a dissociation process[25] where metal–leaving group bond breaking is rate determining. A similar replacement in the analogous bis(ethylenedi-

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amine) complexes is not so effective from the point of view of π bonding possibly because of a structural competition by the H-containing en ligands, as was discussed in the preceding paper.[11b]

The behavior of the *cis*-bis(dipyridyl) complexes described above proves that the presence of acidic protons is essential for the complexes of the type $Co(NH_3)_5X^{n+}$ or $Co(en)_2AX^{n+}$ to undergo base hydrolysis by second-order kinetics and yields further support to the SN1 CB mechanism for the latter reactions (see Introduction). The low reactivity of these complexes, particularly that of the diacetato, reflects their inability to produce a conjugate base from the amino ligands.

It is to be noted that the alternative mechanisms proposed for such reactions in recent years[26,27] are not too different from the SN1 CB mechanism itself. Thus, Chan[27] favors a reaction *via* preliminary ion-pair formation which is also a two-stage process, SN1 IP or SN2 IP. Furthermore, the essential requirement of the presence of acidic protons for a two-stage process indicates that were ion-pair formation rather than an acid–base interaction operative in the first stage, the ion pair would consist of a specific association involving one of the acidic protons in a sort of H-bonding interaction. In this way, the preequilibria related to the SN1 CB and the "ion-pair" mechanisms would only differ in the position of the proton for such an interaction as shown by eq 9 and 10, respectively,

$$\text{ZL–H} + \text{OH}^- \rightleftharpoons \text{ZL}^-\text{-----H–OH} \qquad (9)$$

$$\text{ZL–H} + \text{OH}^- \rightleftharpoons \text{ZL–H-----OH}^- \qquad (10)$$

where Z is a complex residue and LH an H-containing ligand. Both types of mechanisms require that association occurs but to a slight extent. As to the second stage, the ion-pair mechanism does not differ from the SN1 CB if the ion pair breaks down by a unimolecular process whereas the distinction between SN1 IP and SN2 IP (bimolecular internal rearrangement) appears to be a rather subtle one and still experimentally intriguing.

Experimental Section

Materials.—The complexes *cis*-$[Co(dipy)_2(OAc)_2]ClO_4$, *cis*-$[Co(dipy)_2(H_2O)(OAc)](ClO_4)_2$, and *cis*-$[Co(dipy)_2(H_2O)_2](ClO_4)_3$ have been prepared according to the method described in a previous paper.[17] Commercial reagent grade reagents have been used throughout this work. For the kinetic experiments, freshly boiled distilled water was stored in a flask provided with a soda-lime tube just before use.

Hydrolysis of the Complexes.—Product analysis experiments were set up in both acidic and basic conditions by keeping aqueous solutions, 0.003 *M* in diacetato complex and 0.01 *M* in either $HClO_4$ or NaOH, in a bath at 50° for 1 week. Similar experiments were run with the aquoacetato complex in acid solution at 60° for 10 days and in basic solution at 35° for 3 days.

The visible spectra of all of the solutions were recorded at the end of each experiment and compared[17] with the spectrum of the complex ion $Co(dipy)_2(H_2O)_2^{3+}$ or $Co(dipy)_2(OH)_2^+$ depending on pH.

Rate Measurements.—The rates of hydrolysis were followed by a potentiometric method using a Beckman Model G pH meter provided with conventional external glass and calomel electrodes. A 200- or 250-ml volumetric flask was partially filled with a solution containing a calculated amount of the complex and thermally equilibrated in a water thermostat set at the desired temperature with a precision better than ±0.1°. The calculated volume of standard solutions of sodium hydroxide or perchloric acid was then added, and the flask was finally filled to the mark. In order to attain the desired pH value, in the case of the base hydrolysis of $Co(dipy)_2(H_2O)(OAc)^{2+}$ an additional equivalent of base was used, as required for the neutralization of the aquo complex. Alternatively, in the case of the faster reactions, the acidic or basic reagent was added last and under efficient mechanical stirring to the kinetic solution. The reaction flasks were protected from daylight by wrapping them with an aluminum sheet.

A number of 20- or 25-ml samples were withdrawn at convenient time intervals and analyzed potentiometrically for acids. Each sample was quenched by adding perchloric acid (basic runs) or by chilling (acidic runs) and the resulting solution was titrated with CO_2-free 0.01 *N* sodium hydroxide. Quenched solutions were never more acid than pH 4.5.

The mean error in the rate constant values was better than 4%. In all experiments $NaClO_4$ was used to adjust the ionic strength to the desired value.

Spectrophotometric Measurements.—The visible spectra of aqueous solutions of complexes were determined with a Beckman DU quartz spectrophotometer.

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