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Base Hydrolysis of Some Isomers of the Dichloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Cation

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The kinetics of the base-catalyzed hydrolysis of three isomers of the dichloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) cation have been studied in buffer solutions in the pH range 6–8. The second-order rate constants at 25.0 °C and μ = 0.050 ($NaNO_3$) and the enthalpies and entropies of activation respectively for the trans *R,S,S,R*, the trans *R,R,R,R*(*S,S,S,S*), and the cis *R,R,R,R*(*S,S,S,S*) isomers are as follow: 6.5×10^4, 10.7, 0; 1.57×10^5, 11.3, +2; 2.3×10^6, 9.3, +2 ($k_{OH}/M^{-1}\ s^{-1}$, $\Delta H^{\ddagger}$/kcal mol^{-1}, $\Delta S^{\ddagger}$/cal $K^{-1}\ mol^{-1}$). The Eyring plot for the trans *R,S,S,R* isomer is curved at temperatures below 20 °C, the slope becoming more negative. The reactions are discussed in terms of the relative importance of the reprotonation and dissociation of the amido conjugate base.

Introduction

In the past few years we have examined the base-catalyzed reactions of the three available isomers of the dichloro–cobalt(III) complex containing the linear tetraamine 1,9-diamino-3,7-diazanonane (=2,3,2-tet), namely, *trans*-[Co(*R,S*-2,3,2-tet)Cl_2]$^+$,[1] *trans*-[Co(*R,R*(*S,S*)-2,3,2-tet)Cl_2]$^+$,[2] and β-*cis*-[Co(*R,R*(*S,S*)-2,3,2-tet)Cl_2]$^+$.[3] In the first two cases it was shown that the rate-limiting step was the removal of a secondary amine proton by hydroxide, the subsequent aquation of the amido base being much more rapid than any reprotonation process. In addition, the reactions were found to respond to general base catalysis.[4] The β-cis complex, on the other hand, reverted to the more usual pattern and the rate constant for base hydrolysis was much less than that for proton exchange, so that, while the same secondary amine proton was removed by hydroxide, the rate constant for reprotonation was some 2 orders of magnitude greater than that for the solvolysis of the conjugate base. As part of our program to investigate and understand this behavior, we have extended our studies to other tetraamine systems, and this paper reports our investigations of the known isomers of the dichloro complexes with the macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane (=cyclam). The trans isomer, with the ligand in the *R*-3-*S*-2-*S*-3-*R*-2 form, has been examined previously and the kinetics of base hydrolysis reported.[5] This was the first example of a rate-limiting deprotonation in the base hydrolysis of cobalt(III)–amine complexes.[6] The base hydrolysis of the recently described labile trans isomer with the ligand in the *R,R,R,R*(*S,S,S,S*) form[7] and of the previously reported cis isomer (also with the ligand in the *R,R,R,R*(*S,S,S,S*) form are herein discussed.

Experimental Section

Reagents. *cis*-dichloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) chloride was prepared by the method of Poon and Tobe.[5] Anal. Calcd for $C_{10}H_{24}N_4Cl_3Co$: C, 32.8; H, 6.56; N, 15.3; Cl, 29.1. Found: C, 32.0; H, 6.47; N, 15.0; Cl, 29.2.

trans-Dichloro[(*R,S,S,R*)-1,4,8,11-tetraazacyclotetradecane]cobalt(III) chloride was prepared by the method of Bosnich et al.[8] Anal. Calcd for $C_{10}H_{24}N_4Cl_3Co$: C, 32.8; H, 6.56; N, 15.3. Found: C, 32.5; H, 6.54; N, 15.1.

trans-dichloro[(*R,R,R,R*(*S,S,S,S*))-1,4,8,11-tetraazacyclotetradecane]cobalt(III) perchlorate was part of the sample used in ref 7.

Buffers. Reagent grade 2,6-dimethylpyridine and 2,4,6-trimethylpyridine were dissolved in water and partly neutralized with dilute nitric acid until the desired pH was reached. The concentration was adjusted by further dilution and the ionic strength maintained at 0.050 with AnalaR sodium nitrate. The dimethylpyridine buffer was used for pH <7 and the trimethylpyridine buffer was used for the higher pH measurements. The pH of the buffer solution was measured accurately at the reaction temperature with a glass electrode and a calomel reference electrode and a Radiometer PHM 26 pH meter. This instrument was calibrated with potassium hydrogen phthalate buffers at the same ionic strength and temperature.[9]

Kinetics. The buffer solutions were brought to reaction temperature in the thermostated cell compartment of a Pye-Unicam SP 1750 spectrophotometer. The ancillary equipment is described elsewhere.[7] The reaction was started by adding the complex, and the mixture was shaken and replaced in the cell compartment. The cis complex was added as finely powdered solid, while 0.02 cm^3 of freshly prepared aqueous solutions were used to provide the trans complexes. The measurements were then started. Separate experiments showed that, under the conditions used, the temperature did not change by more than 0.1 °C. The reaction was followed by the change in absorbance at a single wavelength, and the first-order rate constants were determined in the usual way.

Results

In the presence of excess hydroxide, the two chlorines of *cis*-[Co(cyclam)Cl_2]$^+$ are rapidly displaced and it has been shown that the first identifiable reaction product is *cis*-[Co(cyclam)$(OH)_2$]$^+$,[5,10] presumably with the ligand in the same configuration as the starting material. Attempts to stop the reaction after the displacement of the first chloride by acidifying the reaction mixture within 2 s of adding excess sodium hydroxide were unsuccessful and, in all cases, two extra equivalents of chloride and the *cis*-[Co(cyclam)$(H_2O)_2$]$^{3+}$ cation were present. The *cis*-[Co(cyclam)Cl_2]$^+$ cation is labile with respect to aquation ($t_{1/2}$ = 40 s at 25 °C)[5] and, at room temperature, the pH has to be increased above 6 before any base catalysis can be observed. Because of the solvolytic lability, it was not possible to study the base hydrolysis by a stopped-flow technique, and it was necessary to start the reaction by dissolving the solid chloride salt in a suitable buffer and observe it by the change in absorbance at one wavelength. The scope for the variation of temperature and pH was limited on the one hand by the spontaneous aquation and on the other by the time required to ensure complete dissolution of the complex. The convenient pH range could be obtained using a 2,6-dimethylpyridine–nitric acid buffer, and within this range, the first step, which is pH dependent, is followed by a slower pH-independent process which can be identified as the previously studied cis to trans isomerization of the *cis*-[Co(cyclam)(OH)(H_2O)]$^{2+}$ cation.[10] The reaction was followed at 340 nm and the first-order rate constants are collected in Table I. Each entry is the average of at least two independent runs.

The labile *trans*-[Co(*R,R,R,R*(*S,S,S,S*)-cyclam)Cl_2]$^+$ cation, in the presence of excess hydroxide, gives a quantitative yield of the *cis*-[Co(cyclam)$(OH)_2$]$^+$ cation and, as in the case of the *cis*-dichloro complex, it was not possible to stop the reaction before the second chlorine was displaced. Because the uncatalyzed aquation was slower than that of the cis isomer, the base-catalyzed process was easier to study but it was still not convenient to use the stopped-flow method and so the technique adopted for the cis isomer was also followed

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Table I. First-Order and Derived Second-Order[a] Rate Constants for the Base-Catalyzed Hydrolysis of Some Dichloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Cations[b,c]

isomer	T/°C	pH	$10^8[\mathrm{OH^-}]$/M	10^2k_{obsd}[d]/$\mathrm{s^{-1}}$	10^5k_{OH}[a]/$\mathrm{M^{-1}\,s^{-1}}$
cis *R,R,R,R*(*S,S,S,S*)	10.4	2.00	0.00	0.32[e]	
	10.4	6.69	2.25	2.4	9.6
	10.4	6.80	2.90	3.5	
	10.4	7.00	4.60	4.4	
	15.2	2.00	0.00	0.59[e]	
	15.2	6.63	2.96	4.3	13.2
	15.2	6.72	3.64	5.5	
	19.8	2.00	0.00	0.95[e]	
	19.8	6.57	3.75	7.4	17.9
	19.8	6.62	4.21	8.9	
	24.5	2.00	0.00	1.41[e]	
	24.5	6.45	4.13	10.6	21.5
	24.5	6.55	5.20	14.3	
	24.5	6.75	8.25	18.4	
trans *R,R,R,R*(*S,S,S,S*)	10.7	2.00	0.00	0.02[f]	
	10.7	7.64	20.7	1.18	
	10.7	7.73	25.4	1.45	0.56
	10.7	7.88	35.9	2.03	
	10.7	7.97	44.2	2.47	
	15.0	2.00	0.00	0.03[f]	
	15.0	7.51	22.0	1.70	
	15.0	7.63	29.0	2.41	0.77
	15.0	7.83	46.0	3.3	
	15.0	7.87	50.4	4.1	
	20.0	2.00	0.00	0.08[f]	
	20.0	6.62	4.26	0.55	
	20.0	6.80	6.46	0.77	1.10
	20.0	7.41	26.3	3.0	
	20.0	7.56	37.2	4.2	
	25.0	2.00	0.00	0.20[f]	
	25.0	6.45	4.27	0.95	
	25.0	6.75	8.52	1.46	1.57
	25.0	7.32	31.7	5.2	
	25.0	7.47	44.7	7.1	
	29.6	2.00	0.00	0.34[f]	
	29.6	6.47	6.33	1.58	
	29.6	6.65	9.58	2.37	2.11
	29.6	7.22	35.6	7.8	
	29.6	7.35	48.0	10.3	
	34.6	2.00	0.00	0.74[f]	
	34.6	6.25	5.44	2.36	
	34.6	6.35	6.85	2.77	2.90
	34.6	6.54	10.6	4.0	
	34.6	7.12	40.3	12.1	
trans *R,S,S,R*[g]	10.9	7.64	21.1	0.44	
	10.9	7.73	25.9	0.56	0.196
	10.9	7.88	36.6	0.72	
	10.9	7.97	45.1	0.88	
	15.0	7.51	22.0	0.73	
	15.0	7.63	29.0	0.99	0.32
	15.0	7.80	42.9	1.39	
	15.0	7.87	50.4	1.57	
	19.4	7.41	25.3	1.10	
	19.4	7.56	35.7	1.58	0.44
	19.4	7.69	48.1	2.09	
	19.4	7.77	57.9	2.52	
	24.8	7.32	31.3	2.04	
	24.8	7.47	44.2	2.84	0.64
	24.8	7.60	59.6	3.8	
	24.8	7.69	73.3	4.5	
	29.9	7.22	36.3	3.2	
	29.9	7.35	48.9	4.4	0.91
	29.9	7.49	67.5	6.3	
	29.9	7.58	83.1	7.6	
	35.4	6.35	7.24	0.92	
	35.4	6.54	11.21	1.44	1.25
	35.4	7.12	42.6	5.3	
	35.4	7.28	61.6	7.8	

[a] Slope of the plot of k_{obsd} vs. $[\mathrm{OH^-}]$. [b] In 2,6-dimethylpyridine–nitric acid or 2,4,6-trimethylpyridine–nitric acid buffers. [c] $\mu = 0.050$. [d] Average from at least two independent runs. [e] Data from ref 5. [f] Data from ref 7. [g] No correction required for the spontaneous aquation.

Table II. Rate Constants, Activation Parameters, and Products of the Base Hydrolysis of Some $[Co(L_4)Cl_2]^+$ Cations[a]

L_4	isomer	$10^{-5}k_{OH}$ at 25 °C/M^{-1} s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	product
2,3,2-tet	trans *R,S*	0.34[b]	14	+10	100% trans *R,S*
2,3,2-tet	trans *R,R(S,S)*	0.68[b]	13.7	+12	100% trans *R,S*
2,3,2-tet	β-cis *R,R(S,S)*	0.25[b]	17.5	+19	100% trans *R,S*
cyclam	trans *R,S,S,R*	0.65	10.7[c]	0[c]	100% trans *R,S,S,R*
cyclam	trans *R,R,R,R(S,S,S,S)*	1.57	11.3	+2	100% cis *R,R,R,R(S,S,S,S)*
cyclam	cis *R,R,R,R(S,S,S,S)*	23	9.3	+2	100% cis *R,R,R,R(S,S,S,S)*

[a] Measured in 2,6-dimethylpyridine–nitric acid and 2,4,6-trimethylpyridine–nitric acid buffers; $\mu = 0.050$ except where otherwise indicated. [b] $\mu = 0.046$. [c] The Eyring plot curves downward at lower temperatures. The activation parameters are calculated from the linear portion in the range 20–35 °C.

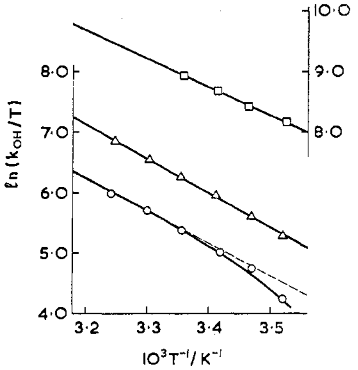

Figure 1. Plots of ln (k_{OH}/T) against T^{-1} for the complexes: ○, *trans*-dichloro(*R,S,S,R*-cyclam)cobalt(III) chloride; Δ, *trans*-dichloro(*R,R,R,R(S,S,S,S)*-cyclam)cobalt(III) perchlorate; □, *cis*-dichloro(*R,R,R,R(S,S,S,S)*-cyclam)cobalt(III) chloride.

here. The first-order rate constants were measured at 320 nm and are collected in Table I.

The base hydrolysis of the solvolytically inert *trans*-$[Co(R,S,S,R\text{-cyclam})Cl_2]^+$ isomer has been studied before and has been shown to give the *trans*-$[Co(R,S,S,R\text{-cyclam})(OH)Cl]^+$ species as the initial reaction product.[5] The kinetics were reexamined under the conditions of the other studies, special attention being paid to the lower reaction temperatures, and the first-order rate constants are also collected in Table I. For all three complexes the plots of k_{obsd} vs. $[OH^-]$ are linear with intercepts corresponding to the first-order rate constants for the spontaneous aquation. The slopes of the lines, $=k_{OH}$, are also givn in Table I.

Discussion

The second-order rate constants at 25 °C, activation parameters, and stereochemistries of the base hydrolysis of the three dichloro(cyclam)cobalt(III) complexes are summarized in Table II where they are compared with data for the analogous complexes of the open-chain tetradentate amine ligand 1,9-diamino-3,7-diazanonane (2,3,2-tet). It is now reasonably certain that the mechanism of the base-catalyzed aquation of such cobalt(III) complexes can be labeled D_{cb} (or S_N1cb)[11,12,13] and represented diagramatically as

$$\mathrm{RNHCl^+ + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RNCl + H_2O}$$

$$\mathrm{RNCl \xrightarrow{k_2} RN^+ + Cl^- \xrightarrow[+H_2O]{fast} RNHOH^+}$$

where $RNHCl^+$ represents $[Co(L_4)Cl_2]^+$, where L_4 is the tetradentate amine ligand. Provided the concentration of the amido conjugate base remains very small, this mechanism predicts the observed second-order rate law, $-d[RNHCl^+]/dt = k_{OH}[RNHCl^+][OH^-]$, where $k_{OH} = k_1k_2/(k_{-1} + k_2)$. When there is more than one proton present in the substrate, the expression should be written $k_{OH} = \sum_i n^ik_1^ik_2^i/(k_{-1}^i + k_2^i)$, where the superscript "*i*" refers to the rate constants appropriate to the *i*th set of n^i equivalent protons and the conjugate base resulting from the removal of one of them. In the cases where the study can be made, it appears that one possible pathway dominates the material transfer.

All of these complexes are extremely sensitive to base catalysis. The detailed study of the 2,3,2-tet complexes has shown that the lability toward base hydrolysis did not parallel the aquation lability and, in the case of the *R,S* and *R,R(S,S)* trans isomers,[1,2] the rate-determining step involved the removal of one of the secondary amine protons so that $k_{OH} \approx 2k_1$ and the difference in the dissociative labilities of the two complexes, which might be reflected in k_2, did not enter into the kinetic expression. On the other hand, it has been shown that the β-cis *R,R(S,S)* isomer follows the normal pattern for base hydrolysis (i.e., $k_{-1} \gg k_2$) and $k_{OH} = k_1k_2/k_{-1}$, the reactive conjugate base being formed by the removal of the secondary amine proton on the nitrogen trans to chlorine.[3] Thus, while k_1 is some 50–100 times greater in the β-cis complex (it is usual to find that protons on nitrogens trans to chlorine are some 2 orders of magnitude greater than equivalent ones on nitrogens trans to other amines[14–16]), k_{OH} is some 5–10 times smaller.

The *trans*-$[Co(R,S,S,R\text{-cyclam})Cl_2]^+$ cation provided the first known example of a base hydrolysis of a cobalt(III) complex where k_{-1} was not very much greater than k_2.[6] However, a quantitative evaluation of the ratio k_{-1}/k_2 was never made and, whereas a comparison of the extent of isotopic exchange in the recovered unreacted material and in the product indicated that this ratio was not far from unity, the low activation energy[13,17] and the observation of general base catalysis[6] suggested that $k_2 \approx 5k_{-1}$. A detailed quantitative examination of the proton exchange is now under way and will be reported elsewhere in due course. The original isotopic exchange studies were carried out at much lower temperatures than the experiments seeking evidence for general base catalysis and, since the ratio k_{-1}/k_2 would be expected to decrease considerably with increasing temperature,[4] the two sets of experiments do not give incompatible results. The variation of k_{-1}/k_2 with temperature is such that the expression for k_{OH} would be changing between the high-temperature limit of $4k_1$ and the low-temperature limit of $4k_1k_2/k_{-1}$ so that the plot of ln (k_{OH}/T) against $1/T$ would not be linear. A reexamination of the data of Poon,[17] measured within the temperature range 20–40 °C, indicates that the value of k_{OH} at 20 °C is lower than expected for a linear Eyring plot. We have remeasured the kinetics, paying special attention to the rate constants at low temperatures, but we were unable, with the equipment at our disposal, to obtain reliable rate constants in the critical region between 0 and 10 °C. Nevertheless, there seems to be a marked increase in the negative slope of the

Eyring plot at temperatures below 20 °C. The high-temperature slope tends toward $\Delta H_{OH}^\ddagger \approx \Delta H^\ddagger \approx 10$ kcal/mol but the data do not possess sufficient accuracy for us to attempt to estimate a value for $\Delta H_2^\ddagger - \Delta H_{-1}^\ddagger$.

Although the *trans*-[Co(*R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*)-cyclam)$Cl_2]^+$ cation is some 10^3 times more labile than the trans *R*,*S*,*S*,*R* isomer with respect to aquation[7] (probably as a result of ligand strain that is released in the five-coordinate intermediate[18]), the base hydrolysis is little more than twice as fast. This is consistent with a situation where k_2 (which should respond to the dissociative labilities of the substrates) does not make a major contribution to the value of k_{OH}, i.e., $k_2 \approx k_{-1}$. Since it is not unreasonable to believe that k_2 for the more dissociatively labile *R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*) trans isomer is likely to be considerably greater than that for the *R*,*S*,*S*,*R* isomer, the former should be closer to the limit when $k_2 \gg k_{-1}$, i.e., $k_{OH} = 4k_1$. It has not yet been possible to make any reliable isotopic labeling studies in order to verify this point but the Eyring plot is linear with $\Delta H_{OH}^\ddagger = 11.3$ kcal mol^{-1}. In many respects there is a great similarity between the behavior of the 2,3,2-tet (open-chain) and the cyclam (macrocyclic) complexes, the *R*,*S* open-chain species (gauche–chair–gauche) resembling the *R*,*S*,*S*,*R* macrocyclic complex (gauche–chair–gauche–chair) and the *R*,*R*(*S*,*S*) open-chain species (gauche–skew–gauche) resembling the *R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*) macrocyclic complex (gauche–skew–gauche–skew). This is seen in the similarity of the ratio of the deprotonation rate constants (ratio of the k_{OH} values at the $k_{OH} \approx nk_1$ limit) for both pairs and also suggests that the difference in ring strain in the two macrocyclic isomers is not greatly reflected in the rate constants for deprotonation.

In contrast to the behavior of the β-*cis*-$[Co(2,3,2\text{-tet})Cl_2]^+$ cation, the rate constant for the base hydrolysis of the *cis*-$[Co(cyclam)Cl_2]^+$ cation is nearly 20 times larger than that for the most labile trans complex. This could be due to the greater dissociative lability of the cis isomer (reflected in k_2) allowing the overall rate to take advantage of the greater exchange lability of protons on nitrogens trans to chlorine (reflected in k_1). However, there is no reason for believing that k_1 remains unchanged, and so an independent estimation of the ratio k_{-1}/k_2 is necessary. The rate constant for base hydrolysis ($k_{OH} = 1.8 \times 10^6$ M^{-1} s^{-1} at 20 °C) is of a similar magnitude to that observed for the exchange of the secondary amine proton trans to chlorine in β-*cis*-$[Co(2,3,2\text{-tet})Cl_2]^+$ ($k_1 = 3 \times 10^6$ M^{-1} s^{-1} at 20 °C) and it might have been expected that the high dissociative lability of the cis cyclam complex might make $k_2 > k_{-1}$. The low enthalpy of activation would also be consistent with a rate-determining deprotonation. However, preliminary studies of the proton exchange behavior of the *cis*-$[Co(cyclam)Cl_2]^+$ cation indicate extensive exchange of protons on the nitrogens trans to chlorine in the unreacted complex recovered in the course of the base hydrolysis. This would indicate that $k_{-1} > 5k_2$. This study, when complete, will be reported elsewhere and it is hoped that this apparent contradiction will be resolved.

Studies of the reaction products indicate that none of the three base hydrolyses proceed with any inversion of configuration at nitrogen. Therefore, unlike the case of the 2,3,2-tet isomers, there is no common intermediate, but neither is one to be expected. The *R*,*S*,*S*,*R* and *R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*) cyclam species differ in the configuration of *two* nitrogens but only one can be involved in any act of base hydrolysis. The absence of overall nitrogen inversion therefore does not rule out the planar geometry for the amido nitrogen in the five-coordinate species produced when the conjugate base dissociates. The cis and trans *R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*) species yield a common product, presumably through a common trigonal-bipyramidal intermediate. The conversion of the cis *R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*) form to the more stable trans *R*,*S*,*S*,*R* form has been observed to take place in the hydroxoaquo species and this involves the exchange of at least two protons.[10]

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Registry No. *trans*-[Co(*R*,*S*,*S*,*R*-cyclam)$Cl_2]^+$, 66841-18-7; *trans*-[Co(*R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*)-cyclam)$Cl_2]^+$, 66841-17-6; *cis*-[Co-(*R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*)-cyclam)$Cl_2]^+$, 66841-16-5.

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