(for log k_2 vs. log K) and $\beta_{-1} = -0.45$ (for log k_{-1} vs. log K). Therefore, in the transition state the configuration around the rhodium would be in the middle of those of the reactant and product. Thus, in the activated complex the two trans phosphorus or arsenic ligands may be moderately bent back and considerable electron transfer from the metal to TCNE may take place.

Finally, it can be concluded from the ΔH_2^* values and the k_2 values at 25 °C (Tables II and III) that the nucleophilicity of the metal substrate increases in the order of RhCl(CO)$(PPh_3)_2$ < $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]^+$ < IrCl(CO)$(PPh_3)_2$.

Registry No. *trans*-$RhCl(CO)(PPh_3)_2$, 15318-33-9; *trans*-$RhCl(CO)(PPh_2Me)_2$, 19552-34-2; *trans*-$RhCl(CO)(AsPh_3)_2$, 16970-35-7; *trans*-$RhCl(CO)(P(OPh)_3)_2$, 53275-15-3; *trans*-$RhCl(CO)(P(O\text{-}o\text{-}CH_3C_6H_4)_3)_2$, 59349-69-8; *trans*-$RhCl(CO)(P(p\text{-}ClC_6H_4)_3)_2$, 17966-82-4; *trans*-$RhCl(CO)(P(p\text{-}CH_3C_6H_4)_3)_2$, 17070-18-7; *trans*-$RhCl(CO)(P(p\text{-}CH_3OC_6H_4)_3)_2$, 16970-33-5; *trans*-$RhCl(CS)(PPh_3)_2$, 59349-68-7; *trans*-$Rh(NCO)(CO)(PPh_3)_2$, 23028-37-7; *trans*-$Rh(NCS)(CO)(PPh_3)_2$, 17966-78-8; *trans*-$RhBr(CO)(PPh_3)_2$, 17070-17-6; *trans*-$RhI(CO)(PPh_3)_2$, 21006-49-5; *trans*-$IrCl(CO)(PPh_3)_2$, 15318-31-7; $[Rh(C_8H_{12})Cl]_2$, 12092-47-6; $RhCl(CO)(P(p\text{-}CH_3OC_6H_4)_3)_2(TCNE)$, 59389-60-5; $RhCl(CO)(PPh_3)_2(TCNE)$, 32613-67-5; $RhCl(CO)(PPh_2Me)_2(TCNE)$, 59389-66-1; $RhCl(CO)(AsPh_3)_2(TCNE)$, 59389-65-0; $RhCl(CO)(P(OPh)_3)_2(TCNE)$, 59389-64-9; $RhCl(CO)(P(O\text{-}o\text{-}CH_3C_6H_4)_3)_2(TCNE)$, 59389-70-7; $RhCl(CO)(P(p\text{-}ClC_6H_4)_3)_2(TCNE)$, 59389-68-3; $RhCl(CO)(P(p\text{-}CH_3C_6H_4)_3)_2(TCNE)$, 59389-67-2; $RhCl(CS)(PPh_3)_2(TCNE)$, 59389-63-8; $Rh(NCO)(CO)(PPh_3)_2(TCNE)$, 59389-62-7; $Rh(NCS)(CO)(PPh_3)_2(TCNE)$, 59389-61-6; $RhBr(CO)(PPh_3)_2(TCNE)$, 30103-58-3; $RhI(CO)(PPh_3)_2(TCNE)$, 30103-59-4; $IrCl(CO)(PPh_3)_2(TCNE)$, 20741-47-3; TCNE, 670-54-2.

References and Notes

(1) S. Carra and R. Ugo, *Inorg. Chim. Acta, Rev.*, **1**, 49 (1967).
(2) W. H. Baddley, *Inorg. Chim. Acta, Rev.*, **2**, 5 (1968).
(3) J. Ashley-Smith, M. Green, and D. C. Wood, *J. Chem. Soc. A*, 1847 (1970).
(4) W. Strohmeier and R. Fleischmann, *Z. Naturforsch., B*, **24**, 1217 (1969).
(5) M. Haga, K. Kawakami, and T. Tanaka, *Inorg. Chim. Acta*, **12**, 93 (1975).
(6) P. J. Krusic, H. Stoklose, L. E. Manzer, and P. Meakin, *J. Am. Chem. Soc.*, **97**, 667 (1975).
(7) L. H. Elson, D. G. Morrell, and J. K. Kochi, *J. Organomet. Chem.*, **84**, C7 (1975).
(8) F. G. Mann and E. J. Chaplin, *J. Chem. Soc.*, 527 (1937).
(9) E. N. Walsh, *J. Am. Chem. Soc.*, **81**, 3023 (1959).
(10) R. F. Hudson and J. E. Wardill, *J. Chem. Soc.*, 1731 (1950).
(11) (a) D. Evans, J. A. Osborn, and G. Wilkinson, *Inorg. Synth.*, **11**, 99 (1968); (b) M. A. Jennings and A. Wojcicki, *Inorg. Chem.*, **6**, 1854 (1967); (c) M. C. Baird and G. Wilkinson, *Chem. Commun.*, 267 (1966); (d) L. Vallarino, *J. Chem. Soc.*, 2473 (1957); (e) K. Vrieze, *Inorg. Synth.*, **11**, 101 (1968).
(12) W. H. Baddley, *J. Am. Chem. Soc.*, **88**, 4545 (1966).
(13) Y. S. Varshavskii, T. G. Cherkasova, M. M. Singh, and N. A. Buzina, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **15**, 1427 (1970).
(14) (a) O. W. Webster, W. Mahler, and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3678 (1962); (b) P. H. Reiger, I. Bernal, and G. K. Fraenkel, *ibid.*, **83**, 3918 (1961).
(15) G. S. Reddy and C. D. Weis, *J. Org. Chem.*, **28**, 1822 (1963).
(16) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2d ed, Wiley, New York, N.Y., 1961, p 186.
(17) M. F. Rettig and R. M. Wing, *Inorg. Chem.*, **8**, 2685 (1969).
(18) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
(19) M. Kubota, G. W. Kiefer, R. M. Ishikawa, and K. E. Bencala, *Inorg. Chim. Acta*, **7**, 195 (1973).
(20) J. F. Harrod and C. A. Smith, *J. Am. Chem. Soc.*, **92**, 2699 (1970).
(21) C. K. Jørgensen, *Coord. Chem. Rev.*, **1**, 164 (1966).
(22) N. Kushibiki and H. Yoshida, *J. Am. Chem. Soc.*, **98**, 268 (1976).
(23) L. Vaska and M. F. Werneke, *Trans. N.Y. Acad. Sci.*, **33**, 70 (1971).
(24) There are marked deviations from the linear relationships in the $P(OPh)_3$ complex. The Tolman cone angle for $P(OPh)_3$ is 128°, whereas those for $P(p\text{-}XC_6H_4)_3$ (X = CH_3O, CH_3, H, Cl) and $P(O\text{-}o\text{-}CH_3C_6H_4)_3$ are 145 and 141°, respectively;[25] the steric release for the $P(OPh)_3$ complex is considered to reflect the deviations. Thus, the reaction is suggested to involve different mechanistic details which presumably arise from steric effect.
(25) (a) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970); (b) C. A. Tolman, W. C. Seidel, and L. W. Gosser, *ibid.*, **96**, 53 (1974).
(26) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, N.Y., 1963, p 128.
(27) L. Vaska, *Acc. Chem. Res.*, **1**, 335 (1968).

Contribution from the Department of Chemistry,
University of Hong Kong, Hong Kong

Structural and Mechanistic Studies of Coordination Compounds. 15.[1] Evidence of an SN1cB Mechanism for the Base Hydrolysis of Some *trans*-Chloro- and -Bromoisothiocyanato Macrocyclic Quadridentate Amine Complexes of Cobalt(III)

P. W. MAK and C. K. POON*

Received January 22, 1976 AIC60058W

The kinetics of base hydrolysis of *trans*-$[CoL(NCS)X]^+$ [L = cyclam (1,4,8,11-tetraazacyclotetradecane), teta (*meso*-1,4,8,11-tetraaza-5,5,7,12,12,14-hexamethylcyclotetradecane), and trans[14]diene (1,4,8,11-tetraaza-5,5,7,12,12,14-hexamethylcyclotetradeca-1,7-diene); X = Cl and Br] have been studied in buffer solutions. Steric acceleration has been observed which strongly supports a dissociative mechanism for these reactions. In the teta and trans[14]diene systems, general base catalysis has been detected and the second-order rate constant with respect to hydroxide ion concentration is virtually independent of the nature of both orienting (NCS^- and Cl^-) and leaving (Cl^- and Br^-) groups. These together with the observations that the activation enthalpies fall within 12–16 kcal mol^{-1} and activation entropies fall within 8–16 cal mol^{-1} deg^{-1} are good evidence for a "limiting" SN1cB mechanism, in which the deprotonation of an amine ligand becomes the rate-determining step, for the base hydrolysis of these two systems of complexes. For the cyclam complexes, the base hydrolysis is "normal" (nonlimiting) and the rate constant then depends on the nature of both orienting (NCS^- and Cl^-) and leaving (Cl^- and Br^-) groups.

Introduction

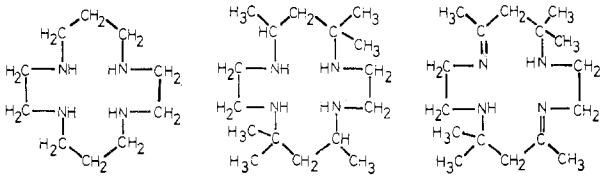
The base hydrolysis of amine complexes of cobalt(III) has been extensively investigated and a number of mechanisms have been proposed.[2] Much evidence has now been accumulated to support the SN1cB mechanism,[2] as represented in general terms by

$$[CoL_4(amine)X]^{n+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [CoL_4(amine\text{-}H)X]^{(n-1)+} + H_2O \quad (1)$$

$$[CoL_4(amine\text{-}H)X]^{(n-1)+} \xrightarrow{k_2} [CoL_4(amine\text{-}H)]^{n+} + X^- \quad (2)$$

$$[CoL_4(amine\text{-}H)]^{n+} + H_2O \xrightarrow{fast} [CoL_4(amine)OH]^{n+} \quad (3)$$

In general, $k_{-1} >> k_2$ and so the dissociation of the conjugate base (step 2) becomes rate determining. Recently, the base hydrolysis of some complexes of the type *trans*-$[CoLCl_2]^+$ [L = *ms*- and *rac*-2,3,2-tet [3,4] (1,9-diamino-3,7-diazanonane) and cyclam[5] (1,4,8,11-tetraazacyclotetradecane, I)], which are



I II III

unusually sensitive to base, have been shown to approach the other limiting condition in which k_{-1} is less than k_2. Since all of these reactions retained first-order dependence on hydroxide ion concentration, this condition implied that the deprotonations of these amine substrates (i.e., step 1) became the rate-determining step. Since it has been demonstrated that the acid hydrolysis of complexes of the type *trans*-$[CoLAX]^+$ [L = teta (*meso*-1,4,8,11-tetraaza-5,5,7,12,12,14-hexamethylcyclotetradecane, II) and trans[14]diene (1,4,8,11-tetraaza-5,5,7,12,12,14-hexamethylcyclotetradeca-1,7-diene, III)] are more labile than those of the corresponding cyclam complexes, due mainly to steric effects, by a factor of ca. 10^3,[6,7] it seems that these teta and trans[14]diene complexes are ideal for substantiating the SN1cB mechanism. If these reactions indeed proceed by a dissociative mechanism, steric effects may increase the magnitude of their k_2 terms relative to those of cyclam complexes and, therefore, increase the chance of these complexes to react by the limiting pathway in which the k_1 term is rate determining. This paper describes the preparation of *trans*-$[Co(cyclam)NCSBr]^+$ and the base hydrolysis of this complex and *trans*-$[CoL(NCS)X]^+$ (L = teta, trans[14]diene; X = Cl, Br) cations.

Experimental Section

***trans*-Bromoisothiocyanato(1,4,8,11-tetraazacyclotetradecane)-cobalt(III) perchlorate** (*trans*-$[Co(cyclam)NCSBr]ClO_4$), was prepared by adding NH_4NCS (0.3 g, 4 mM) to a filtered aqueous solution of *trans*-$[Co(cyclam)Br_2]Br$[8] (2 g, 4 mM in 150 ml), acidified with hydrobromic acid (48% 1 ml) and maintained at 80 °C for 30 min. The solution immediately turned purple and perchloric acid (1 M, 50 ml), saturated with NaBr, was added to precipitate out a green product which was recrystallized twice by adding $NaClO_4$ to a saturated solution of the crude product in dilute hydrobromic acid (2 M). The compound was further recrystallized by adding ether to a saturated mixed ethanol–acetone (1:1) solution; yield 20%. Anal. Calcd for $[Co(C_{10}H_{24}N_4)NCSBr]ClO_4$: C, 26.6; H, 4.9; N, 14.1; Br, 16.1; Cl, 7.2; S, 6.5. Found: C, 26.6; H, 4.7; N, 14.1; Br, 16.0; Cl, 7.1; S, 6.8.

Other complexes, *trans*-$[Co(cyclam)NCSCl]ClO_4$,[8] *trans*-$[Co(teta)NCSCl]ClO_4$,[7] *trans*-$[Co(teta)NCSBr]ClO_4$,[9] and *trans*-$[Co(trans[14]diene)NCSX]ClO_4$[9] (X = Cl, Br), were prepared by published methods.

Kinetics. The base hydrolysis of these isothiocyanato complexes was started by mixing equal volumes of prethermostated complex and buffer solutions into a glass cell in the temperature-controlled cell holder of a Unicam SP700 or SP8000 spectrophotometer and the reaction was studied in situ by following the changing absorbance with time at a constant wavelength [L = cyclam at 390 (Cl), 400 (Br); L = teta, 400 (Cl), 390 (Br); L = trans[14]diene, 390 (Cl), 410 nm (Br)]. The pH of each reaction solution was measured by inserting a set of microelectrodes of Types K4112 (calomel electrode) and G222C (glass electrode) at the end of the reaction using a Radiometer pH meter, Type PHM26. The Radiometer setup was calibrated against a standard potassium hydrogen phthalate solution contained in the reference cell which was housed in the same temperature-controlled cell holder and hence kept at the same reaction temperature. Measurements on trial solutions indicated that the pH value changed by less than 0.01 unit in the course of the reactions. The reaction temperature was measured also at the end of the reaction and after the pH measurement by inserting a thermometer into the reaction solution.

Results

The behavior of *trans*-$[CoL(NCS)X]^+$ in buffer solutions (2,6-lutidine– or γ-collidine–nitric acid buffer system) was very similar to that of *trans*-$[Co(cyclam)NCSCl]^+$.[10] The visible absorption spectrum slowly changed with time with the absorption peak moving toward a shorter wavelength. Isosbestic points were maintained throughout the entire reaction [L = cyclam, X = Cl (536 and 448), X = Br (547 and 454); L = teta, X = Cl (543 and 453), X = Br (556 and 472); L = trans[14]diene, X = Cl (538 and 448), X = Br (545 and 459 nm)]. The initial spectrum in each case was identical with that of the corresponding starting complex. Volhard's titration confirmed that the release of halide was complete in every case at the end of reactions. Addition of excess sodium chloride to the final acidified solution gave the corresponding *trans*-chloroisothiocyanato complex as confirmed by its visible spectrum. It can, therefore, be concluded that the base hydrolysis of these *trans*-halogenoisothiocyanato complexes is complete and stereoretentive. The reactions were followed spectrophotometrically at a constant wavelength and the pseudo-first-order rate constants, k_{obsd}, were obtained from the standard linear plots of ln $(D_\infty - D_t)$ vs. time. The hydroxide ion concentration for each reaction was obtained from the pH of the solution and the ionic product of water at the same temperature.[11]

The phenomenon of general base catalysis was first examined for each complex at one temperature by following the reactions in a series of buffer solutions of constant buffer ratio, [base]/[salt], and ionic strength and hence of constant pH, but with varying amounts of total buffer concentration.[4,5] Since the base effect, though definite in some cases, was usually very small compared to the hydroxide ion effect, it became essential to maintain the pH value of the series of solutions accurate to within ±0.01 unit. This condition, as well as the temperature (maintained accurate to within ±0.1 °C), was checked for every run. Practically, only about 30% of the runs fell within these pH limits. For each base concentration, the reaction was repeated three to four times in order to obtain the most reliable average value which was then accurate to ca. 2–3%. For cyclam complexes, k_{obsd} was constant at a given pH, being independent of the free base concentration. For teta and trans[14]diene complexes, the following rate expression was observed at any particular pH: $k_{obsd} = k_0 + k_B[base]$, in which k_0 is proportional to the hydroxide ion concentration, i.e., $k_0 = k_{OH}[OH^-]$. The dependence of k_{obsd} on free base concentration, though small, was real. These data are collected in Table I. Since the contribution from $k_B[base]$ was relatively small compared to that from k_0 over the pH range of buffer solutions used, no effort was made to follow these general base catalyses at other temperatures. Reactions were followed at relatively low base (0.001–0.01 M) and complex ($(1–4) \times 10^{-4}$ M) concentrations and at a constant ionic strength of 0.10 M with $NaNO_3$. At these low base concentrations, k_{obsd} was virtually equal to k_0. The contribution from the $k_B[base]$ term was corrected, if necessary, by assuming that the relative contribution from this term remained unchanged with temperature. The second-order base hydrolysis rate constants, k_{OH}, obtained from the slopes of the plots of k_{obsd} vs. $[OH^-]$ over a span of 0.6–1.0 pH unit, are collected in Table II.

Table I. General Base Catalysis for the Base Hydrolysis of Some Complexes of the Type *trans*-[CoL(NCS)X]$^+$ in 2,6-Lutidine-Nitric Acid Buffer Solutions and at $\mu = 0.10$ M with $NaNO_3$

L	X	T, °C	[Base], M	pH	10^8[OH$^-$], M	$10^3 k_{obsd}$,[a,b] s^{-1}	k_{OH},[b] M^{-1} s^{-1}	k_B,[b] M^{-1} s^{-1}
cyclam[c]	Cl	22.0	0.010	7.83	54.0	0.338	6.2×10^2	
cyclam[c]	Cl	22.0	0.100	7.83	54.0	0.328		
cyclam	Br	27.9	0.025	6.67	5.9	1.15	2.0×10^4	
cyclam	Br	27.9	0.050	6.67	5.9	1.16		
cyclam	Br	27.9	0.075	6.67	5.9	1.19		
cyclam	Br	27.9	0.100	6.67	5.9	1.19		
teta	Cl	25.5	0.025	6.68	5.0	1.41	2.5×10^4	4.9×10^{-3}
teta	Cl	25.5	0.050	6.68	5.0	1.48		
teta	Cl	25.5	0.075	6.68	5.0	1.62		
teta	Cl	25.5	0.100	6.68	5.0	1.77		
teta	Br	33.9	0.010	6.23	3.3	6.11	1.8×10^5	3.4×10^{-2}
teta	Br	33.9	0.030	6.23	3.3	7.06		
teta	Br	33.9	0.050	6.23	3.3	7.50		
teta	Br	33.9	0.070	6.23	3.3	8.50		
trans[14]diene	Cl	21.3	0.010	6.64	3.3	4.11	1.2×10^5	1.1×10^{-2}
trans[14]diene	Cl	21.3	0.030	6.64	3.3	4.35		
trans[14]diene	Cl	21.3	0.050	6.64	3.3	4.55		
trans[14]diene	Cl	21.3	0.070	6.64	3.3	4.79		
trans[14]diene	Br	21.5	0.010	6.66	3.5	10.6	2.9×10^5	2.6×10^{-2}
trans[14]diene	Br	21.5	0.030	6.66	3.5	11.0		
trans[14]diene	Br	21.5	0.050	6.66	3.5	11.6		
trans[14]diene	Br	21.5	0.070	6.66	3.5	12.1		

[a] Each entry represents an average of three or four different determinations. [b] $k_{obsd} = k_{OH}[OH^-] + k_B[base]$. [c] In γ-collidine-nitric acid buffer solution.

Discussion

The second-order rate constants, k_{OH}, at 25.0 °C and activation parameters for the base hydrolysis of some related complexes are collected in Table III.

A comparison of these rate constants between teta and corresponding cyclam complexes clearly demonstrates steric acceleration and hence strongly supports a dissociative mechanism for these reactions. The observation of general base catalysis confirms that the hydroxide ion, just like any other base, only plays the role as a reagent to generate the "reactive" amido conjugate base which then undergoes acid hydrolysis in the "normal" manner. In all cases studied, these reactions always have second-order kinetics, being first order with respect to the hydroxide ion concentration. This implies that the standing concentration of the amido conjugate base is very small. It is then possible to apply the steady-state approximation to this intermediate and to obtain the following expression[3] for the second-order base hydrolysis rate constant k for reactions 1–3

$$\text{rate} = k[OH^-][\text{complex}]$$

with

$$k = \frac{k_1 k_2}{k_{-1} + k_2} \tag{4}$$

(or $nk_1k_2/(k_{-1} + k_2)$ in the general case where there are n equivalent amine protons in the complex). To include the effect of general base on the deprotonation reaction, the forward reaction of step 1 is modified into the two separate reactions

$$[CoL_4(\text{amine})X]^{n+} + OH^- \xrightarrow{k_1^{OH}} [CoL_4(\text{amine-H})X]^{(n-1)+} + H_2O$$

$$[CoL_4(\text{amine})X]^{n+} + \text{base} \xrightarrow{k_1^{B}} [CoL_4(\text{amine-H})X]^{(n-1)+} + H(\text{base})$$

Equation 4 still holds with the k_1 term accordingly expressed as

$$k_1 = k_1^{OH} + k_1^{B}\frac{[\text{base}]}{[OH^-]}$$

(usually, $k_1^B << k_1^{OH}$). For tetraammine and bis(ethylenediamine) series of complexes where the base hydrolysis is "normal" (i.e., $k_{-1} >> k_2$), the second-order rate constant k (expression 4) then becomes

$$k = k_{OH} = \frac{k_1}{k_{-1}}k_2 = \frac{K_a}{K_w}k_2$$

where K_a represents the acid dissociation constant (amine proton) of the complex and K_w the ionic product of water. k depends critically on k_2 and is, therefore, strongly dependent on the nature of both orienting group A and leaving group X (e.g., for the *trans*-bis(ethylenediamine) series,[12] $k_{Cl_2}/k_{NCSCl} = 250$ and $k_{OHBr}/k_{OHCl} = 13$). Activation enthalpies fall within the range 22–30 kcal mol^{-1}, which is normal for the acid hydrolysis of most cobalt(III) amine complexes, while activation entropies fall within 20–40 cal mol^{-1} deg^{-1}.[2] At the other extreme end where general base catalysis has been detected for the teta and trans[14]diene series of complexes (i.e., $k_2 >> k_{-1}$), the second-order rate constant of expression 4 becomes

$$k = k_1 = k_1^{OH} + k_1^{B}\frac{[\text{base}]}{[OH^-]}$$

The "so-called" second-order base hydrolysis rate constant with respect to hydroxide ion concentration k_{OH} should then be equated with k_1^{OH} and the base effect k_B with k_1^B making

$$k_{obsd} = k_{OH}[OH^-] + k_B[\text{base}]$$
$$(= k_1^B[OH^-] + k_1^B[\text{base}])$$

It has been demonstrated in a few cases that the effect of acido ligands on the amine–proton exchange rate constant is negligible when they are cis but is relatively much more important when they are trans to the exchanging amines.[13–15] For example, for the $Co(NH_3)_5X^{2+}$ series,[15] the exchange rate constants of cis NH_3 lie within $(1.1–3.8) \times 10^5$ M^{-1} s^{-1} for X = F, Cl, Br, and NO_2 with activation enthalpies lying in the range 12–15 kcal mol^{-1} and activation entropies in the range 3–14 cal mol^{-1} deg^{-1}. The observations here that the second-order base hydrolysis rate constants for these teta and trans[14]diene complexes are virtually independent of the

Table II. Second-Order Base Hydrolysis Rate Constants of Complexes of the Type *trans*-[CoL(NCS)X]$^+$ in 2,6-Lutidine–Nitric Acid Buffer Solutions and at $\mu = 0.10$ M with $NaNO_3$

L	X	T, °C	pH	$10^8[OH^-]$, M	$10^3 k_{osbd}$, s^{-1}	k_{OH}, $M^{-1}\ s^{-1}$
cyclam	Br	20.5	6.41	1.8	0.165	
cyclam	Br	20.5	6.94	6.2	0.580	9.3×10^3
cyclam	Br	20.5	7.03	7.6	0.720	
cyclam	Br	27.9[a]	6.67	5.9		2.0×10^4
cyclam	Br	35.5	6.19	3.4	1.60	
cyclam	Br	35.5	6.71	11	5.30	4.8×10^4
cyclam	Br	35.5	6.79	13	6.60	
cyclam	Br	42.5	6.06	3.9	3.65	
cyclam	Br	42.5	6.57	13	11.5	9.2×10^4
cyclam	Br	42.5	6.68	16	15.0	
cyclam	Br	53.5	5.88	5.0	14.5	
cyclam	Br	53.5	6.22	11	30.0	2.7×10^5
cyclam	Br	53.5	6.42	17	45.0	
cyclam	Br	53.5	6.55	24	58.0	
teta	Cl	23.0	6.91	7.1	1.55	2.1×10^4
teta	Cl	23.0	7.02	9.1	1.85	
teta	Cl	25.5[a]	6.68	5.0		2.5×10^4
teta	Cl	28.5	6.64	5.8	2.00	
teta	Cl	28.5	6.84	9.1	3.00	3.4×10^4
teta	Cl	28.5	6.90	10	3.60	
teta	Cl	35.4	6.18	3.3	2.20	
teta	Cl	35.4	6.48	6.5	4.50	6.8×10^4
teta	Cl	35.4	6.70	11	7.30	
teta	Cl	35.4	6.82	14	9.50	
teta	Cl	42.8	6.07	4.1	5.10	
teta	Cl	42.8	6.56	13	16.5	1.3×10^5
teta	Cl	42.8	6.65	16	21.0	
teta	Cl	48.8	5.98	4.9	9.80	1.9×10^5
teta	Cl	48.8	6.25	9.1	16.5	
teta	Br	12.9	6.38	0.91	0.340	3.9×10^4
teta	Br	12.9	6.63	1.6	0.630	
teta	Br	19.8	6.57	2.5	1.75	
teta	Br	19.8	6.79	4.1	2.50	6.4×10^4
teta	Br	19.8	7.04	7.4	4.70	
teta	Br	19.8	7.19	10	6.30	
teta	Br	26.8	6.34	2.5	2.70	
teta	Br	26.8	6.78	7.5	8.40	1.1×10^5
teta	Br	26.8	7.08	15	15.0	
teta	Br	33.9[a]	6.23	3.3		1.8×10^5
teta	Br	39.6	6.69	14	43.0	3.0×10^5
teta	Br	39.6	6.95	25	72.0	
trans[14]diene	Cl	16.1	6.79	3.2	2.75	8.6×10^4
trans[14]diene	Cl	16.1	7.10	4.9	4.20	
trans[14]diene	Cl	19.8	6.08	0.76	0.94	
trans[14]diene	Cl	19.8	6.44	1.9	2.30	
trans[14]diene	Cl	19.8	6.58	2.6	2.70	1.2×10^5
trans[14]diene	Cl	19.8	6.76	3.9	4.10	
trans[14]diene	Cl	19.8	7.00	6.7	8.60	
trans[14]diene	Cl	21.3[a]	6.64	3.3		1.2×10^5
trans[14]diene	Cl	26.7	6.12	1.7	3.45	
trans[14]diene	Cl	26.7	6.62	5.2	9.30	1.9×10^5
trans[14]diene	Cl	26.7	7.00	13	24.0	
trans[14]diene	Cl	38.0	6.62	11	45.5	4.3×10^5
trans[14]diene	Cl	38.0	6.64	11	48.0	
trans[14]diene	Br	13.2	6.94	3.4	5.20	1.5×10^5
trans[14]diene	Br	13.2	7.33	8.3	11.5	
trans[14]diene	Br	19.8	6.81	4.3	12.0	
trans[14]diene	Br	19.8	6.97	6.3	16.5	2.8×10^5
trans[14]diene	Br	19.8	6.99	6.5	19.0	
trans[14]diene	Br	21.5[a]	6.66	3.5		2.9×10^5
trans[14]diene	Br	26.9	6.12	1.5	6.20	
trans[14]diene	Br	26.9	6.34	2.6	10.5	4.2×10^5
trans[14]diene	Br	26.9	6.97	11	48.5	
trans[14]diene	Br	33.4	6.56	6.8	48.0	
trans[14]diene	Br	33.4	6.75	11	84.0	
trans[14]diene	Br	33.4	6.76	11	78.0	7.3×10^5
trans[14]diene	Br	33.4	6.94	16	115	
trans[14]diene	Br	33.4	7.03	20	155	

[a] Data extracted from Table I.

nature of both orienting (Cl^- and NCS^-) and leaving (Cl^- and Br^-) groups[16] with activation enthalpies lying between 12 and 16 kcal mol^{-1} and activation entropies between 8 and 16 cal mol^{-1} deg^{-1} are fully consistent with the proposed "limiting" SN1cB mechanism for the base hydrolysis of these complexes.[4] This contrasts sharply with the much wider spread of pK_a's for any one series of *trans*-$[CoLAOH_2]^{2+}$ [L = $(NH_3)_4$, $(en)_2$, cyclam] with the nature of A.[17] Here, the acido ligands are

Table III. Second-Order Rate Constants and Activation Parameters for the Base Hydrolysis of Some Complexes of the type *trans*-[CoLAX]$^+$

L	A	X	k_{OH}(25.0 °C), M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}
cyclam[a]	Cl	Cl	6.7×10^4	13.7	12
cyclam[b]	NCS	Cl	9.0×10^2	21.1	25
cyclam[c]	NCS	Br	1.5×10^4	18.8 ± 0.3	24 ± 2
teta[d]	Cl	Cl	5.7×10^5		
teta[c]	NCS	Cl	2.5×10^4	16.3 ± 0.3	16 ± 2
teta[c]	NCS	Br	9.8×10^4	13.0 ± 0.4	8 ± 3
trans[14]diene[d]	Cl	Cl	2.2×10^5		
trans[14]diene[c]	NCS	Cl	1.7×10^5	12.6 ± 0.3	8 ± 2
trans[14]diene[c]	NCS	Br	3.9×10^5	13.6 ± 0.5	13 ± 4
$(en)_2$[e,f]	Cl	Cl	3.2×10^3	22.6	33
$(en)_2$[f,g]	NCS	Cl	1.3×10	22.6	22
$(NH_3)_4$[e]	Cl	Cl	1.8×10^3		
$(NH_3)_4$[b]	NCS	Cl	5.4	29.6	44
RS-2,3,2-tet[h]	Cl	Cl	4×10^4		
RR(*SS*)-2,3,2-tet[h]	Cl	Cl	8.8×10^4	13.6	9

[a] C. K. Poon, Ph.D. Thesis, University of London, 1967. [b] K. S. Mok, C. K. Poon, and H. W. Tong, *J. Chem. Soc., Dalton Trans.*, 1701 (1972). [c] This work. [d] At 19.8 °C; J. A. Kernohan and J. F. Endicott, *Inorg. Chem.*, 9, 1504 (1970). [e] R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Am. Chem. Soc.*, 78, 709 (1956). [f] en = ethylenediamine; activation parameters are extracted from J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta.*, 11, 47 (1974). [g] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1691 (1956). [h] Extrapolated from data published by E. Ahmed, M. L. Tucker, and M. L. Tobe, *Inorg. Chem.*, 14, 1 (1975).

trans to the acidic protons. The base hydrolysis of the cyclam series of complexes is most interesting in that the dichloro complex is "limiting" whereas the chloroisothiocyanato complex is still "normal". Accordingly, the kinetic ratio of k_{Cl_2}/k_{NCSCl} (74) is smaller than the corresponding ratio for bis(ethylenediamine) (250) and tetraammine (330) complexes. Inspection of the rate constant and activation parameters for *trans*-[Co(cyclam)NCSBr]$^+$ seems to indicate that the base hydrolysis of this complex is getting close to but has not yet reached the "limiting" condition as shown by the failure to detect general base catalysis (i.e., $k_{-1} \gtrsim k_2$).

Acknowledgment. We thank the Committee on Higher Degrees and Research Grants of the University of Hong Kong for financial support.

Registry No. *trans*-[Co(cyclam)(NCS)Br]ClO_4, 59204-55-6; *trans*-[Co(cyclam)(NCS)Cl]$^+$, 46931-41-3; *trans*-[Co(teta)(NCS)Cl]$^+$, 55032-63-8; *trans*-[Co(teta)(NCS)Br]$^+$, 55032-93-4; *trans*-[Co(trans[14]diene)(NCS)Cl]$^+$, 55032-53-6; *trans*-[Co(trans[14]diene)(NCS)Br]$^+$, 55032-55-8; *trans*-[Co(cyclam)Br_2]Br, 34460-16-7.

References and Notes

(1) Part 14: C. K. Poon and C. L. Wong, *Inorg. Chem.*, **15**, 1573 (1976).
(2) For useful reviews see (a) M. L. Tobe, *Acc. Chem. Res.*, **3**, 377 (1970); (b) C. K. Poon, *Inorg. Chim. Acta, Rev.*, **4**, 123 (1970); (c) J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta*, **11**, 41 (1974); (d) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2d ed, Wiley, New York, N.Y., 1967; (e) A. M. Sargeson, *Pure Appl. Chem.*, **33**, 527 (1973).
(3) E. Ahmed and M. L. Tobe, *Inorg. Chem.*, **13**, 2956 (1974).
(4) E. Ahmed, M. L. Tucker, and M. L. Tobe, *Inorg. Chem.*, **14**, 1 (1975).
(5) C. K. Poon and M. L. Tobe, *Chem. Commun.*, 156 (1968).
(6) W. K. Chau and C. K. Poon, *J. Chem. Soc. A*, 3087 (1971).
(7) W. K. Chau, W. K. Lee, and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, 2419 (1974).
(8) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).
(9) W. K. Lee and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, 2423 (1974).
(10) K. S. Mok, C. K. Poon, and H. W. Tong, *J. Chem. Soc., Dalton Trans.*, 1701 (1972).
(11) "Handbook of Chemistry and Physics", R. C. Weast, Ed., 48th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1968, p D-92.
(12) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962).
(13) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **8**, 1595 (1969).
(14) D. A. Buckingham, P. J. Cresswell, and A. M. Sargeson, *Inorg. Chem.*, **14**, 1485 (1975).
(15) J. W. Palmer and F. Basolo, *J. Phys. Chem.*, **64**, 778 (1960).
(16) The base hydrolysis of *trans*-[Co(teta)NCSCl]$^+$ may be just at the borderline between "limiting" and "nonlimiting" as reflected by its relatively slower rate constant and higher $\Delta H^{\ddagger}$ than its bromoisothiocyanato and dichloro analogues.
(17) C. K. Poon and H. W. Tong, *J. Chem. Soc., Dalton Trans.*, 930 (1974).

Contribution from the Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Sendai 980, Japan

Preparation and Circular Dichroism of Nickel(II) Complexes Containing Optically Active Tetraamines with Pyrrolidinyl Groups. Nickel(II) Complexes with a Six-Membered Chelate Ring

TASUKU MURAKAMI, SADAO KITAGAWA, and MASAHIRO HATANO*[1]

Received January 7, 1976 AIC60018S

The nickel(II) complexes with 1,3-bis[2(*S*)-aminomethyl-1-pyrrolidinyl]propane (AMPP), 1,3-bis[2(*S*)-*N*-methylaminomethyl-1-pyrrolidinyl]propane (MMPP), and *N*,*N*′-bis[2(*S*)-pyrrolidinylmethyl]-1,3-trimethylenediamine (PMTN) which have the skeleton of 2,3,2-tet were prepared; AMPP and MMPP formed octahedral species, while PMTN formed square-planar ones in aqueous solutions. It was confirmed that whether these tetraamines containing pyrrolidinyl groups form octahedral or planar species of nickel(II) ion depends upon the position of the two pyrrolidinyl groups within the tetraamines themselves. The member of the central chelate ring is not significant for this selective complexation. The mixed complexes of AMPP and PMTN with ethylenediamine were isolated. The CD spectra of these complexes were compared with those of the complexes with the other tetraamines which have the skeleton of trien.

In the previous papers,[2,3] we have reported on the formation of the nickel(II) complexes with the five types of optically active tetraamines which have two pyrrolidinyl groups in each molecule. 1,2-Bis[2(*S*)-aminomethyl-1-pyrrolidinyl]ethane (AMPE)[4] and 1,2-bis[2(*S*)-*N*-methylaminomethyl-1-pyrrolidinyl]ethane (MMPE) formed blue octahedral complexes with nickel(II) ion in aqueous solutions, while *N*,*N*′-bis[2(*S*)-pyrrolidinylmethyl]ethylenediamine (PMEN), *N*,*N*′-bis[2(*S*)-pyrrolidinylmethyl]-1(*R*),2(*R*)-cyclohexanediamine (*RR*-PMCN), and *N*,*N*′-bis[2(*S*)-pyrrolidinylmethyl]-1(*S*),2(*S*)-cyclohexanediamine (*SS*-PMCN) formed yellow square-planar ones. This selectivity may be related to the position of the two pyrrolidinyl groups within the tetraamines; AMPE and MMPE have the two pyrrolidinyl groups