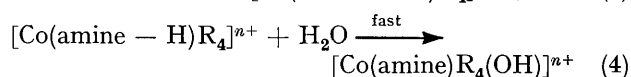
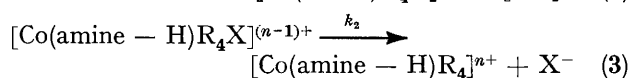
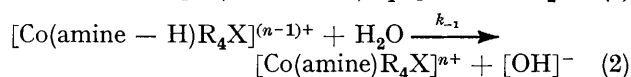
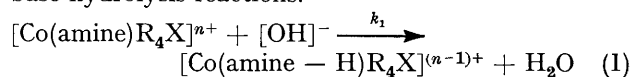


Structural and Mechanistic Studies of Co-ordination Compounds. Part 20.¹ Preparation and Base Hydrolysis of Some Cobalt(III) Complexes of Quadridentate Macrocyclic Amines

By Chung-Kwong Poon* and Pak-Wing Mak, Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

The complexes *trans*-[CoBr(L¹)(N₃)]⁺ (L¹ = 1,4,8,11-tetra-azacyclotetradecane) and *trans*-(*RS*)-[CoA(L²)X]⁺ (L² = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-7,14-diene; A = CN, X = NO₂, NCS, or N₃; A = NO₂, X = Cl or Br) have been prepared and characterized. The kinetics of base hydrolysis of an extensive set of complexes of the type *trans*-[CoA(L)X]⁺ [L = L¹, L², and L³ (= *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane)] have been studied. All the complexes react by second-order kinetics with complete release of the leaving group X and complete retention of configuration. An S_N1(cb) mechanism operating under three different conditions (normal, intermediate, and limiting) has been assigned on the basis of the magnitudes of the second-order rate constants, *k*_{OH}, enthalpies (Δ*H*‡) and entropies (Δ*S*‡) of activation, and the effects of the orientating and leaving groups on *k*_{OH}.

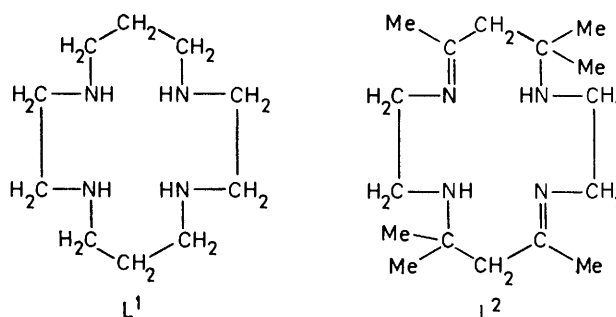
PREVIOUSLY^{2,3} we have shown that the second-order base-hydrolysis rate constants of *trans*-(*RS*)-[CoA(L²)-X]⁺ [L² = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-7,14-diene] are independent of the nature of both the orientating ligands (A = NCS, Cl, or CN) and the leaving groups (X = Cl or Br). This, together with the observation of general base catalysis and the relatively low values of the activation parameters, has been taken to indicate a 'limiting' S_N1(cb) mechanism⁴⁻⁸ [equations (1)–(4)] in which *k*₂ ≫ *k*₋₁ thus making *k*₁ (*k*₁ ≪ *k*₂ and *k*₋₁) the rate-determining step for these base-hydrolysis reactions.



The present paper is designed to extend the study to a wider range of A and X and to search for systems in which the 'intermediate' S_N1(cb) mechanism (*i.e.* *k*₋₁ ~ *k*₂) may be operative. The operation of a 'normal' S_N1(cb) mechanism (*i.e.* *k*₋₁ ≫ *k*₂) is well known in the base hydrolysis of most cobalt(III) amine complexes. This paper describes the preparation and base hydrolysis of *trans*-(*RS*)-[CoL²(NO₂)X]⁺ (X = Cl or Br), *trans*-(*RS*)-[Co(CN)L²(X)]⁺ (X = NO₂, NCS, or N₃), and *trans*-[CoBr(L¹)(N₃)]⁺ (L¹ = 1,4,8,11-tetra-azacyclotetradecane), and the base hydrolysis of *trans*-(*RS*)-[CoL²(N₃)X]⁺ (X = Cl or Br) and *trans*-[CoL¹(OH)-(N₃)]⁺ cations. Unfortunately, the acid hydrolysis of *trans*-(*RS*)-[CoL²(NO₂)X]⁺ (X = Cl or Br) was very fast † and the reaction could not be prevented by the addition of an excess of the appropriate anion X⁻.

† The report of Hay and Lawrance⁹ that *trans*-[CoCl(L²)-(NO₂)]⁺ undergoes base hydrolysis at a rate of 2.5 × 10² dm³ mol⁻¹ s⁻¹ at 25 °C could not be reconciled with our observation that the background aquation of this complex was complete as soon as it was dissolved in ice-cold dilute nitric acid. It seems likely that the discrepancy could be due to the isomer problem with complexes of this type (see Results section). We may be working on an isomer different from that of Hay and Lawrance.

This behaviour makes it impossible to follow the base hydrolysis of these two nitro-complexes. Furthermore, attempts to prepare some other isothiocyanato- and cyano-complexes of L² containing other relatively labile leaving groups (X = NO₃, F, or I), which may possibly react by the limiting path, in a pure crystalline



form were unsuccessful. In some cases, the reactions were followed in both buffer and Na[OH] solutions in order to determine whether various buffer components have any significant effect on the rates.

EXPERIMENTAL

Preparation of the Complexes.—*trans*-Azidobromo(1,4,8,11-tetra-azacyclotetradecane)cobalt(III) perchlorate, *trans*-[CoBr(L¹)(N₃)] [ClO₄]. This complex was prepared by adding with stirring a saturated aqueous solution of KBr (2 cm³) to an aqueous solution of *trans*-[CoL¹(N₃)(OH₂)] [ClO₄]₂¹⁰ (2 g in 10 cm³). On standing, *trans*-[CoBr(L¹)(N₃)] [ClO₄] slowly separated out as light bluish green crystals. The complex could be recrystallized, if desired, by adding diethyl ether to a saturated solution of the complex in acetone (yield 80%) (Found: C, 24.8; H, 4.9; Br, 16.6; Cl, 7.4; N, 20.4. Calc. for C₁₀H₂₄BrClCoN₇O₄: C, 25.0; H, 5.0; Br, 16.6;

¹ Part 19, C. K. Poon and D. A. Isabirye, *J.C.S. Dalton*, 1977, 2115.

² P. W. Mak and C. K. Poon, *Inorg. Chem.*, 1976, 15, 1949.

³ C. K. Poon, C. L. Wong, and P. W. Mak, *J.C.S. Dalton*, 1977, 1931.

⁴ M. L. Tobe, *Accounts Chem. Res.*, 1970, 3, 377.

⁵ F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions', 2nd edn., Wiley, New York, 1967.

⁶ C. K. Poon, *Inorg. Chim. Acta Rev.*, 1970, 4, 123.

⁷ J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta*, 1974, 11, 41.

⁸ A. M. Sargeson, *Pure Appl. Chem.*, 1973, 33, 527.

⁹ R. W. Hay and G. A. Lawrance, *J.C.S. Dalton*, 1975, 1556.

¹⁰ C. K. Poon and H. W. Tong, *J.C.S. Dalton*, 1974, 1.

Cl, 7.4; N, 20.4%) [$\nu(\text{NNN})$ at 2 050 cm^{-1} ; λ_{max} 610 nm in water].

trans-(RS)-*Chloro*(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-7,14-diene)nitrocobalt(III) perchlorate hydrochloride, *trans*-(RS)-[CoCl(L²)(NO₂)](ClO₄)·HCl. This complex was first reported by Hay and Lawrance.⁹ However, it was found more convenient¹¹ to prepare it by treating a saturated aqueous solution of *trans*-(RS)-[CoL²(NO₂)₂](ClO₄)¹² (2.7 g) with concentrated HCl (20 cm^3). After the brown fumes had subsided, the solution was cooled and excess of Na[ClO₄] was added to precipitate pink crystals. The complex was recrystallized by adding diethyl ether to a saturated solution of the complex in ethanol acidified with HCl (yield 50%) (Found: C, 33.5; H, 5.9; Cl, 19.0; N, 12.9. Calc. for C₁₆H₃₃Cl₃CoN₅O₆: C, 34.5; H, 5.9; Cl, 19.0; N, 12.6%) [$\nu(\text{NO}_2)$ at 1 315 and 1 300 cm^{-1} ; $\delta(\text{ONO})$ at 820 cm^{-1} ; λ_{max} 522 nm in methanol].

trans-(RS)-*Bromo*(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-7,14-diene)nitrocobalt(III) perchlorate, *trans*-(RS)-[CoBr(L²)(NO₂)](ClO₄). This complex was prepared by adding a methanolic solution of Na[NO₂] (0.35 g), which was saturated with Na[ClO₄], to *trans*-(RS)-[CoBr(L²)(OH₂)](ClO₄)₂·2H₂O¹³ (3 g) in the minimum amount of methanol. Scratching the side of the container induced slow crystallization of brownish red crystals which were filtered off, washed with several small portions of methanol and diethyl ether, and finally dried *in vacuo* (yield 70%) (Found: C, 33.9; H, 5.5; Br, 14.3; N, 12.4. Calc. for C₁₆H₃₂BrClCoN₅O₆: C, 34.0; H, 5.7; Br, 14.2; N, 12.4%) [$\nu(\text{NO}_2)$ at 1 340 and 1 320 cm^{-1} ; $\delta(\text{ONO})$ at 828 cm^{-1} ; λ_{max} 524 nm in acetone].

trans-(RS)-*Cyano*(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-7,14-diene)nitrocobalt(III) perchlorate, *trans*-(RS)-[Co(CN)L²(NO₂)](ClO₄). A warm (*ca.* 60 °C), filtered, saturated, methanolic solution of Na[NO₂] (0.35 g) was added with stirring to a similarly warmed methanolic solution of *trans*-(RS)-[Co(CN)L²(OH₂)](ClO₄)₂·2H₂O.³ The dark yellow solution turned bright yellow and was allowed to stand in a refrigerator for 4 d. Fine, needle-shaped, pale yellow crystals appeared, which were filtered off, washed with ethanol and diethyl ether, and dried *in vacuo* (yield 80%) (Found: C, 39.5; H, 6.5; Cl, 7.0; N, 16.0. Calc. for C₁₇H₃₂ClCoN₆O₆: C, 40.0; H, 6.3; Cl, 6.9; N, 16.5%) [$\nu(\text{CN})$ at 2 140 cm^{-1} ; $\nu(\text{NO}_2)$ at 1 330 cm^{-1} ; $\delta(\text{ONO})$ at 820 cm^{-1} ; λ_{max} 419 nm in water].

trans-(RS)-*Cyano*(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-7,14-diene)isothiocyanatocobalt(III) perchlorate monohydrate, *trans*-(RS)-[Co(CN)L²(NCS)](ClO₄)·H₂O. Equal molar amounts of *trans*-(RS)-[Co(CN)L²(OH₂)](ClO₄)₂·2H₂O³ (2.9 g) and [NH₄][NCS] (0.38 g) were separately dissolved in minimum amounts of boiling methanol. These solutions were filtered while hot, mixed, and boiled for 10 min. The solvent was removed *in vacuo* and the crude product remaining was dissolved in the minimum amount of ethanol-acetone, filtered, and then reprecipitated with diethyl ether. The product was recrystallized by dissolving it in the minimum amount of dilute HClO₄, adding four times the acid volume of ethanol-acetone (1 : 1), and reprecipitating by dropwise addition of diethyl ether (yield 60%) (Found: C, 39.7; H, 6.2; Cl, 6.8; N, 15.5; S, 5.6. Calc. for C₁₈H₃₄ClCoN₆O₅S: C, 40.0; H, 6.3; Cl, 6.6; N, 15.5; S, 5.9%) [$\nu(\text{CN})$ at 2 140

cm^{-1} ; N-bonded NCS group, $\nu(\text{CN})$ at 2 100 cm^{-1} , $\nu(\text{CS})$ at 830 cm^{-1} ; λ_{max} 436 nm in water].

trans-(RS)-*Azidocyno*(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-7,14-diene)cobalt(III) perchlorate, *trans*-(RS)-[Co(CN)L²(N₃)](ClO₄). This complex was prepared by mixing hot methanolic solutions of *trans*-(RS)-[Co(CN)L²(OH₂)](ClO₄)₂·2H₂O³ (2.9 g) and Na[N₃] (0.33 g). The resulting reddish yellow solution was warmed for 10 min, cooled, and treated with diethyl ether to precipitate the desired product (yield 70%) (Found: C, 40.2; H, 6.5; Cl, 7.1; N, 22.2. Calc. for C₁₇H₃₂ClCoN₈O₄: C, 40.3; H, 6.3; Cl, 7.0; N, 22.1%) [$\nu(\text{CN})$ at 2 120 cm^{-1} ; $\nu(\text{NNN})$ at 2 040 cm^{-1} ; λ_{max} 450 nm in water].

The complexes *trans*-[CoBr(L¹)(NCS)](ClO₄)², *trans*-(RS)-[CoCl₂(L²)](ClO₄)¹² and *trans*-(RS)-[CoCl(L²)(NCS)](ClO₄)¹⁴ were prepared by published methods.

Kinetics.—The base hydrolyses in either buffer or Na[OH] solutions were followed spectrophotometrically *in situ* using a Unicam SP 8000 recording spectrophotometer, equipped with a Weyfringe ADCP-2 digital printer, or an Aminco-Morrow stopped-flow spectrophotometer equipped with an Aminco DASAR (data acquisition, storage, and retrieval) system. For relatively labile complexes (*i.e.* those having relatively fast background-aquation rate constants), the reaction was started by adding a drop of a concentrated methanolic or acetonitrile solution of the complex to the appropriate reaction medium (buffer solution or Na[OH]) previously brought to the reaction temperature in a 4-cm open-top optical cell housed in the thermostatted compartment of a Unicam SP 8000 spectrophotometer. The solution was rapidly stirred with a thin glass paddle which had also been brought to the reaction temperature in the reaction medium. After removing the glass paddle, the instrument was immediately switched on to record the changing absorbance at a fixed wavelength. The above process between adding the drop of complex solution and the first spectrophotometric reading could be accomplished in *ca.* 3 s. The change in temperature on adding the drop of complex solution to the reaction medium was found to be negligible. The pH of the buffer solutions in the optical cell was measured with a set of microelectrodes, type K4112 (calomel electrode) and G222C (glass electrode), using a Radiometer type PHM26 pH meter. The pH meter was calibrated against a standard buffer solution contained in the reference cell and hence kept at the same reaction temperature. The hydroxide-ion concentration of the buffer solution in each run was calculated as described previously.³ For these fast reactions, the spectral isosbestic points were determined by rapid scanning at *ca.* 10-nm intervals. Usually, the experiments had to be repeated a number of times in order to obtain the desired information. As a general precaution to prevent general base catalysis,^{2,3} the base concentration of the buffer solutions was usually kept at a relatively low value (1×10^{-3} — 1×10^{-2} mol dm⁻³).

For complexes having relatively slow background-aquation rate constants, the reaction was followed either by the method described above (here, the open-top optical cell was covered by a lid) or by the stopped-flow method. The complex in HNO₃ (*ca.* 10⁻³—10⁻⁴ mol dm⁻³) was stored in one reservoir while Na[OH] of suitable concentration (at least ten times that of the complex) and ionic strength was

¹¹ W. K. Lee, M. Phil. Thesis, University of Hong Kong, 1974.

¹² N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, 1967, **6**, 770.

¹³ W. K. Lee and C. K. Poon, *J.C.S. Dalton*, 1974, 2423.

¹⁴ W. K. Chau, W. K. Lee, and C. K. Poon, *J.C.S. Dalton*, 1974, 2419.

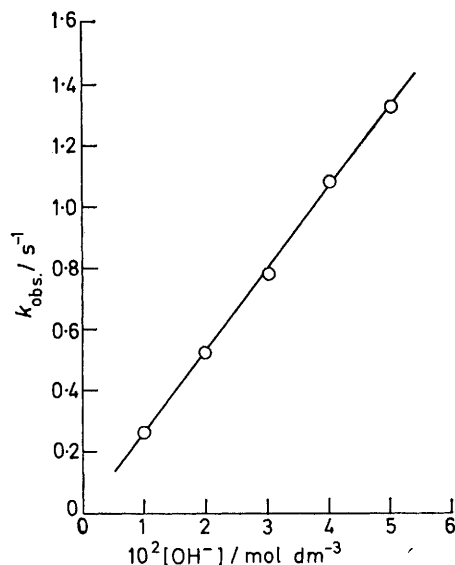
kept in the other reservoir. After thermal equilibration, the solutions were mixed and the changing light intensity at a preset wavelength was stored in the Aminco DASAR system. The kinetic data were then either printed out on a Teletype typewriter or plotted on graph paper using a Houston Omnigraphic 2000 X-Y recorder. It was found that the reservoir temperature depended not only on the temperature of the thermostatted water, from a Forma Masterline model 2800 refrigerated thermostat bath, but also on the flow rate and temperature of the surroundings. In order to overcome this problem, the instrument was placed in a thermostatted box and calibration curves of reservoir temperature as a function of bath and box temperature and flow rate were determined independently.

RESULTS

Complexes of the general type $trans\text{-}[\text{CoA}(\text{L}^2)\text{X}]^+$ can have several different diastereoisomers depending on the relative orientations of the N-H bonds of the two secondary nitrogen donors. Only one isomer is expected from the N-meso (RS) configuration while two can occur with the N-rac (RR,SS) configuration. All the L^2 complexes reported are prepared either directly or indirectly from the isomerically pure N-meso isomer of $trans\text{-}[\text{CoCl}_2(\text{L}^2)]^+$ under controlled conditions. At each stage of the preparation only one isomer was detected by chromatography using Dowex 50W-X8 (20-50 mesh) or Sephadex C-25 cation-exchange resins. For relatively stable complexes, the isomeric purity was further confirmed by noting that the electronic-absorption spectrum was unaffected by several recrystallization processes. An N-meso (RS) configuration is, tentatively, assigned to all these L^2 complexes.

The spectral behaviour for the base hydrolysis of $trans\text{-}(\text{RS})\text{-}[\text{Co}(\text{CN})\text{L}^2(\text{X})]^+$ ($\text{X} = \text{N}_3, \text{NCS}, \text{or } \text{NO}_2$) and $trans\text{-}[\text{CoBr}(\text{L}^1)(\text{N}_3)]^+$ was very similar to that of the corresponding

solution. This is due to the relatively very rapid aquation of the chlorohydroxo-intermediate. The base hydrolysis of $trans\text{-}[\text{CoL}^1(\text{OH})\text{X}]^+$ ($\text{X} = \text{Cl}$ or N_3) was most conveniently studied in $\text{Na}[\text{OH}]$ solution starting with $trans\text{-}[\text{CoCl}_2(\text{L}^1)]^+$ and $trans\text{-}[\text{CoBr}(\text{L}^1)(\text{N}_3)]^+$ respectively. The release

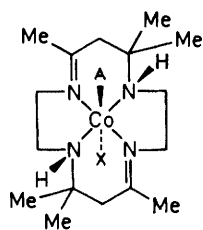
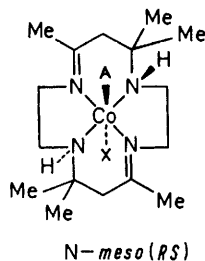


A representative plot of $k_{\text{obs.}}$ against $[\text{OH}^-]$ for the base hydrolysis of $trans\text{-}(\text{RS})\text{-}[\text{Co}(\text{CN})\text{L}^2(\text{NCS})]^+$ in $\text{Na}[\text{OH}]$ at $I = 0.10 \text{ mol dm}^{-3}$ and 15.4°C

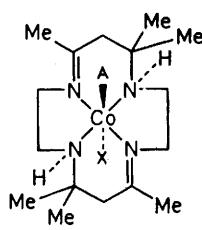
of the first halide from these two complexes was virtually complete as soon as they were dissolved, giving the corresponding $trans\text{-}[\text{CoL}^1(\text{OH})\text{X}]^+$. All these reactions are complete and stereoretentive. Pseudo-first-order rate constants, $k_{\text{obs.}}$, were obtained from standard plots of $\ln(D_\infty - D_t)$ against time, where D_t and D_∞ represent the absorbances at time t and after 10 half-lives respectively. These plots are linear to more than two half-lives. The second-order rate constants, k_{OH} , were obtained from the gradients of linear plots of k_{OH} against $[\text{OH}^-]$ over an approximately five-fold range of $[\text{OH}^-]$ (Figure).

The base hydrolysis of $trans\text{-}(\text{RS})\text{-}[\text{CoL}^2(\text{N}_3)\text{X}]^+$ ($\text{X} = \text{Cl}$ or Br) was complicated by the subsequent release of azide from the azidohydroxo-product. The second steps do not show any isosbestic points to enable the first steps to be followed more conveniently at these wavelengths. The base hydrolysis of the first step was followed spectrophotometrically for about two half-lives when the interference due to the second step was not serious, and the pseudo-first-order rate constants were obtained by Guggenheim's method.¹⁵ The kinetic data for $trans\text{-}(\text{RS})\text{-}[\text{CoCl}_2(\text{L}^2)]^+$ and $trans\text{-}(\text{RS})\text{-}[\text{CoL}^2(\text{N}_3)\text{X}]^+$ ($\text{X} = \text{Cl}$ or Br) were not very accurate. Due to the rapid aquation of these complexes, the base hydrolysis had to be followed in buffers of high pH so that the base hydrolysis might constitute the major contribution to the observed rate constants. However, this increased the observed rate constants to within the range 10^{-2} – 10^{-1} s^{-1} , and a large portion of the complex had frequently reacted before the first absorbance measurement could be made. Furthermore, the Guggenheim plots for the azido-complexes were appreciably curved at about two half-lives due to the participation of the second step, and

¹⁵ A. A. Frost and R. G. Pearson, 'Kinetics and Mechanisms,' 2nd edn., Wiley, New York, 1961.



N-rac (RR,SS)



cyanohalogeno-³ and azidochloro-complexes¹⁰ respectively. Isosbestic points were maintained throughout the reaction with the initial spectrum being identical to that of the starting complex and the final acidified spectrum to that of the corresponding $trans\text{-}aqua\text{-}cyano\text{-}$ and $trans\text{-}aqua\text{-}azido\text{-}$ complexes respectively. The base hydrolysis of $trans\text{-}(\text{RS})\text{-}[\text{CoCl}_2(\text{L}^2)]^+$, however, gave a final spectrum identical to that of $trans\text{-}(\text{RS})\text{-}[\text{CoL}^2(\text{OH})_2]^+$ in the same buffer

only the initial gradients were used for the calculation of the rate constants. For these fast reactions, the kinetic experiments were repeated many times in order to obtain a relatively reliable average value. These rate constants, which might not be as accurate as the others, however, gave a good measure of the reactivity of these complexes, at least for comparison purposes. The activation parameters, however, have probably errors of *ca.* 20–30%.

For some systems, reactions were carried out in two or more different media (*i.e.* in buffer or Na[OH] solutions), and in one case in Na[OH] to which an additional base (2,6-dimethylpyridine) had been added, in order to determine the effect of buffer on k_{OH} and the associated activation parameters. The reactivity of *trans*-(*RS*)-[Co(CN)(L²)(NO₂)]⁺ in Na[OH] was such that the reaction could be conveniently followed by the 'normal' method of mixing using the Unicam SP 8000 recording spectrophotometer and by the stopped-flow method using the Aminco-DASAR system. The combined set of kinetic data from two different methods gave a linear activation plot of $\ln k_{OH}/T$ against $1/T$ where T is the absolute temperature. The reaction conditions are summarized in Table 1 and values of k_{OH} in Table 2. Activation enthalpies, ΔH^\ddagger , and entropies,

TABLE 1

Spectral characteristics for the base hydrolysis of some complexes of the type *trans*-[CoA(L)X]⁺.

L	A	X	Reaction ^a medium	Isosbestic points (λ/nm)	λ ^b /nm
L ¹	N ₃	Br	2,6Me ₂ -py-HNO ₃ (U)	468, 568	390
			γ-collidine-HNO ₃ (U)	468, 568	390
			Na[OH](S)	<i>c</i>	390
			Na[OH](U)	<i>c</i>	360
L ²	OH	N ₃	Na[OH](U)	<i>c</i>	400
			Na[OH](S)	<i>c</i>	400
	NCS	Br	γ-collidine-HNO ₃ (U)	464, 542	390
			γ-collidine-HNO ₃ (U)	466, 544	400
	CN	NO ₂	Na[OH](U and S)	386, 583	650
			H ₃ BO ₃ -Na[OH](U)	355, 429	470
L ³	NCS	Cl	Na[OH](S)	<i>c</i>	345
			H ₃ BO ₃ -Na[OH](U)	<i>c</i>	345
			Na[OH](S)	<i>c</i>	345
			Na[OH](S)	<i>c</i>	400

^a Letters in parentheses indicate the method used to follow the reactions: U = normal spectrophotometric method using a Unicam SP 8000 spectrophotometer; S = stopped-flow method. ^b Wavelength at which the reaction was followed.

^c The reaction was too fast to allow isosbestic points to be determined; however, in the 2,6Me₂-py-HNO₃ buffer system, isosbestic points have been reported² to occur at 454 and 547 nm for *trans*-[CoBr(L¹)(NCS)]⁺ and at 453 and 543 nm for *trans*-[CoCl(L³)(NCS)]⁺.

ΔS^\ddagger , were obtained from the above plots by the method of least squares.

DISCUSSION

The second-order rate constants extrapolated to 25.0 °C, and activation parameters for the base hydrolysis of some cobalt(III) complexes of macrocyclic amines L¹, L², and L³ (L³ = *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane), are collected in Table 3. Although these values do depend slightly on the nature of the reaction medium, the differences are small and, therefore, do not appear to upset the following discussion. The discrepancy could be due to error in the estimation of [OH⁻] in buffer solutions from the relation

TABLE 2

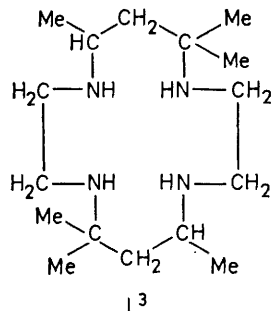
Second-order base-hydrolysis rate constants of complexes of the type *trans*-[CoA(L)X]⁺ at $I = 0.10$ mol dm⁻³ (Na[NO₃])

L	A	X	Reaction medium	θ _c °C	k_{OH}^a dm ³ mol ⁻¹ s ⁻¹			
L ¹	N ₃	Br	2,6Me ₂ -py-HNO ₃	10.7	(5.6 ± 0.3) × 10 ³			
				21.1	(2.0 ± 0.1) × 10 ⁴			
				27.8	(3.7 ± 0.1) × 10 ⁴			
				32.7	(6.1 ± 0.3) × 10 ⁴			
				42.7	(1.6 ± 0.1) × 10 ⁵			
				53.5	(4.2 ± 0.2) × 10 ⁵			
			γ-collidine-HNO ₃	15.9	(9.9 ± 0.5) × 10 ³			
				25.5	(2.9 ± 0.1) × 10 ⁴			
				31.0	(4.9 ± 0.3) × 10 ⁴			
				18.1	(8.8 ± 0.3) × 10 ³			
				21.8	(1.3 ± 0.05) × 10 ⁴			
				24.1 ^b	(1.7 ± 0.1) × 10 ⁴			
			OH	N ₃	Na[OH]	Na[OH]	26.9	(2.2 ± 0.1) × 10 ⁴
28.4 ^b	(2.6 ± 0.2) × 10 ⁴							
30.5	(3.1 ± 0.2) × 10 ⁴							
40.2	(3.0 ± 0.2) × 10 ⁻²							
47.1	(8.1 ± 0.4) × 10 ⁻²							
56.3	(2.9 ± 0.1) × 10 ⁻¹							
NCS	Br	Na[OH]				Na[OH]	22.3	(5.9 ± 0.3) × 10 ³
							28.1	(1.1 ± 0.05) × 10 ⁴
							33.5	(2.0 ± 0.1) × 10 ⁴
							18.3	(1.0 ± 0.2) × 10 ⁵
							21.1	(1.2 ± 0.2) × 10 ⁵
							24.9	(1.6 ± 0.2) × 10 ⁵
L ²	N ₃	Cl	γ-collidine-HNO ₃	9.6	(5.9 ± 1.0) × 10 ⁴			
				14.8	(9.0 ± 2.0) × 10 ⁴			
				20.2	(1.3 ± 0.2) × 10 ⁵			
				11.0	(6.0 ± 2.0) × 10 ⁴			
				14.8	(9.0 ± 2.5) × 10 ⁴			
				20.2	(1.3 ± 0.3) × 10 ⁵			
	CN	NO ₂	Na[OH]	Na[OH]	10.6 ^c	(1.2 ± 0.05)		
					13.3 ^c	(2.0 ± 0.1)		
					18.6 ^c	(4.0 ± 0.3)		
					21.8 ^d	(5.8 ± 0.3)		
					25.2 ^c	(9.2 ± 0.5)		
					26.8 ^d	(1.3 ± 0.1) × 10		
CN	NCS	H ₃ BO ₃ -Na[OH]	H ₃ BO ₃ -Na[OH]	31.8 ^d	(2.1 ± 0.1) × 10			
				23.0	(1.0 ± 0.05) × 10 ²			
				28.1	(2.0 ± 0.1) × 10 ²			
				33.7	(4.5 ± 0.2) × 10 ²			
				38.9	(9.2 ± 0.6) × 10 ²			
				15.4	(2.7 ± 0.1) × 10			
	CN	N ₃	H ₃ BO ₃ -Na[OH]	Na[OH]	22.3	(6.7 ± 0.3) × 10		
					28.1	(1.4 ± 0.1) × 10 ²		
					33.5	(3.1 ± 0.1) × 10 ²		
					25.0	(8.7 ± 0.5) × 10		
					40.4	(6.3 ± 0.4) × 10 ²		
					46.7	(1.4 ± 0.1) × 10 ³		
L ³	NCS	Cl	Na[OH]	15.6	(1.9 ± 0.1) × 10			
				26.8	(7.8 ± 0.5) × 10			
				31.7	(1.5 ± 0.1) × 10 ²			
				18.1	(6.3 ± 0.4) × 10 ³			
				21.8	(8.7 ± 0.4) × 10 ³			
				24.1	(1.1 ± 0.05) × 10 ⁴			
26.9	(1.4 ± 0.1) × 10 ⁴							
28.4	(1.6 ± 0.1) × 10 ⁴							
31.7	(2.1 ± 0.1) × 10 ⁴							

^a k_{OH} was obtained from the gradient of a linear plot of k_{obs} against [OH⁻] for up to five different runs by the method of least squares over an approximately five-fold range of [OH⁻]. ^b Containing 0.10 mol dm⁻³ 2,6-Me₂-py. ^c By the 'normal' method of mixing the reactants using the Unicam SP 8000 spectrophotometer. ^d By the stopped-flow method using the Aminco-DASAR system.

$K_W = a_H a_{OH}$, where K_W , a_H , and a_{OH} represent the ionic product of water and the activity of hydrogen ion and hydroxide ion respectively. Values of a_H were obtained directly from the pH of the buffer solutions and the values of K_W at different temperatures were those for

pure water.¹⁶ The actual reaction medium, however, contained 0.10 mol dm⁻³ 1:1 electrolyte and *ca.* 0.01



mol dm⁻³ amine. Although allowance has been made for the effect of ionic strength and temperature on the

the entire range of [OH⁻] studied. It has been shown¹⁷ that the second-order rate constant, k_{OH} , for reactions (1)–(4) is given by expression (5) where $k_{OH} = k_1 k_2 /$

$$\text{rate} = k_{OH}[\text{OH}^-][\text{complex}] \quad (5)$$

$(k_{-1} + k_2)$ or $n k_1 k_2 / (k_{-1} + k_2)$ in the general case where there are n equivalent amine protons in the complex.

Inspection of the kinetic data in Table 3 shows clearly that k_{OH} for *trans*-(RS)-[CoA(L²)X]⁺ is indeed virtually independent of the nature of both the orientating [CN]⁻, [NCS]⁻, Cl⁻, and [N₃]⁻ ligands, of different electronic-displacement properties, and the leaving Cl⁻ and Br⁻ groups. With relatively 'inert' leaving groups, such as [NO₂]⁻, [N₃]⁻, and [NCS]⁻, however, the reactivity of *trans*-(RS)-[Co(CN)L²(X)]⁺ does depend on the nature of X. This kinetic behaviour constrasts

TABLE 3

Second-order rate constants at 25.0 °C and activation parameters for the base hydrolysis of some macrocyclic amine complexes of the type *trans*-[CoA(L)X]⁺

L	A	X	Reaction medium	k_{OH} dm ³ mol ⁻¹ s ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J K ⁻¹ mol ⁻¹	Classification
L ²	Cl	Cl	γ -collidine-HNO ₃ ^a	1.6×10^5	49 ± 6	19 ± 30	I
	NCS	Cl	2,6Me ₂ -py-HNO ₃ ^b	1.3×10^5	51.5 ± 1.5	25 ± 12	I
	N ₃	Cl	γ -collidine-HNO ₃ ^a	1.8×10^5	49 ± 6	20 ± 30	I
	CN ⁻	Cl	γ -collidine-HNO ₃ ^c	1.6×10^5	56.5 ± 1.0	44 ± 8	I
	NCS	Br	2,6Me ₂ -py-HNO ₃ ^b	2.9×10^5	52.8 ± 2.0	37 ± 15	I
	N ₃	Br	γ -collidine-HNO ₃ ^a	1.9×10^5	55 ± 10	40 ± 40	I
	CN ⁻	Br	2,6Me ₂ -py-HNO ₃ ^c	1.1×10^6	52.4 ± 1.0	46 ± 8	I
L ³	NCS	Br	2,6Me ₂ -py-HNO ₃ ^b	7.5×10^4	53.9 ± 2.0	29 ± 15	I
L ¹	Cl	Cl	2,6Me ₂ -py-HNO ₃ ^d	6.7×10^4	56.5 ± 1.5	37 ± 12	I
	N ₃	Cl	γ -collidine-HNO ₃ ^e	2.8×10^3	98.1 ± 1.0	150 ± 8	II
	NCS	Cl	γ -collidine-HNO ₃ ^f	9.0×10^2	87.8 ± 1.5	106 ± 12	II
	NO ₂	Cl	H ₃ BO ₃ -Na ₂ [B ₄ O ₇] ^g	6.0×10^2	81.2 ± 1.0	81 ± 8	II
	CN ⁻	Cl	2,6Me ₂ -pip-HNO ₃ ^h	2.8×10	94.6 ± 1.0	100 ± 8	II
	CN ⁻	Br	γ -collidine-HNO ₃ ^e	5.0×10^2	84.1 ± 1.5	88 ± 12	II
	OH ⁻	N ₃	Na[OH] ^a	2.8×10^{-3}	118 ± 1.0	103 ± 8	II
	OH ⁻	Cl	Na[OH] ^a	4.8	96.4 ± 1.5	92 ± 12	II
L ²	CN ⁻	NCS	H ₃ BO ₃ -Na[OH] ^a	1.3×10^2	105 ± 1.5	149 ± 12	II
			Na[OH] ^a	9.9×10	96.2 ± 1.0	116 ± 8	II
	CN ⁻	N ₃	H ₃ BO ₃ -Na[OH] ^a	8.7×10	98.9 ± 1.5	124 ± 12	II
			Na[OH] ^a	6.5×10	90.7 ± 2.0	94 ± 15	II
	CN ⁻	NO ₂	Na[OH] ^a	9.2	93.9 ± 1.5	89 ± 12	II
L ¹	NCS	Br	2,6Me ₂ -py-HNO ₃ ^b	1.1×10^4	78.8 ± 1.3	97 ± 8	III
			Na[OH] ^a	8.0×10^3	80.0 ± 2.0	98 ± 15	III
	N ₃	Br	2,6Me ₂ -py-HNO ₃ ^a	2.8×10^4	74.7 ± 1.0	91 ± 8	III
			γ -collidine-HNO ₃ ^a	2.7×10^4	75.2 ± 2.0	92 ± 15	III
			Na[OH] ^a	1.8×10^4	72.9 ± 1.5	81 ± 12	III
	NO ₂	Br	γ -collidine-HNO ₃ ^g	1.4×10^4	79.2 ± 2.0	100 ± 15	III
L ³	NCS	Cl	2,6Me ₂ -py-HNO ₃ ^b	1.9×10^4	66.7 ± 1.2	61 ± 10	III
			Na[OH] ^a	1.2×10^4	63.4 ± 1.0	46 ± 8	III

^a This work. ^b Ref. 2; in that paper, no allowance was made for the deviation of the activity coefficient of hydroxide ion from unity at $I = 0.10$ mol dm⁻³. From the primary data in Table 2 of the paper, the concentrations of hydroxide ion were recalculated as described in ref. 3 and the new entries for k_{OH} , ΔH^\ddagger , and ΔS^\ddagger are presented in this Table. It should be noted that the k_{OH} values are effectively lowered by a factor of *ca.* 0.75 while the ΔH^\ddagger values remain virtually unchanged. ^c Ref. 3. ^d C. K. Poon, Ph.D. Thesis, University of London, 1967; data recalculated by the method of least squares. ^e Ref. 9. ^f K. S. Mok, C. K. Poon, and H. W. Tong, *J.C.S. Dalton*, 1972, 1701. ^g C. K. Lui and C. K. Poon, *J.C.S. Dalton*, 1972, 216. ^h C. K. Poon and H. W. Tong, *J.C.S. Dalton*, 1973, 1301; 2,6Me₂-pip = 2,6-dimethylpiperidine.

activity coefficient of hydroxide ion by the Debye-Hückel method,³ the effect of amines, which can form hydrogen bonds with water or its ions, has been neglected. It has been shown that the addition of 2,6-dimethylpyridine (2,6Me₂-py) to the Na[OH] solutions does not affect the observed rate constants of *trans*-[CoBr(L¹)-(N₃)⁺].

The kinetic results show that all these complexes undergo base hydrolysis with second-order kinetics over

rather sharply with that of *trans*-[CoA(L¹)Cl]⁺ where k_{OH} varies over a factor of *ca.* 2×10^3 for these same orientating ligands. In terms of this varied kinetic behaviour and the magnitudes of k_{OH} (at 25.0 °C), ΔH^\ddagger , and ΔS^\ddagger , the complexes in Table 3 may be conveniently classified into three groups.

¹⁶ 'Handbook of Chemistry and Physics,' 48th edn., ed. R. C. Weast, Chemical Rubber Co., Ohio, 1968, D-92.

¹⁷ E. Ahmed and M. L. Tobe, *Inorg. Chem.*, 1974, **13**, 2956.

The group I 'limiting' complexes are characterized by a nearly constant value of k_{OH} of *ca.* $10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25.0°C , with relatively low values of ΔH^\ddagger (49–57 kJ mol⁻¹) and ΔS^\ddagger (19–46 J K⁻¹ mol⁻¹). Tobe⁴ pointed out that these values are very similar to those found for the amine proton-exchange reactions of most cobalt(III) amine complexes of the same charge type. Coupled with the observation of general base catalysis in most of these systems,^{2,18} a 'limiting' $S_{\text{NI}}(\text{cb})$ mechanism, in which $k_{-1} \ll k_2$ thus making $k_{\text{OH}} = k_1$, has been assigned²⁻⁴ to the base hydrolysis of these macrocyclic amine complexes. The observation that k_{OH} is independent of the nature of both A and X (X = Cl or Br), which are *cis* to the amine ligands, is fully consistent with previous observations¹⁹⁻²² that the amine proton-exchange rate constants of most cobalt(III) amine complexes are independent of the nature of the ligands *cis* to the exchanging nitrogen.

The group II complexes are 'normal' with $k_{-1} \gg k_2$, thus making $k_{\text{OH}} = k_1 k_2 / k_{-1}$ ($= K_a k_2 / K_{\text{W}}$), where K_a represents the acid-dissociation constant of the amine complex. Here, the values of k_{OH} are much lower ($\leq 3 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25.0°C), with much higher ΔH^\ddagger (80–120 kJ mol⁻¹) and ΔS^\ddagger (80–150 J K⁻¹ mol⁻¹). For these complexes, K_a (*i.e.* k_1 and k_{-1}) would not vary greatly and differences in k_{OH} are essentially due to differences in k_2 . This immediately explains the dependence of k_{OH} on the nature of the orientating ligands A in *trans*-[CoA(L¹)Cl]⁺ and on the leaving groups X in *trans*-[CoL¹(OH)X]⁺ (X = Cl or N₃) and *trans*-(RS)-[Co(CN)L²(X)]⁺ (X = NO₂, N₃, or NCS). The dependence of acid-hydrolysis rate constants of cobalt(III) amine complexes on the nature of the orientating and leaving group is well known.⁵⁻⁷

Comparing *trans*-[CoCl(L³)(NCS)]⁺ with the corresponding bromo-complex, the lower value of k_{OH} and higher activation parameters of the former imply that this complex has probably not yet reached the 'limiting' group I behaviour. However, the observation of general base catalysis² suggests that k_2 would not be much less than k_{-1} and, more probably, might even be marginally greater. Inspection of the rate constants and activation parameters for *trans*-[CoA(Br)L¹]⁺ (A = NO₂, NCS, or N₃) shows that they are very similar to those of *trans*-[CoCl(L³)(NCS)]⁺ in that they lie between

¹⁸ C. K. Poon and M. L. Tobe, *Chem. Comm.*, 1968, 156.

¹⁹ D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 1969, **8**, 1595.

²⁰ D. A. Buckingham, P. J. Cresswell, and A. M. Sargeson, *Inorg. Chem.*, 1975, **14**, 1485.

those of the group I and II complexes. It seems reasonable to group these four complexes together as 'intermediate' complexes having $k_{-1} \sim k_2$. The observation that k_{OH} (*ca.* $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) for *trans*-[CoA(Br)-L¹]⁺ is independent of the nature of A (A = NCS, NO₂, or N₃) is consistent with this. However, the failure to detect general base catalysis in these three L¹ complexes indicates that k_2 is probably less than k_{-1} (*i.e.* $k_{-1} \geq k_2$). Since a change from group II to I behaviour is accompanied by a change in activation enthalpy from $\Delta H^\ddagger = \Delta H^\ddagger(k_1) + \Delta H^\ddagger(k_2) - \Delta H^\ddagger(k_{-1})$ (*ca.* 100 kJ mol^{-1}) to $\Delta H^\ddagger = \Delta H^\ddagger(k_1)$ (*ca.* 53 kJ mol^{-1}), it was suggested²³ that when the base hydrolysis of complexes having $k_{-1} \sim k_2$ were studied over a range of *ca.* 60°C the relative values of k_{-1} to k_2 might change from $k_{-1} = 5k_2$ to $k_{-1} = \frac{1}{5}k_2$. This would probably result in a change from group II to I behaviour, and in a curved Arrhenius plot. Experimentally, it is impracticable to follow the base hydrolysis of the four group III complexes over such a wide range of temperature in the *same* reaction medium since most of the common non-interfering buffers have a working range of only *ca.* 1 pH unit. The use of two or more buffer systems does not give the desired information since k_{OH} slightly depends on the nature of the buffer. On the other hand, the base hydrolysis of these complexes in Na[OH] near the high-temperature end of this 60°C range is too fast to follow even by the stopped-flow method. When the base hydrolysis of these group III complexes were studied over the range *ca.* 30 – 40°C , however, no deviation from linearity was observed in the Arrhenius plots.

It should be noted that the above classification of these macrocyclic complexes into three different groups is rather tentative and that there would not be any definitive lines of demarcation between them. Finally, the higher value of k_{OH} for *trans*-[CoCl(L³)(NCS)]⁺ compared to the L¹ analogue is a good indication of steric acceleration associated with the dissociative k_2 reaction. The values of K_a for these two complexes would not be greatly different.

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

[1/740 Received, 3rd May, 1977]

²¹ J. W. Palmer and F. Basolo, *J. Phys. Chem.*, 1960, **64**, 778.

²² E. Ahmed and M. L. Tobe, *Inorg. Chem.*, 1976, **15**, 2635.

²³ E. Ahmed, M. L. Tucker, and M. L. Tobe, *Inorg. Chem.*, 1975, **14**, 1.