Labilization by steric crowding. Hydrolysis and racemization kinetics of Co(tmen)$_3^{3+}$, tmen = 2,3-diamino-2,3-dimethylbutane

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Abstract

Hydrolysis and racemization of Co(tmen)$_3^{3+}$ (tmen = 2,3-diamino-2,3-dimethylbutane) follow the rate law, rate = k[Co(tmen)$_3^{3+}$][OH⁻] in the pH range 4.8 to 13.8. Kinetic parameters are k(hydr) = 2.5 ± 0.8 M⁻¹ s⁻¹ (298 K), ΔH^*(hydr) = 132 ± 3 kJ mol⁻¹, ΔS^*(hydr) = 144 ± 23 J K⁻¹ mol⁻¹, ΔV^*(hydr) = 57.6 ± 0.9 cm³ mol⁻¹; k(rac) = 273 ± 14 M⁻¹ s⁻¹ (298 K), ΔH^*(rac) = 117 ± 3 kJ mol⁻¹, ΔS^*(rac) = 87 ± 20 J K⁻¹ mol⁻¹. A conjugate base mechanism D(CB) is assigned to the hydrolysis reaction which proceeds from the singly deprotonated complex via a five-coordinate intermediate followed by a rapid dissociation of the monodentate *trans*-ligand and *cis-trans* isomerization to the final *trans*-Co(tmen)$_2$(H$_2$O)$_2^{3+}$. The operation of a D(CB) mechanism is supported by a large positive activation entropy and a remarkably large activation volume of +60 cm³ mol⁻¹. For the faster racemization the deprotonation is followed by the inversion process without Co−N bond cleavage corresponding to a Bailar twist. As a consequence of the steric crowding of the twelve peripheral methyl groups, both processes are faster by at least nine orders of magnitude than for the parent Co(en)$_3^{3+}$ complex.

Introduction

The best established example of a robust coordination compound is the tris-chelate Co(en)$_3^{3+}$ (en = 1,2-diaminoethane). This complex ion is inert to substitution in acidic and neutral solution up to 100 °C. Base hydrolysis occurs at reasonable rates only above 70 °C, with an apparent second order rate constant of 3 × 10⁻⁹ M⁻¹ s⁻¹ at 298 K. This reaction is catalyzed by charcoal, the rate of the reaction being approximately first order in absorbed [Co(en)$_3^{3+}$] and [OH⁻] [1].

Resolved Co(en)$_3^{3+}$ is apparently racemized at high temperatures and high pH. The observed loss of rotatory power of the solution, however, is due to the hydrolysis reaction and to the formation of *cis*- and *trans*-[Co(en)$_2$(OH)$_2$]⁺, which are in rapid equilibrium. Racemization occurs without net hydrolysis in the presence of a large excess of free en. Ligand exchange, however, proceeds as a competing reaction implying Co−N bond cleavage in the mechanism of racemization [2]. Both processes are catalyzed by surface catalysts such as charcoal. In contrast to the vast amount of kinetic data for the pentaammine species, very little data are available for other tris-bidentate complexes [3].

In a recent study of the reduction kinetics of the Co(tmen)$_3^{3+/2+}$ couple (tmen = 2,3-diamino-2,3-dimethylbutane) an enormous acceleration of the hydrolysis for this fully methylated complex ion was observed in comparison to the parent Co(en)$_3^{3+}$ [4]. This, for low-spin Co(III) compounds, completely atypical labile behavior prompted the study of the hydrolysis and racemization kinetics of the title complex. In addition we studied the pressure dependence of the hydrolysis process to serve as a comparison for all the activation volumes available for base hydrolysis of 30 Co(III) amine complexes [5–7]. To our surprise we found the largest pressure dependence ever detected for such reactions.

Experimental

Samples and solutions

The preparation of Co(tmen)$_3$Cl$_3$ followed published procedures [4]. Partial resolution of the

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racemic salt into its enantiomeric forms was achieved with (−)tris(catecholato)arsenate(V) [8]. (+)Co(tmen)$_3{}^{3+}$, forming a very sparingly soluble salt, was removed by filtration. Addition of conc. HCl to the remaining solution precipitated solid (−)Co(tmen)$_3$Cl$_3$.

The following solutions ($\mu = 1.0$ M (NaClO$_4$)) were employed for hydrolysis and racemization: 0.2 M CAPS (3-(cyclohexylamino)-1-propanesulfonic acid); 0.2 M TRIS (tris(hydroxymethyl)aminomethane); 0.2 M HEPES (N-2-hydroxyethyl-piperazine-N'-2-ethanesulfonic acid); 0.1 M citric acid + 0.2 M Na$_2$HPO$_4$.

Instrumentation

Conventional kinetics was followed in the UV − Vis range by using a HP 8451 A diode array spectrophotometer and a PE 241 MC polarimeter. Stopped-flow experiments at high pH were carried out with a Hi-Tech Scientific instrument equipped with a HP computer at ambient conditions and a home-made high pressure stopped-flow instrument for pressures up to 100 MPa [9]. pH was measured with a standard glass electrode and converted to OH$^-$ concentration using a pK_w value for water of 13.77 at 1.0 M ionic strength [10].

Kinetic measurements

Hydrolysis and racemization reactions were studied by using buffer concentrations adequate to ensure pseudo-first order conditions. For the hydrolysis kinetics the decrease in absorbance at 504 nm (λ_{max} of Co(tmen)$_3{}^{3+}$) was monitored. Racemization kinetics was monitored by measuring the decrease of optical rotation at 589 nm. All measurements were carried out in thermostatted cells (±0.1 °C) in the temperature range 5.5 to 40 °C.

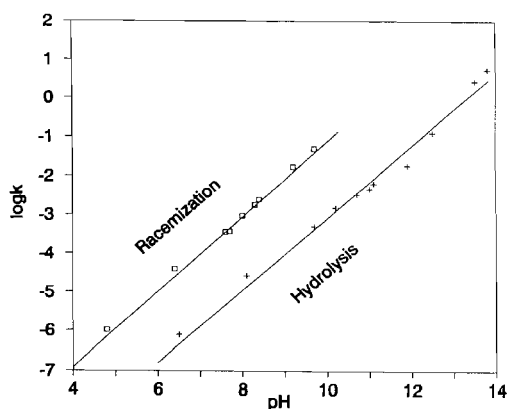Fig. 1. Log k vs. pH plot for first order rate constants.

Results and discussion

Kinetic data at room temperature (24.6 ± 0.1 °C) are collected as observed pseudo-first order rate constants k_{obs} in Table 1. Whereas hydrolysis could be studied in the pH range 6.5 − 13.8, racemization became too fast at pH > 9.7 to be followed by conventional procedures. The kinetics of racemization was also followed in 0.1 M HClO$_4$ over a period of 10 months. During this long-term semiquantitative experiment at a temperature fluctuating between 20 and 24 °C the chirality decayed with a first order rate constant of about 1.5×10^{-8} s^{-1}, whereas an apparent rate constant of less than 10^{-9} s^{-1} was estimated from an analogous experiment for hydrolysis in the same medium.

A log k_{obs} versus pH plot (Fig. 1) clearly demonstrates that both reactions follow a general rate law of the form k[Co(tmen)$_3{}^{3+}$][OH$^-$] over the entire pH range studied. The corresponding slopes are 0.91 ± 0.04 and 0.94 ± 0.02 for the hydrolysis and racemization reactions, respectively. From these data we extract the two second-order rate constants k(hydrolysis) = 2.5 ± 0.8 M^{-1} s^{-1} and k(racemization) = 273 ± 14 M^{-1} s^{-1} (298 K). Both reactions proceed faster by many orders of magnitude for the Co(tmen)$_3{}^{3+}$ ion than for the parent Co(en)$_3{}^{3+}$. The magnitude of the difference is indicated by the comparison of the estimated half-lives in 0.5 M NaOH, for hydrolysis about 14 years and 0.5 s for Co(en)$_3{}^{3+}$ [1] and for Co(tmen)$_3{}^{3+}$, respectively. The half-life for racemization of Co(tmen)$_3{}^{3+}$ is only 5 ms. The complete methylation of the carbon backbone of en obviously causes a radical change from a very inert to a truly labile behavior.

Variation of the buffer concentration does not affect the kinetics of the two reactions, a general acid or base dependent path can therefore be excluded. Likewise the reactions have no dependence on counter ion, with the exception of phosphate, which will be discussed below.

The observed kinetic data measured under pseudo-first order conditions (Table 2) were converted into k(hydr) and k(rac) and analyzed according to $k = (k_B T/h) \exp(\Delta S^*/R - \Delta H^*/RT)$. The kinetic parameters for hydrolysis are k (298 K) = 2.5 ± 0.8 M^{-1} s^{-1}, $\Delta H^* = 132 ± 3$ kJ mol^{-1} and $\Delta S^* = 144 ± 23$ J K^{-1} mol^{-1}. For the racemization process the following values are obtained: k (298 K) = 273 ± 14 M^{-1} s^{-1}, $\Delta H^* = 117 ± 3$ kJ mol^{-1} and $\Delta S^* = 87 ± 20$ J K^{-1} mol^{-1}.

The pressure dependence of the hydrolysis reaction was studied for 0.1 M base at 0.1 and 1.0 M ionic strength, and the results are summarized in Table 3. The lower ionic strength was selected in order

TABLE 1. Pseudo-first order rate constants for hydrolysis and racemization of $Co(tmen)_3^{3+}$; 1 M $NaClO_4$, pH adjusted by NaOH or HCl when no buffer is given; temperature: 24.6 ± 0.1 °C

	Hydrolysis			Racemization	
	pH	k_{obs} (s^{-1})		pH	k_{obs} (s^{-1})
1 M NaOH	13.8	5.28 ± 0.19	0.2 M CAPS	9.7	$(5.01 \pm 0.18) \times 10^{-2}$
0.5 M NaOH	13.5	2.66 ± 0.06	0.2 M TRIS	9.2	$(1.71 \pm 0.04) \times 10^{-2}$
0.05 M NaOH	12.5	0.125 ± 0.004	0.2 M TRIS	8.4	$(2.52 \pm 0.04) \times 10^{-3}$
0.012 M NaOH	11.9	$(1.83 \pm 0.05) \times 10^{-2}$	0.2 M TRIS	8.3	$(1.81 \pm 0.03) \times 10^{-3}$
0.05 M tmen	11.1	$(6.33 \pm 0.38) \times 10^{-3}$	0.2 M TRIS	8.0	$(9.62 \pm 0.32) \times 10^{-4}$
0.2 M CAPS	11.0	$(4.69 \pm 0.12) \times 10^{-3}$	0.2 M HEPES	7.7	$(3.81 \pm 0.08) \times 10^{-4}$
0.2 M CAPS	10.7	$(3.37 \pm 0.10) \times 10^{-3}$	0.2 M TRIS	7.6	$(3.7 \pm 0.19) \times 10^{-4}$
0.2 M CAPS	10.2	$(1.52 \pm 0.04) \times 10^{-3}$		6.4	$(4.06 \pm 0.81) \times 10^{-5}$
0.2 M CAPS	9.7	$(5.14 \pm 0.32) \times 10^{-4}$		4.8	$(1.05 \pm 0.05) \times 10^{-6}$
0.2 M HEPES	8.1	$(2.73 \pm 0.6) \times 10^{-5}$			
	6.5	$(7.84 \pm 0.41) \times 10^{-7}$			

to be able to compare the results of this study with earlier reported data for a series of Co(III) amine complexes [5–7]. Plots of ln k_{obs} versus pressure are linear in both cases and result in the activation volumes, calculated from the slope $(= -\Delta V^*/RT)$ of such plots, included in Table 3.

Within the pH range considered racemization is always faster than hydrolysis. In phosphate buffers between pH 4 and 7, however, the rate of hydrolysis apparently exceeds that of racemization (Table 4). This implies the loss of one tmen ligand to be a crucial step for both reactions, indicating in turn a specific interaction between $Co(tmen)_3^{3+}$ and the protonated phosphate anion. This interaction is also observed in the absorption spectrum of the complex ion; in the presence of phosphate the two ligand field bands are shifted to higher energies by about 160 cm^{-1}. An analogous effect is observed for $Co(en)_3^{3+}$ and is attributed to a strong ion-pair formation due to H bonds N—H...O—P. The amine protons are correctly oriented for this strong H-bonding only when the complex is in the lel_3 conformation. The presence of phosphate ions thus stabilizes the lel_3 conformation which produces a slightly stronger ligand field than the ob_3 form [3, 11–13]. Interestingly the rate of racemization in phosphate buffers at pH 6.2 and 7.2 is lower than in the absence of phosphate. This implies that the interaction with phosphate deactivates the complex to racemization but activates its hydrolysis. Thus the decrease in the rate of racemization is not simply due to an increase in pK_a of the coordinated amines in the presence of phosphate. It is more likely that the lel_3 structure, apparently stabilized by phosphate, is less prone to racemization than the conformer predominating in solution in the absence of phosphate. In the solid state the ob_3 conformation is observed [14].

Mechanistic considerations

In contrast to $Co(en)_3^{3+}$ its methylated derivative $Co(tmen)_3^{3+}$ easily hydrolyzes and racemizes in neutral and alkaline media at room temperature. The observed rate law for both reactions depends linearly on the OH$^-$ concentration. We thus conclude that a conjugate base D(CB) mechanism applies for hydrolysis as well as racemization. This conclusion is supported by the activation parameters, in particular ΔS^* and ΔV^*.

Since hydrolysis leads to $trans$-$Co(tmen)_2Aq^{n+}$, where Aq represents H_2O or OH$^-$, we propose the following reaction scheme (see page 88).The step following the deprotonation of one coordinated amine involves the cleaving of a Co—N bond, presumably that $trans$ to the deprotonated amino group [15]. This resulting five-coordinate intermediate is converted into the final $trans$-$Co(tmen)_2Aq_2^{n+}$ via loss of a tmen ligand and rapid cis—$trans$ isomerization.

The observed second order rate constant essentially consists of the deprotonation constant K_a and the rate of dissociation k_D of the ligand from the deprotonated complex. This interpretation implies a pK_a value of the coordinated amine in the order of 15 or greater in order to observe an overall second order rate constant, i.e. a linear dependence of k_{obs} on [OH$^-$], $k_{obs} = K_a k_D[OH^-] = k(hydr)[OH^-]$.

The extremely high values for ΔV^*(hydr) are also in line with the suggested mechanism. In terms of an overall reaction volume profile [5–7], ΔV^*(hydr) $= \Delta V(K_a) + \Delta V^*(k_D)$ since $k(hydr) = K_a k_D$. Both these quantities will depend on intrinsic and solvational volume changes [16] associated with the hydrolysis process. For the deprotonation of $Co(tmen)_3^{3+}$ we expect $\Delta V(K_a)$ to have a value of approximately 27 cm^3 mol^{-1}, based on that found for the deprotonation of a series of 3+ charged octahedral complexes [7, 17]. The introduction of

86

TABLE 2. k_{obs} as a function of temperature for hydrolysis and racemization of Co(tmen)$_3^{3+a}$

Hydrolysis

pH = 12.5		pH = 9.7		pH = 8.1		pH = 6.5	
T (°C)	k_{obs} (s^{-1})	T (°C)	k_{obs} (s^{-1})	T (°C)	k_{obs} (s^{-1})	T (°C)	k_{obs} (s^{-1})
25.2	0.150 ± 0.004	18.1	$(1.08 \pm 0.06) \times 10^{-4}$	18.3	$(7.63 \pm 0.31) \times 10^{-6}$	24.7	$(7.84 \pm 0.41) \times 10^{-7}$
30.0	0.325 ± 0.009	24.0	$(5.14 \pm 0.31) \times 10^{-4}$	24.6	$(2.47 \pm 0.05) \times 10^{-5}$	30.0	$(1.97 \pm 0.09) \times 10^{-6}$
35.0	0.883 ± 0.015	30.1	$(8.62 \pm 0.60) \times 10^{-4}$	30.0	$(6.50 \pm 0.16) \times 10^{-5}$	35.0	$(4.52 \pm 0.16) \times 10^{-6}$
40.0	1.966 ± 0.039	40.0	$(6.11 \pm 0.24) \times 10^{-3}$	35.1	$(1.57 \pm 0.06) \times 10^{-4}$	40.1	$(1.15 \pm 0.04) \times 10^{-5}$
				40.0	$(3.58 \pm 0.11) \times 10^{-4}$		

Racemization

pH = 8.0		pH = 7.7		pH = 6.4	
T (°C)	k_{obs} (s^{-1})	T (°C)	k_{obs} (s^{-1})	T (°C)	k_{obs} (s^{-1})
10.0	$(1.02 \pm 0.02) \times 10^{-4}$	10.6	$(3.35 \pm 0.08) \times 10^{-5}$	24.2	$(4.06 \pm 0.38) \times 10^{-5}$
24.1	$(9.62 \pm 0.08) \times 10^{-4}$	27.7	$(3.58 \pm 0.02) \times 10^{-4}$	30.0	$(1.03 \pm 0.07) \times 10^{-4}$
30.0	$(1.80 \pm 0.03) \times 10^{-3}$	30.0	$(8.41 \pm 0.06) \times 10^{-4}$	35.0	$(2.03 \pm 0.10) \times 10^{-4}$
40.0	$(1.41 \pm 0.05) \times 10^{-2}$	35.0	$(1.83 \pm 0.03) \times 10^{-3}$	40.0	$(3.87 \pm 0.22) \times 10^{-4}$
		40.0	$(3.88 \pm 0.03) \times 10^{-3}$		

[a][Co(III)] approximately 10^{-3} M; ionic strength and buffers: see Table 1.

TABLE 3. k_{obs} as function of pressure for the base hydrolysis of $Co(tmen)_3^{3+}$ [a]

Pressure (MPa)	k_{obs} [b] (s^{-1})	k_{obs} [c] (s^{-1})
5	0.29 ± 0.01	1.62 ± 0.02
25	0.180 ± 0.007	1.04 ± 0.01
50	0.101 ± 0.002	0.56 ± 0.01
75	0.055 ± 0.003	0.310 ± 0.005
100	0.030 ± 0.003	0.183 ± 0.008
ΔV^* (cm^3 mol^{-1})	59.1 ± 0.3	57.6 ± 0.9

[a] $[Co(III)] = 2.5 \times 10^{-3}$ M; $[OH^-] = 0.1$ M; temperature = 25 °C. [b] Ionic strength = 0.1M, mean value of at least four kinetic runs. [c] Ionic strength = 1.0 M ($NaClO_4$ medium), mean value of at least four kinetic runs.

TABLE 4. k_{obs} for hydrolysis and racemization of $Co(tmen)_3^{3+}$ in phosphate buffers

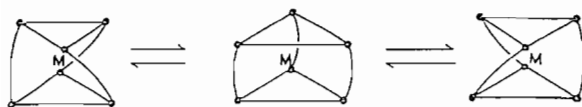| pH	k_{obs} (s^{-1})	
	Hydrolysis	Racemization
4.1	$(3.2 \pm 0.1) \times 10^{-7}$	$(2.9 \pm 0.4) \times 10^{-7}$
5.1	$(3.1 \pm 0.1) \times 10^{-6}$	$(1.9 \pm 0.1) \times 10^{-6}$
6.2	$(9.9 \pm 0.5) \times 10^{-6}$	$(6.8 \pm 0.2) \times 10^{-6}$
7.2	$(2.4 \pm 0.02) \times 10^{-5}$	$(1.6 \pm 0.05) \times 10^{-5}$

Fig. 2. Bailar twist mechanism for the racemization for tris bidentate coordination (adapted from ref. 18).

the methyl substituents is not expected to influence this value significantly, since very similar ΔV^*(hydr) values were reported for the base hydrolysis of $Co(NH_3)_5Cl^{2+}$, $Co(NH_2Me)_5Cl^{2+}$ and $Co(NH_2Et)_5Cl^{2+}$ [5, 7]. It follows that $\Delta V^*(k_D)$ has a value of approximately 30 cm^3 mol^{-1}. Earlier values found for the hydrolysis of other 3+ charged complexes are 13 cm^3 mol^{-1} for $Co(NH_3)_5Me_2SO^{3+}$ and 16 cm^3 mol^{-1} for $Co(NH_3)_5)OC(Me)N(Me)_2^{3+}$ [5, 7]. The significantly higher value for $\Delta V^*(k_D)$ found in this study must be due to a large volume increase associated with the ring-opening process of the bulky tmen ligand. In the other quoted examples, $\Delta V^*(k_D)$ is associated with the dissociation of the leaving group, which obviously causes a smaller increase in volume. All in all, the observed ΔV^*(hydr) of approximately 60 cm^3 mol^{-1} is the largest value

found so far for the base hydrolysis of Co(III) complexes. In the case of neutral leaving groups and the present ring-opening reaction, no major change in solvation is expected to contribute towards $\Delta V^*(k_D)$. Naturally, the observed values of ΔV^*(hydr) do show a trend to smaller values with increasing negative charge on the leaving group, due to an increase in electrostriction associated with charge creation [5–7].

The reaction sequence for racemization appears to be simpler, the reaction (i) also being the first step in agreement with the observed linear $[OH^-]$ dependence. Configuration inversion of this deprotonated complex ion is faster by two orders of magnitude than the hydrolysis discussed above. Since the dissociation process in the hydrolytic path, as for $Co(en)_3^{3+}$, would be the same for hydrolysis and racemization, the latter cannot proceed via this route. Obviously the CoN_6 core is retained during the $\Delta \rightarrow \Lambda$ conversion of $Co(tmen)_3^{3+}$, the alternative path consisting of a concerted breaking and remaking of three chelate rings can safely be ruled out.

The most likely pathway is a trigonal twist (Bailar twist) where the transition state has a trigonal prismatic geometry (Fig. 2) [18]. This mechanism is supported by the crystal structure of $[Co(tmen)_3]$(tosylate)$_3$ showing the coordination geometry already trigonally deformed by 16° towards the prismatic structure [14]. The forming of a chelate ring with a dangling monodentate en has also been ruled out by a study of the hydrolysis of $[Co(en)_2(enH)Cl]^{3+}$ [19]. A rather different situation exists for earlier racemization experiments of Co(III) complexes with 1,2-diaminopropane where the reactants were absorbed on charcoal [20].

The labile kinetic behavior of $Co(tmen)_3^{3+}$ towards hydrolysis and racemization is a direct consequence of the steric crowding imposed by the 12 peripheral methyl groups. This strain produces an enlarged cavity available for the metal atom combined with a trigonally deformed octahedral arrangement of the ligating nitrogen atoms. Further support for this strain-induced enhancement of the reactivity is furnished by preliminary data for the mixed ion $Co(tmen)_2en^{3+}$. The partial relief of strain is reflected in the kinetics of base hydrolysis with a second order rate constant of 2×10^{-2} M^{-1} s^{-1}, i.e. two orders of magnitude less labile than the homoleptic tmen complex.
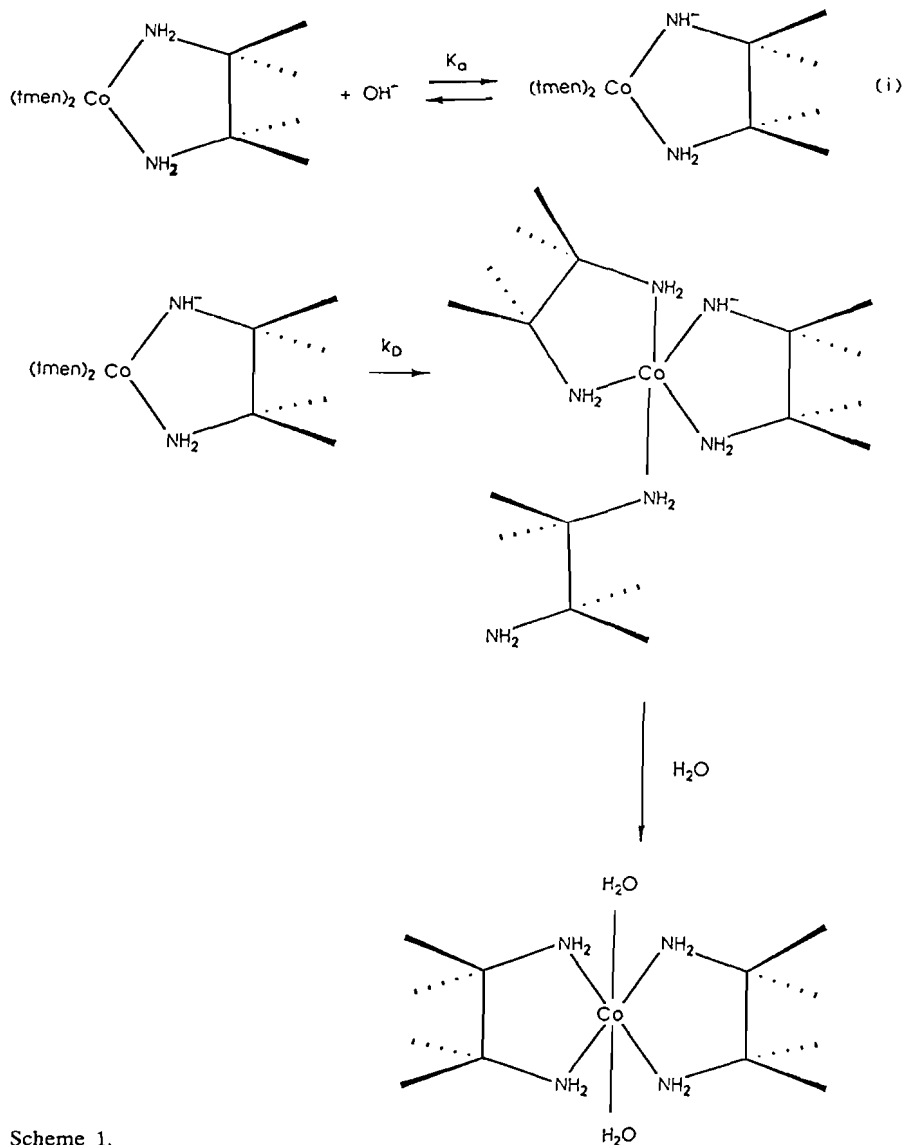
Scheme 1.

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