Structural and Mechanistic Studies of Co-ordination Compounds. Part XIII.† Preparation and Acid Hydrolysis of Some *trans*-Azidochloro- and Azidobromo-cobalt(III) Complexes containing Macrocyclic Quadridentate Amine Ligands having Different Degrees of Unsaturation

By **Chung-Kwong Poon** * and **Chung-Lai Wong**, Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

The preparation and characterization of *trans*-$[CoX(L)(N_3)]^{n+}$ [L = 2,3-dimethyl-1,4,8,11-tetra-azacyclotetradeca-1,3-diene (L^1), X = Cl^- and Br^-; L = 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene (L^2), X = Cl^-, Br^-, N_3^-, and H_2O] cations are described. The acid hydrolysis of these azidohalogeno-cations and of *trans*-$[CoBr(L^3)(N_3)]^+$ (L^3 = 1,4,8,11-tetra-azacyclotetradecane, cyclam) has been studied over a range of temperature. The rate constants of corresponding complexes increase in the following order of L: $L^3 < L^1 < L^2$ (1 : 440 : 2 400 for the chloro- and 1 : 58 : 260 for the bromo-series at 25.0 °C respectively). This, coupled with the observation that the quotient of the rate constant with bromide to that with chloride as leaving group, k_{Br}/k_{Cl}, at the same temperature decreases in the same order of L (11 : 1.4 : 1.1), strongly supports an earlier proposition that the kinetic lability of these macrocyclic amine complexes increases with the ' softness ' of the central cobalt(III) ion, as brought about by the increasing extent of electronic delocalization between the metal ion and the encircling macrocycle.

In a previous paper [1] we have outlined a programme to examine the systematic changes in the kinetics and mechanisms of substitution reactions of complexes of the type *trans*-$[CoLAX]^{n+}$ (L = a macrocyclic quadridentate amine ligand, A = a unidentate orienting ligand, and X = a unidentate leaving group) with progressive degrees of unsaturation in the amine macrocycles. The programme was designed to substantiate experimentally

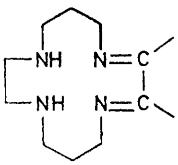
---

† Part XII, P. K. Chan and C. K. Poon, *J. C. S. Dalton*, 1976, 858.

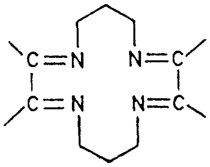
[1] Part XI, W. K. Lee and C. K. Poon, *J.C.S. Dalton*, 1974, 2423.

the earlier deliberation [2] that the kinetic lability of these complexes is markedly affected by the degree of ' softness ' of the central cobalt(III) ion. As the extent of unsaturation of the amine macrocycle increases, the ' softness ' of the central metal ion progressively increases, probably due to an increasing extent of electronic delocalization between the metal ion and the encircling macrocycle. This enhanced delocalization might help to stabilize five-co-ordinate intermediates and increase the kinetic lability of these complexes.

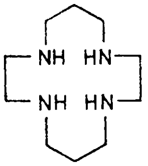
This paper describes the preparation of *trans*-[CoX(L)-$(N_3)]^+$ [L = 2,3-dimethyl-1,4,8,11-tetra-azacyclotetradeca-1,3-diene (L^1) and 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene (L^2); X = Cl and Br], and the acid hydrolysis of these cations and *trans*-$[CoBr(L^3)(N_3)]^+$ (L^3 = 1,4,8,11-tetra-azacyclotetradecane, cyclam). The acid hydrolysis of *trans*-$[CoCl(L^3)$-$(N_3)]^+$ has been reported previously.[3,4]



L^1



L^2



L^3 (cyclam)

EXPERIMENTAL

Preparation of the Complexes.—trans-Azidobromo(2,3-*dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-1,3-*diene*)*cobalt*(III) *perchlorate*. This complex was prepared by adding an aqueous solution of $Na[N_3]$ (0.1 g in 5 cm³) with stirring to a boiling aqueous solution of *trans*-$[CoBr_2(L^1)][ClO_4]$ (1 g in 50 cm³).[5] The blue solution was immediately cooled in a bath of ice–water and filtered to remove the unchanged *trans*-$[CoBr_2$-$(L^1)][ClO_4]$, if any. Addition of an excess of $Na[ClO_4]$ to the filtrate slowly precipitated the desired bluish green product which was recrystallized from a minimum amount of boiling water (25 cm³). The product was filtered off, washed with ethanol and diethyl ether, and dried in air (yield 0.4 g) (Found: C, 28.6; H, 4.8; Br, 15.8; Cl, 7.0; N, 19.0. Calc. for $C_{12}H_{24}BrClCoN_7O_4$: C, 28.6; H, 4.8; Br, 15.8; Cl, 7.0; N, 19.4%) [$\lambda_{max.}$ 564 (ε 385), $\lambda_{min.}$ 484 nm (ε 107 dm³ mol⁻¹ cm⁻¹)].

trans-*Azidochloro*(2,3-*dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-1,3-*diene*)*cobalt*(III) *perchlorate*. This complex was prepared by adding $Ag[ClO_4]$ (0.54 g) to a hot aqueous solution of *trans*-$[CoBr(L^1)(N_3)][ClO_4]$ (1 g in 25 cm³) and, after removing the AgBr formed by filtration, an excess of NaCl (0.5 g) and $Na[ClO_4]$ were added to the hot filtrate. The solution was immediately cooled in a bath of ice–water and purple crystals of the desired complex slowly appeared, which were filtered off and recrystallized from a minimum amount of hot water (15 cm³). The complex was filtered off, washed with ethanol and diethyl ether, and dried in air (yield 0.6 g) (Found: C, 31.4; H, 5.1; Cl, 15.6; N, 21.2. Calc. for $C_{12}H_{24}Cl_2CoN_7O_4$: C, 31.3; H, 5.2; Cl, 15.4; N, 21.3%) [$\lambda_{max.}$ 558 (ε 408), $\lambda_{min.}$ 492 nm (ε 119 dm³ mol⁻¹ cm⁻¹)].

trans-*Diazido*(2,3,9,10-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-1,3,8,10-*tetraene*)*cobalt*(III) *perchlorate*. This complex was prepared by adding an excess of $Na[N_3]$ (2 g) with stirring to a hot aqueous suspension of *trans*-$[CoBr_2(L^2)]$-$[ClO_4]$ (5 g in 50 cm³).[5] The complex rapidly dissolved and the solution immediately became dark red. Addition of an excess of $Na[ClO_4]$ to the cooled solution precipitated the brown complex, which was filtered off, washed with ethanol and diethyl ether, and dried in air (yield 4 g) (Found: C, 34.2; H, 5.0; Cl, 7.1; N, 28.1. Calc. for $C_{14}H_{24}ClCoN_{10}O_4$: C, 34.3; H, 4.9; Cl, 7.2; N, 28.6%) [$\lambda_{max.}$ 525 (ε 506), $\lambda_{min.}$ 490 nm (ε 466 dm³ mol⁻¹ cm⁻¹)].

trans-*Aqua-azido*(2,3,9,10-*tetramethyl*-1,4,8,11,-*tetra-azacyclotetradeca*-1,3,8,10-*tetraene*)*cobalt*(III) *perchlorate monohydrate*. This complex was prepared by adding an aqueous solution of $Ag[ClO_4]$ (4.4 g in 5 cm³) to a hot aqueous suspension of *trans*-$[CoL^2(N_3)_2][ClO_4]$ (10 g in 25 cm³). The solution was heated with constant stirring to coagulate the $Ag[N_3]$ precipitate, which was then filtered off. Addition of an excess of $Na[ClO_4]$ to the cooled filtrate precipitated the desired reddish brown complex, which was recrystallized by adding an equal volume of acetone to a filtered saturated solution of the complex in ethanol (95%, 50 cm³), followed by an excess of diethyl ether. The complex was filtered off, washed with diethyl ether, and dried in air (yield 8 g) (Found: C, 29.2; H, 4.6; Cl, 12.2; N, 17.0. Calc. for $C_{14}H_{28}Cl_2CoN_7O_{10}$: C, 28.8; H, 4.8; Cl, 12.2; N, 16.8%) [$\lambda_{max.}$ 526 (ε 275), $\lambda_{min.}$ 473 nm (ε 127 dm³ mol⁻¹ cm⁻¹)].

trans-*Azidochloro*(2,3,9,10-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-1,3,8,10-*tetraene*)*cobalt*(III) *perchlorate*. An ethanolic solution of $[NH_4]Cl$ (0.1 g in 10 cm³) was added to a solution of *trans*-$[CoL^2(N_3)(OH_2)][ClO_4]_2\cdot H_2O$ (1 g) in ethanol–acetone (1 : 1, 50 cm³). The brown solid which gradually formed was filtered off, washed with ethanol and diethyl ether, and dried in air (yield 0.7 g) (Found: C, 33.8; H, 5.0; Cl, 15.0; N, 20.2. Calc. for $C_{14}H_{24}Cl_2CoN_7O_4$: C, 34.7; H, 5.0; Cl, 14.7; N, 20.3%) [$\lambda_{max.}$ 537 (ε 349), $\lambda_{min.}$ 480 nm (ε 140 dm³ mol⁻¹ cm⁻¹)].

trans-*Azidobromo*(2,3,9,10-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-1,3,8,10-*tetraene*)*cobalt*(III) *perchlorate*. This complex was similarly prepared with a similar yield to its chloro-analogue, except that here an aqueous solution of NaBr was used instead of the ethanolic solution of $[NH_4]Cl$ (Found: C, 31.6; H, 4.5; Br, 14.8; Cl, 7.1; N, 18.5. Calc. for $C_{14}H_{24}BrClCoN_7O_4$: C, 31.8; H, 4.5; Br, 15.1; Cl, 6.7; N, 18.6%) [$\lambda_{max.}$ 546 (ε 394), $\lambda_{min.}$ 486 nm (ε 166 dm³ mol⁻¹ cm⁻¹)].

trans-*Azidobromo*(1,4,8,11-*tetra-azacyclotetradecane*)*cobalt*-(III) *perchlorate*. This complex was kindly supplied by Mak.[6]

Kinetics.—The acid hydrolysis was followed spectrophotometrically *in situ* using Unicam SP 700 or SP 8000 recording spectrophotometers, separately equipped with a thermostatted cell holder and either a set of scale-expansion

---

[2] C. K. Poon, *Co-ordination Chem. Rev.*, 1973, **10**, 1.

[3] C. K. Poon and H. W. Tong, *J.C.S. Dalton*, 1974, 1.

[4] W. K. Chau, W. K. Lee, and C. K. Poon, *J.C.S. Dalton*, 1974, 2419.

[5] S. C. Jackels, K. Farmery, E. K. Barefield, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, 1972, **11**, 2893.

[6] P. K. Mak, unpublished work.

accessories and a Unicam AR25 external recorder (for SP 700) or a Weyfringe ADCP-2 digital printer (for SP 8000), in a conventional manner as described previously.[7] The reaction temperature, maintained to ±0.1 °C with a Lauda model WB-20/R thermostat bath, was taken by inserting a thermometer into the reacting solution at the end of the reaction. For kinetic studies at temperatures well below room temperature, the optical windows were demisted by constant flushing of the cell compartment of the spectrophotometer with a stream of dry air. The kinetics of these reactions were studied by following the changing absorbances at a fixed wavelength [at 645 (L^3, X = Br, $\varepsilon_r = 157$, $\varepsilon_p = 61$), 600 (L^1, X = Cl, $\varepsilon_r = 199$; X = Br, $\varepsilon_r = 260$, $\varepsilon_p = 138$), 575 (L^2, X = Cl, $\varepsilon_r = 200$, $\varepsilon_p = 126$), and 585 nm (L^2, X = Br, $\varepsilon_r = 255$, $\varepsilon_p = 90$ dm^3 mol^{-1} cm^{-1})].*

RESULTS

The acid hydrolysis of the complexes involved complete replacement of the co-ordinated halide by water, as confirmed by Volhard's titration. The changing visible absorption spectra, with peaks slightly shifted to the blue, maintained isosbestic points during the course of the entire reaction [at 463 and 588 (L^3, X = Br), 465 and 550 (L^1, X = Cl), 465 and 557 (L^1, X = Br), 453 and 529 (L^2, X = Cl), and 467 and 528 nm (L^2, X = Br)]. Addition of excess of the corresponding halide reversed the reaction, retracing the same set of isosbestic points. For complexes of L^2 and L^3,[3] where the corresponding aqua-azido-complexes are well characterized, it was found that the final reaction spectra were very similar to those of the authentic samples of the corresponding *trans*-$[CoL(N_3)(OH_2)]^{2+}$. All these observations strongly indicated that these reactions followed equation (1).

$$\textit{trans}\text{-}[CoX(L)(N_3)]^+ + H_2O \overset{k}{\rightleftharpoons} \textit{trans}\text{-}[CoL(N_3)(OH_2)]^{2+} + X^- \quad (1)$$

Although the visible spectrum of *trans*-$[CoL^1(N_3)(OH_2)]^{2+}$ was not available for a confirmation of the stereoretentive nature of the acid hydrolysis of the L^1 complexes, the way in which the associated spectral change was very similar to those of the complexes of L^2 and L^3, coupled with the complete reversibility of the reactions, strongly supported that the reactions of L^1 complexes also followed equation (1). The first-order rate constants were obtained from gradients of standard semilogarithmic plots of $\ln(D_\infty - D_t)$ against time, where D_∞ and D_t represent absorbances at a given wavelength after 10 aquation half-lives and at time t respectively. These plots were linear to three half-lives. The data are collected in Table 1.

TABLE 1

First-order rate constants for the acid hydrolysis of *trans*-$[CoX(L)(N_3)]^+$ in 0.01 mol dm^{-3} HNO_3 [a]

L	X	θ_c/°C	10^3k [b]/s^{-1}
L^3	Br [c]	35.9	0.167
		39.2	0.247
		43.9	0.418
		49.3	0.827
		53.4	1.38
L^1	Cl [d]	21.8	0.99
		22.7	1.11
		24.6	1.47
		27.1	2.17
		29.8	3.41
		32.4	4.32
		33.1	5.15
		33.6	5.41
		34.4	6.47
L^1	Br [e]	22.2	1.61
		24.4	2.05
		28.1	3.27
		30.2	4.04
		34.4	6.78
L^2	Cl [e]	7.3	0.84
		11.5	1.53
		14.0	2.06
		16.4	2.91
L^2	Br [e]	10.7	1.72
		14.7	2.89
		16.5	3.59
		20.3	5.83

[a] These reactions were independent of acid (0.001—0.05 mol dm^{-3}) and complex concentration. [b] Each entry represents an average of two or three different determinations. [c] [complex] = 5.0×10^{-4}–1.30×10^{-3} mol dm^{-3}. [d] [complex] = 3.0×10^{-3}–9×10^{-3} mol dm^{-3}. [e] [complex] = 2.0×10^{-3}–6.0×10^{-3} mol dm^{-3}.

TABLE 2

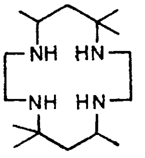
First-order acid hydrolysis rate constants [a] of some complexes of the type *trans*-$[CoX(L)(N_3)]^+$ at 25.0 °C

L	k_{Br}/s^{-1}	k_{Cl}/s^{-1}	k_{Br}/k_{Cl}
L^3	3.8×10^{-5} [b]	3.6×10^{-6} [c]	10.6
L^1	2.2×10^{-3} [b]	1.6×10^{-3} [b]	1.4
L^2	1.0×10^{-2} [b]	8.8×10^{-3} [b]	1.1
L^4	7.1×10^{-2} [d]	6.5×10^{-3} [c]	10.9
L^5	5.5×10^{-2} [d]	2.1×10^{-2} [d]	2.6

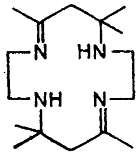
[a] k_{Br} and k_{Cl} represent the rate constants with X = Br and Cl respectively. [b] This work. [c] Ref. 4. [d] Ref. 1.

DISCUSSION

It was extensively discussed in a previous paper[1] that the kinetic quotient k_{Br}/k_{Cl} for the acid hydrolysis of a corresponding pair of *trans*-$[CoLAX]^{n+}$ complexes ($X = Br^-$ and Cl^-), which could be taken as a measure of the 'softness' of the central metal ion, would probably decrease as the extent of electronic delocalization between the central cobalt(III) ion and the encircling macrocycle, L, increased. The discussion was made on the basis of a dissociative model of these reactions with tetragonal-pyramidal intermediates, which was convincingly supported by various experimental observations.[4,8] It is obvious from Table 2 that this kinetic ratio for complexes of saturated L^3 and L^4 (L^4 = *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane, teta) is indeed much greater than that for those of partially unsaturated L^1, L^2, and L^5 (L^5 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene).



L^4



L^5

The correlation between kinetic lability and the extent of electronic delocalization should be considered with care. Only when one is convinced of the absence of or insignificant contribution from other factors can one then proceed to ascribe the variation in kinetic lability

---

* ε_r and ε_p represent the molar absorption coefficients of the reactant and product.

[7] K. S. Mok and C. K. Poon, *Inorg. Chem.*, 1971, **10**, 225.

[8] C. K. Poon and M. L. Tobe, *J. Chem. Soc.* (*A*), 1968, 1549.

to electronic effects. Among other factors, steric effects may play an important role in the kinetic lability of these methyl-substituted macrocyclic amine complexes. Simple molecular models showed that any methyl substituent attached to an unsaturated imine carbon would not contribute significantly to steric effects since this methyl group must lie in a plane defined by the four nitrogen donors with the cobalt(III) ion sitting at the centre. In other words, this methyl group is lying on a plane perpendicular to the N_3–Co–X axis and will not exert any significant steric effect on the release of X. As regards the solvation effect, the addition of extra methyl groups to a macrocycle may change the gross solvation energy of the complex. However, these additional methyl groups are rather remote from the axial reaction site. In terms of a dissociative mechanism with tetragonal-pyramidal intermediates, the major solvation change accompanying these reactions would most probably be associated with that in the immediate surroundings of the Co–X bond.[9] Therefore, solvation effects would not be expected to contribute significantly to the variation in lability of the axial ligands in these complexes. It seems reasonable, therefore, to assume that the progressive increase in the kinetic lability of these complexes in the order $L^3 < L^1 < L^2$ may be ascribed to electronic effects of these macrocycles. The greater effect on chloro- (1 : 440 : 2 400) than on bromo-complexes (1 : 58 : 260) seems to imply that the former are more sensitive to the ' hard ' and ' soft' character of the central metal ion than the latter,[2] but the reason behind this is not known.

The situation for complexes of L^4 and L^5 is less straightforward. Since serious steric effects have been observed [4,10] in substitution reactions of complexes of L^4, it might be expected that even a slight distortion of the conformation of the methyl-containing six-membered chelate rings in complexes of L^5 as compared to those of L^4 would affect the steric effects and hence the kinetic lability. Therefore, a comparison of the acid-hydrolysis rate constants of corresponding pairs of L^4 and L^5 complexes might not reflect electronic effects. It should be emphasized that this ' hard and soft concept ' may not be the best explanation of the kinetic results. It is, however, reasonable and, at least, it is compatible with the observation [2] that the increasing kinetic lability of these complexes with the extent of unsaturation of the amine macrocycles is accompanied by a decreasing kinetic quotient of $k_{\mathrm{Br}}/k_{\mathrm{Cl}}$ (or $k_{\mathrm{I}}/k_{\mathrm{Br}}$).

The activation parameters for the acid hydrolysis of these azido-complexes are collected in Table 3. With the limited amount of experimental data available, these parameters do not appear to conform to any regular pattern. In particular, the exceptionally large value of $\Delta S^\ddagger$ for *trans*-$[\mathrm{CoCl(L^1)(N_3)}]^+$ is rather puzzling and the reason for this is not known.

TABLE 3

Activation parameters for the acid hydrolysis of some complexes of the type *trans*-$[\mathrm{CoX(L)(N_3)}]^+$ [a]

L	X	$\Delta H^\ddagger$/kcal mol^{-1}	$\Delta S^\ddagger$/cal K^{-1} mol^{-1}
L^3	Cl [b]	23.7 ± 0.3	-4 ± 2
L^3	Br	23.7 ± 0.3	1 ± 1
L^1	Cl	25.8 ± 0.5	13 ± 4
L^1	Br	20.8 ± 0.2	0 ± 1
L^2	Cl	21.5 ± 0.2	4 ± 1
L^2	Br	20.4 ± 0.2	1 ± 1

[a] This work except for *trans*-$[\mathrm{CoCl(L^3)(N_3)}]^+$; 1 cal = 4.184 J. [b] The activation parameters were calculated from the combined aquation and thiocyanate-substitution kinetic data over a much wider range of temperature; refs. 3 and 4.

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

[5/1440 *Received*, 21*st July*, 1975]

---

[9] C. K. Poon and H. W. Tong, *J.C.S. Dalton*, 1974, 930.

[10] W. K. Chau and C. K. Poon, *J. Chem. Soc.* (*A*), 1971, 3087.