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Reaction Sequence in the Hydroxo-Bridge Cleavage of the Tri-μ-hydroxo-bis[triamminecobalt(III)] Complex. Identification of an Isomerization Step

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Further details of hydroxo-bridge cleavage of the tri-μ-hydroxo-bis[triamminecobalt(III)] complex, $[(NH_3)_3Co(\mu\text{-}(OH,OH,OH))Co(NH_3)_3]^{3+}$, have been obtained, $I = 1.00$ M ($LiClO_4$). The faster equilibration stopped-flow step, forward rate constant $k_a = 4.22$ M^{-1} s^{-1} at 25 °C, which was previously assigned to slow protonation, is here alternatively assigned to first bridge cleavage. Activation parameters ($\Delta H^{\ddagger} = 11.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -18.3$ cal K^{-1} mol^{-1}) and deuterium isotope effects support such an assignment. The slower equilibration stopped-flow step is now believed to correspond to a process involving isomerization of water ligands into trans (opposed) positions. Details of the $[H^+]$ dependence for the slower (conventional) third observable step, involving cleavage of the second bridge, are clarified. The final product *fac*-$[Co(NH_3)_3(H_2O)_3]^{3+}$ is formed with cleavage of the third bridge in a relatively fast non-rate-determining step. Rate constants and activation parameters have now been obtained for three forward and two reverse steps in the reaction sequence.

Introduction

Kinetic studies on the hydroxo-bridge cleavage of the tri-μ-hydroxo complex $[(NH_3)_3Co(\mu\text{-}(OH,OH,OH))Co(NH_3)_3]^{3+}$ have been reported previously.[1-3] Involvement of an isomerization step first became a possibility once it had been demonstrated that the di-μ-hydroxo-bisaquo intermediate $[(NH_3)_3(H_2O)Co(\mu\text{-}(OH,OH))Co(H_2O(NH_3)_3]^{4+}$ (isolated as the nitrate salt) had H_2O ligands in trans (opposed) positions.[4] Studies reported here have yielded further relevant information regarding the mechanism.

Experimental Section

Reactants. These were prepared as described previously.[2] To obtain a completely deuterated sample of the tri-μ-hydroxo complex, $[(NH_3)Co(\mu\text{-}(OH,OH,OH))Co(NH_3)_3](ClO_4)_3\cdot 2H_2O$, the latter (6 g) was first left in vacuo over P_2O_5 for 2 weeks to remove the $2H_2O$. The complex was then dissolved in D_2O (99.75%, Merck) and a few drops of 0.1 M NaOD in D_2O added. Analar (dehydrated) $NaClO_4$ was added after a few minutes and the solution cooled to 0 °C. Crystals of the perchlorate salt were filtered off, and the sample was recrystallized twice, when the IR spectrum showed no ν(O–H) or ν(N–H) stretching frequencies at 3600–3100 cm^{-1}. Dehydration experiments over P_2O_5 were consistent with the formula $[(ND_3)_3Co(\mu\text{-}(OD,OD,OD))Co(ND_3)_3](ClO_4)_3\cdot 2D_2O$.

Kinetic Studies. There are three observable stages in conversion to a mononuclear complex, the first two of which can be monitored using a stopped-flow (Durrum Instrument). The first stage was monitored at 544 nm (increased in absorbance). A full study has already been made of the second stage at 450 and 544 nm (also an increase in absorbance).[2] Conventional spectrophotometry, Unicam SP500, was used to study the third stage at 362 nm (decrease in absorbance). The third stage was also studied at 295 nm, $I = 3.00$ M ($LiClO_4$). Incidence of the second stage prevented accurate absorbance A_∞ values for the first stage being obtained from oscilloscope traces. Instead the Guggenheim method of evaluating rate constants was used.[5]

The ionic strength was adjusted to $I = 1.00$ M ($LiClO_4$) or (for more extensive range of $[H^+]$ for third stage) $I = 3.00$ M ($LiClO_4$).

First-order plots of log ΔA against time for the third stage were linear to 95% completion.

An unweighted nonlinear least-squares program[6] was used in evaluating all parameters.

Results

First-order rate constants k_{eq}, Table I,[7] give a dependence (eq 1) on $[H^+]$ (Figure 1), where k_a and k_{-a} are believed to

$$k_{eq} = k_a[H^+] + k_{-a} \tag{1}$$

correspond to forward and reverse (equilibration) steps. Rate constants and activation parameters are summarized in Table IV. Rate constants $k_{eq}{}^D$ for the deuterated complex in D_2O solution $[D^+] = 0.05$, 0.10, 0.25, and 0.50 M were $k_{eq}{}^D = 1.58$ (3), 2.12 (2), 2.91 (5), and 4.76 (2) s^{-1}, respectively (number of runs averaged in parentheses). These give at 25 °C $k_a/k_a{}^D = 0.64$ and $k_{-a}/k_{-a}{}^D = 1.3$, where $k_a{}^D$ and $k_{-a}{}^D$ are parameters as defined in eq 1 for the deuterated complex.

Crossover points from spectra of tri-μ-hydroxo and di-μ-hydroxo-bisaquo (trans) complexes are at 269 ± 3, 341 ± 5, and 511 ± 3 nm. By varying the wavelength setting on the stopped-flow three isosbestic points were identified for the first stage at 265 ± 3, 339 ± 10, and 524 ± 2 nm ($[H^+] = 0.25$ and 1.00 M). For the second stage (the study reported in ref 2) isosbestics were at 265 ± 6, 358 ± 10 and 504 ± 3 ($[H^+] = 1.0$ M; with $[H^+] = 0.25$ M the latter was at 513 ± 2).

Rate constants k_{obsd} for the third stage are given in Table II.[7] The best fit of data is given by eq 2 where k'_c is small.

$$k_{obsd} = k_c[H^+] + k'_c \tag{2}$$

This same dependence was observed for a wider $[H^+]$ range, 0.05–3.00 M at $I = 3.00$ M ($LiClO_4$), Table III.[7] No evidence was obtained for a less than first-order dependence on $[H^+]$ as suggested in ref 1. Since the final step yielding *fac*-$Co(NH_3)_3(H_2O)_3{}^{3+}$ is believed to be rapid, k_{obsd} is not an equilibration process, and k'_c is therefore assigned to an $[H^+]$-independent contribution to bridge cleavage. Rate constants and activation parameters are again listed in Table IV.

Table IV. Summary of Kinetic and Thermodynamic Data for the Hydroxo-Bridge Cleavage of the Tri-μ-hydroxo-bis[triamminecobalt(III)] Complex, Reaction Sequence, and Rate Constants as Defined in Eq 3-5, I = 1.00 M ($LiClO_4$)

Constant	Value at 25 °C	Enthalpy, kcal mol^{-1}	Entropy, cal K^{-1} mol^{-1}	Comment
k_a	4.22 M^{-1} s^{-1}	11.2 ± 2.0[a]	−18.3 ± 6.7[a]	This work
k_{-a}	1.80 s^{-1}	17.4 ± 1.6[a]	0.8 ± 5.0[a]	This work
K_a	2.34 M^{-1}	−6.2[b]	−19.1[b]	Ratio k_a/k_{-a}
k_b	0.186 s^{-1}	23.4[a]	16.6[a]	k_1 of ref 1
k_{-b}	0.0066 s^{-1}	22.8[a]	7.6[a]	k_1 of ref 1
K_b	27.9	0.6[b]	9.0[b]	Ratio k_b/k_{-b}
k_c	6.07 × 10^{-5} M^{-1} s^{-1}	18.1 ± 0.8[a]	−17.1 ± 2.7[a]	This work
k'_c	0.095 × 10^{-5} s^{-1}	32 ± 6[a]	21 ± 20[a]	This work

[a] Activation parameters. [b] Thermodynamic parameters.

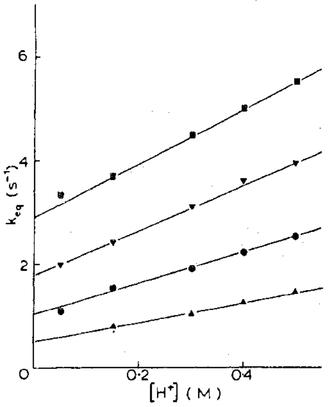


Figure 1. The dependence of equilibration rate constants, k_{eq}, for the first stage in the hydroxo-bridge cleavage of the tri-μ-hydroxo-bis[triamminecobalt(III)] complex, $[(NH_3)_3Co(\mu\text{-}(OH,OH,OH))Co(NH_3)_3]^{3+}$, on [$H^+$], I = 1.00 M ($LiClO_4$).

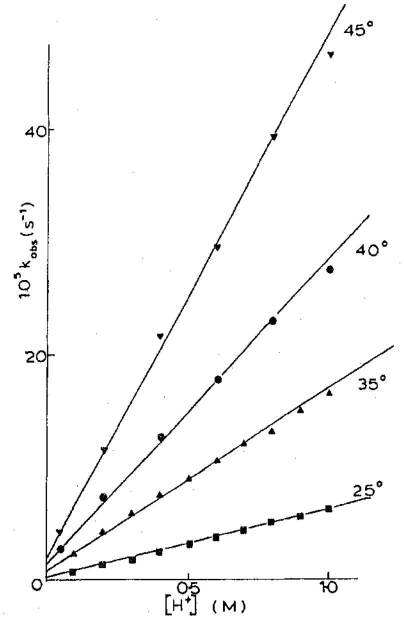
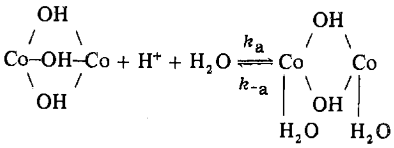
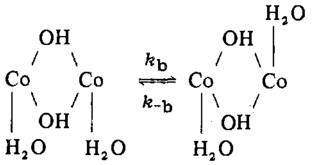
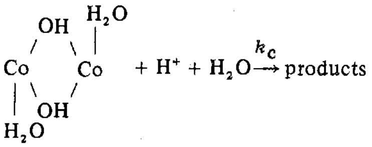


Figure 2. The dependence of rate constants, k_{obsd}, for the third stage in the hydroxo-bridge cleavage of the tri-μ-hydroxo-bis[triamminecobalt(III)] complex, $[(NH_3)_3Co(\mu\text{-}(OH,OH,OH))Co(NH_3)_3]^{3+}$, on [$H^+$], I = 1.00 M ($LiClO_4$).


(3)


(4)


(5)

Discussion

Three stages have been monitored in the hydroxo-bridge cleavage of the tri-μ-hydroxo complex to mononuclear product. A feature of the mechanism (eq 3–5) now proposed is the inclusion of an isomerism step (eq 4). If, as proposed,[1] the first equilibration to be monitored corresponded to protonation without bridge cleavage, protonation rate constant 4.22 M^{-1} s^{-1} (deprotonation rate constant 1.85 s^{-1}), it would indeed be an exceptionally slow process.[8] Slow proton-transfer steps are known. For example in the reaction $H^+ + OH^- \rightleftharpoons H_2O$ which is written as

$$H_3O^+ + OH^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_2O + H_2O \qquad (6)$$

rate constants (25 °C) are k_f = 1.4 × 10^{11} M^{-1} s^{-1} and k_r = 2.5 × 10^{-5} s^{-1}.[9] The widely different rate constants observed reflect the different basicities of H_3O^+ (strongly acidic) and H_2O. In the proton-transfer equilibration (eq 7), both H_3O^+

$$\mu\text{-}(OH,OH,OH) + H_3O^+ \rightleftharpoons \mu\text{-}(OH,OH,OH_2) + H_2O \qquad (7)$$

and μ-(OH,OH,OH_2) are strongly acidic. While it would be reasonable for one of the forward or reverse rate constants here to be slow (providing there were a sufficiently large difference in acidities), we feel that two slow proton transfer steps are unlikely in this situation. Assuming bridge cleavage (eq 3) occurs, the activation parameters for k_a (a composite constant) are similar in magnitude to those obtained for other hydroxo-bridge cleavage processes involving binuclear cobalt(III) complexes.[10] Furthermore deuterium isotope effects give $k_a/k_a{}^D$ = 0.63 and $k_{-a}/k_{-a}{}^D$ = 1.3 which do not support protonation without bridge cleavage. If protonation alone were involved, a primary isotope effect (factor of 2–10) and a secondary solvent effect (>1) would be expected.[11] This is clearly not the case. The observed ratios are satisfactorily accounted for in terms of eq 3, where k_a is the product of the protonation equilibrium constant (K_p) and rate constant for bridge cleavage. For a strongly acidic species such as is formed in eq 3, it is estimated that K_p will be $<K_p{}^D$ by a factor of between 1 and 2.[12] Only a small isotope effect is expected for the bridge cleavage (and formation) rate constant since no bonds to H or D are directly involved. Finally three isosbestic points were observed for both the first and second stages (eq 3 and 4), where these are in fairly close agreement. The two isomeric bisaquo complexes in eq 4 probably have very similar spectra.

The second stage (eq 4) although primarily an isomerization step results in a displacement of eq 3 and therefore exhibits an $[H^+]$ dependence. We reassign the kinetics as presented in ref 2 to this second stage. The $[H^+]$ dependence observed experimentally can accordingly be written as in eq 8. Although agreement of $K_a = 1.51\ M^{-1}$, $\Delta H_a = -9.7 \pm 3.7$, $\Delta S_a = -31.2 \pm 12.2$, with K_a ($= k_a/k_{-a}$) in Table IV is satisfactory (bearing in mind the complexity of eq 6), the possibility that an $[H^+]$-independent pathway makes some small contributions to the forward reaction in eq 3 cannot be ruled out. Such contributions would be difficult to detect since the reverse step k_{-a} is effective. The activation parameters for k_b and k_{-b}, Table IV, are consistent with an isomerization process at the cobalt(III).[13]

$$k_{obsd} = \frac{k_b K_a[H^+]}{1 + K_a[H^+]} + k_{-b} \qquad (8)$$

The interpretation given in ref 2 for the di-μ-hydroxo-μ-amido-bis[triamminecobalt(III)] complex remains unchanged. The question which remains unanswered with regard to the latter is whether k_{-2} includes (as a relatively rapid equilibration) an isomerization step and indeed whether isomerization to the trans form takes place at all. The introduction of an isomerization step in the present study is a direct consequence of the crystal structure of the hydrated nitrate salt of the di-μ-hydroxo complex $[(NH_3)_3(H_2O)Co(\mu\text{-}(OH,OH))Co(H_2O)(NH_3)_3](NO_3)_4 \cdot H_2O$ (refined to $R = 0.032$).[4] In the latter, H-atom positions were obtained from a difference synthesis, which resulted in an unambiguous assignment of all H-bonds and enabled the H_2O and NH_3 groups to be distinguished. Thus the H_2O ligands were found to donate two short H-bonds (2.62 and 2.72 Å) as can be expected for a water molecule bonded to a trivalent cation, while the NH_3 in question (occupying the position that would have been occupied by a cis H_2O) forms three long H-bonds (2.94, 3.16, and 3.21 Å) as do other NH_3 ligands present. The number and length of these contacts leave no doubt as to the H_2O and NH_3 site occupancies. No similar crystallographic study has been carried out for the μ-hydroxo-μ-amido-bisaquo complex.

A simple hydrogen-ion dependence (eq 2) applies to the third stage for the tri-μ-hydroxo complex where k'_c corresponds to an $[H^+]$-independent contribution to the bridge-cleavage process. No evidence was obtained for an equilibration process, and since bridge cleavage of the singly bonded μ-hydroxo complex $[(NH_3)_5Co(\mu\text{-}OH)Co(NH_3)_5]^{5+}$ is known to be significantly more rapid,[9] we interpret in terms of a subsequent more rapid cleavage of the third and final bridge. The reverse step in eq 5 does not therefore, for the range of $[H^+]$ investigated, contribute. We do not rule out bridge cleavage of the cis bisaquo di-μ-hydroxo complex as an effective path. However $K_b = 27.9$ at 25 °C, and the cis complex is very much a minority species compared to the trans form. Unless there is an exceptionally large rate enhancement, contributions from such a path would not be expected to be significant.

The overall picture for hydroxo-bridge cleavage which emerges from this study is one of relatively rapid first bridge cleavage, slow cleavage of the second bridge, and relatively rapid cleavage of the final bridge. Interestingly $\Delta H^{\ddagger}$ for k_c (eq 5) is similar in magnitude to that observed by Hoffman and Taube[14] for the di-μ-hydroxo complex $(NH_3)_4Co(\mu\text{-}(OH,OH))Co(NH_3)_4{}^{4+}$ ($\Delta H^{\ddagger} = 16.3$ kcal mol^{-1}; $\Delta S^{\ddagger} = -17$ cal K^{-1} mol^{-1}). Both values are greater than $\Delta H^{\ddagger}$ for cleavage of triply bridged complexes (11.2 kcal mol^{-1} for k_a, 12.4 kcal mol^{-1} for the μ-(NH_2,OH,OH) complex[2]) and a singly bridged complex (12.0 kcal mol^{-1}).[4]

The isomerization step proceeds by an $[H^+]$-independent path, and the mechanism is presumably one involving hydrogen bonding between a water ligand and one of the two hydroxo bridges. Synchronous proton transfer and displacement of the hydroxo bridge are envisaged, the latter taking up the new aquo ligand position. Accompanying rearrangement of NH_3 ligands is required.

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Registry No. $[(NH_3)_3Co(\mu\text{-}(OH,OH,OH))Co(NH_3)_3]^{3+}$, 45976-80-5; deuterium, 7782-39-0.

Supplementary Material Available: Listings of rate constants, Tables I–III (3 pages). Ordering information is given on any current masthead page.

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