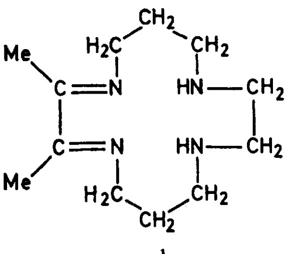
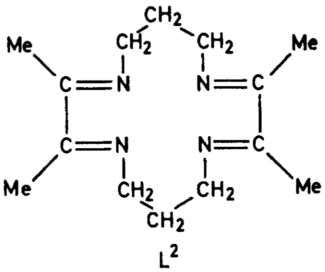
Structural and Mechanistic Studies of Co-ordination Compounds. Part 16.[1] Preparation and Acid Hydrolysis of *trans*-Bromo- and *trans*-Chloro-nitrocobalt(III) Complexes of 2,3-Dimethyl-1,4,8,11-tetra-azacyclotetradeca-1,3-diene and 2,3,9,10-Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene

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

The complexes *trans*-$[CoX(L)(NO_2)]^{n+}$ [L = 2,3-dimethyl-1,4,8,11-tetra-azacyclotetradeca-1,3-diene (L^1), X = Cl^- and Br^-; and L = 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene (L^2), X = Cl^-, Br^-, NCS^-, or OH_2] have been prepared and the acid hydrolysis of the halogeno-complexes has been investigated. The specific rates of acid hydrolysis of these nitro-complexes are nearly independent of the extent of unsaturation in the amine macrocycles, whereas k_{Br}/k_{Cl} decreases. The order of the labilizing power of A (A = Cl, N_3, NCS, or NO_2) on the acid hydrolysis of *trans*-$[CoX(L)A]^+$ (X = Cl or Br) gradually changes with the extent of unsaturation in L [L = L^3 (1,4,8,11-tetra-azacyclotetradecane, cyclam), L^4 (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane), L^1, and L^2]. In L^2 complexes, the order becomes very similar to that for the base hydrolysis of *trans*-$[CoCl(L^3)A]^+$. This observation suggests that unsaturation in macrocyclic amines and amido-groups in amine conjugate bases have similar effects in promoting the hydrolysis of cobalt(III) complexes.


L^1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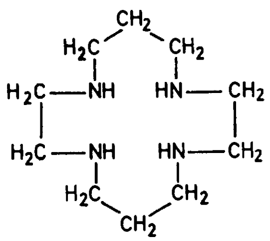
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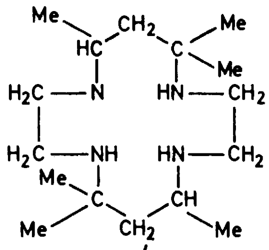
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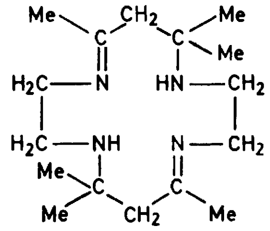
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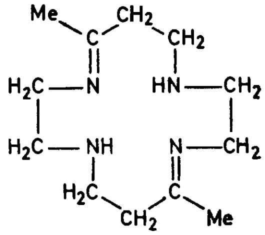
L^6

In a series of papers [2-5] we have shown that, for a given pair of orientating ligand A (A = Cl, N_3, or NCS) and leaving group X (X = Cl or Br), the specific rates of acid hydrolysis of complexes of the type *trans*-$[CoX(L)A]^+$ increased with increasing extent of unsaturation in the macrocyclic quadridentate amine L. For example, L^1 and L^5 complexes (L^1 = 2,3-dimethyl-1,4,8,11-tetra-azacyclotetradeca-1,3-diene and L^5 = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-7,14-diene) are more reactive than the corresponding L^3 complexes [L^3 = 1,4,8,11-tetra-azacyclotetradecane (cyclam)] by factors of *ca.* 10^2—10^3 and 10^3—10^4 respectively. This increase in kinetic reactivity was accompanied by a corresponding decrease in the kinetic quotient k_{Br}/k_{Cl}

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[1] Part 15, P. W. Mak and C. K. Poon, *Inorg. Chem.*, 1976, **15**, 1949.

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

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

[4] C. K. Poon and C. L. Wong, *J.C.S. Dalton*, 1976, 966.

[5] C. K. Poon and C. L. Wong, *Inorg. Chem.*, 1976, **15**, 1573.

(with X = Br and Cl respectively for the same L and A). These two systematic changes were reasonably accounted for [2-5] in terms of an increased polarizability, or 'softness,' of the central cobalt(III) ion with the increasing extent of electronic delocalization between the metal ion and the encircling unsaturated macrocycle. This enhanced polarizability might help stabilize five-coordinate intermediates and increase the reactivity of the complexes. However, it was recently reported [6] that the aquation rates of *trans*-$[CoCl(L)(NO_2)]^+$ (L = L^5 or L^6 where L^6 = 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene) are not much different from those of the saturated L^3 analogue.

This study was designed to investigate other unsaturated macrocyclic systems of the type *trans*-$[CoX(L)(NO_2)]^+$ (L = L^1 or L^2 where L^2 = 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene, X = Cl or Br) to see whether these nitro-complexes also behave differently from other analogous complexes with A = Cl,[7] N_3,[4] and NCS.[5]

EXPERIMENTAL

Preparation of the Complexes.—trans-*Chloro*(2,3-*dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-1,3-*diene*)*nitrocobalt*(III) *perchlorate*, *trans*-$[CoCl(L^1)(NO_2)][ClO_4]$. This complex was prepared by adding concentrated hydrochloric acid (15 cm^3) with stirring to *trans*-$[CoL^1(NO_2)_2][ClO_4]$.[8] After the evolution of brown fumes had subsided, the solution was filtered and a few drops of perchloric acid (70%) were added to the filtrate to precipitate out a light red solid. The product was filtered off, washed with ethanol and diethyl ether, and dried in air (yield 60%) (Found: C, 30.7; H, 5.1; Cl, 15.4; N, 15.2. Calc. for $C_{12}H_{24}Cl_2CoN_5O_6$: C, 31.0; H, 5.2; Cl, 15.3; N, 15.1%) [$\lambda_{max.}$ 504 (ε 130), $\lambda_{min.}$ 442 nm (ε 87 dm^3 mol^{-1} cm^{-1})].

trans-*Bromo*(2,3-*dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-1,3-*diene*)*nitrocobalt*(III) *perchlorate*, *trans*-$[CoBr(L^1)(NO_2)][ClO_4]$. This complex was similarly prepared with a similar yield to its chloro-analogue, except that here hydrobromic acid (48%, 15 cm^3) was used instead of HCl (Found: C, 27.9; H, 4.8; Br, 15.4; Cl, 6.8; N, 13.7. Calc. for $C_{12}H_{24}BrClCoN_5O_6$: C, 28.3; H, 4.7; Br, 15.7; Cl, 7.0; N, 13.8%) [$\lambda_{max.}$ 514 (ε 140), $\lambda_{min.}$ 458 nm (ε 81 dm^3 mol^{-1} cm^{-1})].

trans-*Chloronitro*(2,3,9,10-*tetramethyl*-1,4,8,11-*tetra-aza-cyclotetradeca*-1,3,8,10-*tetraene*)*cobalt*(III) *perchlorate*, *trans*-$[CoCl(L^2)(NO_2)][ClO_4]$. This complex was similarly prepared with a lower yield (20%) to its L^1 analogue starting with *trans*-$[CoL^2(NO_2)_2][ClO_4]$ [8] (Found: C, 34.2; H, 5.0; Cl, 14.8; N, 14.5. Calc. for $C_{14}H_{24}Cl_2CoN_5O_6$: C, 34.4; H, 4.9; Cl, 14.6; N, 14.4%) [$\lambda_{max.}$ 477 (ε 129), $\lambda_{min.}$ 431 (ε 100 dm^3 mol^{-1} cm^{-1})].

trans-*Bromonitro*(2,3,9,10-*tetramethyl*-1,4,8,11-*tetra-aza-cyclotetradeca*-1,3,8,10-*tetraene*)*cobalt*(III) *perchlorate*, *trans*-$[CoBr(L^2)(NO_2)][ClO_4]$. This complex was also similarly prepared to its L^1 analogue starting with *trans*-$[CoL^2(NO_2)_2][ClO_4]$.[8] For an analytically pure sample, the product had to be recrystallized from the minimum amount of boiling water. Addition of a concentrated aqueous solution of $Na[ClO_4]$ to the cooled solution precipitated the desired orange-brown crystals which were filtered off, washed with ethanol and diethyl ether, and dried in air (yield 50%) (Found: C, 31.3; H, 4.5; Br, 15.1; Cl, 6.9; N, 12.9. Calc. for $C_{14}H_{24}BrClCoN_5O_6$: C, 31.6; H, 4.5; Br, 15.0; Cl, 6.8; N, 13.2%) [$\lambda_{max.}$ 493 (ε 157), $\lambda_{min.}$ 451 nm (ε 125 dm^3 mol^{-1} cm^{-1})].

trans-*Isothiocyanatonitro*(2,3,9,10-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-1,3,8,10-*tetraene*)*cobalt*(III) *perchlorate*, *trans*-$[CoL^2(NCS)(NO_2)][ClO_4]$. This complex was prepared by adding $[NH_4][NCS]$ (0.14 g, 1.9 mmol) with stirring to a hot aqueous suspension of *trans*-$[CoBr(L^2)(NO_2)][ClO_4]$ (1 g, 1.9 mmol in 30 cm^3). The resulting reddish-brown solution was cooled and filtered. Addition of a concentrated aqueous solution of $Na[ClO_4]$ precipitated out a solid which was recrystallized from the minimum amount of hot water. Brownish-red crystals which formed on cooling were filtered off, washed with ethanol and diethyl ether, and dried in air (yield 75%) (Found: C, 35.1; H, 4.5; Cl, 7.1; N, 16.6. Calc. for $C_{15}H_{24}ClCoN_6O_6S$: C, 35.3; H, 4.7; Cl, 7.0; N, 16.5%) [$\lambda_{max.}$ 494 (sh) nm (ε 189 dm^3 mol^{-1} cm^{-1})].

trans-*Aquanitro*(2,3,9,10-*tetramethyl*-1,4,8,11-*tetra-aza-cyclotetradeca*-1,3,8,10-*tetraene*)*cobalt*(III) *perchlorate*, *trans*-$[CoL^2(NO_2)(OH_2)][ClO_4]_2$. This complex was prepared by adding $Ag[ClO_4]$ (0.39 g, 1.9 mmol) to a suspension of *trans*-$[CoBr(L^2)(NO_2)][ClO_4]$ (1 g, 1.9 mmol) in hot water (25 cm^3). The suspension was warmed to coagulate the AgBr precipitate which was filtered off. Excess of $Na[ClO_4]$ was added to the filtrate to precipitate a yellow solid which was recrystallized from the minimum amount of boiling water, followed by the addition of a concentrated solution of $Na[ClO_4]$ to the cooled solution. The orange-yellow crystals were filtered off, washed with ethanol–diethyl ether (1 : 4) and then with diethyl ether, and dried *in vacuo* at 65 °C (yield 70%) (Found: C, 28.4; H, 4.7; Cl, 12.2; N, 12.1. Calc. for $C_{14}H_{26}Cl_2CoN_5O_{12}$: C, 28.6; H, 4.8; Cl, 12.1; N, 11.9%) [$\lambda_{max.}$ 454 (ε 145), $\lambda_{min.}$ 428 nm (ε 130 dm^3 mol^{-1} cm^{-1})].

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 a suitable scale-expansion accessory as described previously.[4] The kinetics of these reactions were studied by following the changing absorbances at a fixed wavelength [at 550 (L^1, X = Cl, ε_r = 75; X = Br, ε_r = 105, ε_p = 45), 510 (L^2, X = Cl, acid hydrolysis, ε_r = 103, ε_p = 65), 450 (L^2, X = Cl, thiocyanate-substitution reaction, ε_r = 111, ε_p = 294), and 520 nm (L^2, X = Br, ε_r = 128, ε_p = 51 dm^3 mol^{-1} cm^{-1})].*

RESULTS

The isomeric purity of the complexes was checked by dissolving them in HCl (0.01 mol dm^{-3}) and then absorbing them on a Dowex 50 W-X8 (20—50 mesh) cation-exchange resin in the acid form. On eluting with HCl of different concentrations, in each case, only a single band developed on the column, which could be eluted.

Complexes of L^2, having equivalent *trans* sites, only give rise to one *trans* isomer. However, a number of isomers are possible for L^1 complexes [N-*rac* (*RR*,*SS*) only gives one geometrical isomer while N-*meso* (*RS*) gives two isomers resulting from the non-equivalence of the two *trans* sites]

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

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

[7] D. P. Rillema, J. F. Endicott, and J. R. Barber, *J. Amer. Chem. Soc.*, 1973, **95**, 6987.

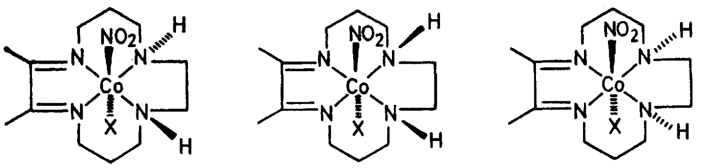
[8] S. C. Jackels, K. Farmery, E. K. Barefield, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, 1972, **11**, 2893.

TABLE 1

First-order rate constants for the acid hydrolysis of *trans*-$[CoX(L)(NO_2)]^+$ in 0.01 mol dm^{-3} HNO_3 [a]

L	X	θ_c/°C	$10^3k/s^{-1}$ [b]
L^1	Cl	24.9	0.53
		27.3	0.68
		31.7	1.10
		33.8	1.40
		37.2	1.90
		39.8	2.6
L^1	Br	25.2	1.15
		25.8	1.25
		27.2	1.45
		28.7	1.70
		29.6	1.80
		29.9	1.95
		33.1	2.7
		34.2	3.1
		34.8	3.3
		36.4	3.9
L^2	Cl	25.5	0.25
		28.5	0.35
		30.0	0.45
		34.5	0.75
		36.1	0.94
		40.9	1.60
L^2	Br	31.2	0.56
		33.5	0.72
		34.9	0.84
		38.0	1.10
		39.8	1.30
		40.7	1.45
		41.5	1.55
L^2 [c]	Cl	27.6	0.32
		36.3	0.88
		38.5	1.20

[a] These reactions were independent of the acid (0.01—0.05 mol dm^{-3}) and complex concentrations (1.0×10^{-3}—3.1×10^{-3} mol dm^{-3}). [b] Each entry represents an average of two to four different determinations. [c] Thiocyanate-substitution reactions: $[HNO_3] = 0.01$ mol dm^{-3}; $[NCS^-] = 0.1$ mol dm^{-3}.



N-*rac* (*RR,SS*)-L^1 N-*meso* (*RS*)-L^1

with the N-*rac*-isomer the most stable. Since the isomerically pure L^1 complexes were prepared under acidic conditions from the isomerically pure *trans*-$[CoL^1(NO_2)_2][ClO_4]$ which had been recrystallized several times under basic conditions, a condition which enabled inversion of co-ordinated nitrogen through deprotonation and reprotonation to bring the complex to the most stable configuration, it seemed very likely that these L^1 complexes adopted the N-*rac* (*RR,SS*) configuration.

The acid hydrolysis of these complexes is very similar to that of analogous complexes of the type *trans*-$[CoX(L)A]^+$ ($L = L^1$ or L^2, X = Cl or Br, and $A = N_3$ [4] or NCS [5]). The changing visible-absorption spectra, with peaks slightly shifted to the blue, maintained isosbestic points during the course of the entire reaction [at 421 and 489 (L^1, X = Cl), 440 and 486 (L^1, X = Br), 420 and 468 (L^2, X = Cl), and 437 and 467 nm (L^2, X = Br)]. Volhard's titration confirmed the complete replacement of the co-ordinated halide by water. In the case of L^2 complexes, where the aquanitro-complex is available, the final reaction spectra were identical to that of *trans*-$[CoL^2(NO_2)(OH_2)]^{2+}$. Contrary to the analogous azido- [4] and isothiocyanato-complexes,[5] these reactions are not reversible. In view of the stereoretentive nature of all the substitution reactions of complexes of macrocyclic amines [2] and the above observations, these reactions can be represented by equation (1). The first-order rate constants k were obtained from

$$trans\text{-}[CoX(L)(NO_2)]^+ + H_2O \xrightarrow{k} trans\text{-}[CoL(NO_2)(OH_2)]^{2+} + X^- \quad (1)$$

gradients of standard semilogarithmic plots of $\ln(D_t - D_\infty)$ against time, where D_t and D_∞ represent absorbances at a given wavelength at time t and after 10 aquation half-lives respectively. These plots were linear to three half-lives. The data are collected in Table 1.

The thiocyanate-substitution reaction of *trans*-$[CoCl(L^2)(NO_2)]^+$ was examined to see if this reaction gave a correct measure of the corresponding aquation rate constant. The absorption spectrum of the substrate changed gradually to that of *trans*-$[CoL^2(NCS)(NO_2)]^+$ as the reaction proceeded. The first-order rate constants, obtained from standard semilogarithmic plots, were independent of thiocyanate concentration and agree well with the corresponding aquation rate constants of the substrate. These data are also collected in Table 1. Activation parameters and the rate constants extrapolated to 25.0 °C are collected in Table 2.

The aquation rate constant of *trans*-$[CoCl(L^5)(NO_2)]^+$ (5.5×10^{-4} s^{-1} at 25 °C) reported by Hay and Lawrance [6]

TABLE 2

Activation parameters and first-order rate constants [a] at 25.0 °C for the acid hydrolysis of some complexes of the type *trans*-$[CoX(L)(NO_2)]^+$

L	$\frac{k_{Br}}{s^{-1}}$	$\frac{\Delta H_{Br}^{\ddagger}}{kJ\ mol^{-1}}$	$\frac{\Delta S_{Br}^{\ddagger}}{J\ K^{-1}\ mol^{-1}}$	$\frac{k_{Cl}}{s^{-1}}$	$\frac{\Delta H_{Cl}^{\ddagger}}{kJ\ mol^{-1}}$	$\frac{\Delta S_{Cl}^{\ddagger}}{J\ K^{-1}\ mol^{-1}}$	k_{Br}/k_{Cl}
L^3	5.5×10^{-4} [b]	86.9 ± 1.3	-13 ± 4	4.3×10^{-5} [c]	86.1 ± 1.0	-38 ± 4	13
L^4				4.1×10^{-2} [d]	92.8 ± 1.7	42 ± 8	
L^5				5.5×10^{-4} [e]			
L^6				4.4×10^{-4} [e]	77.3	-50	
L^1	1.1×10^{-3} [f]	80.7 ± 1.3	-29 ± 4	5.3×10^{-4} [f]	79.8 ± 1.3	-42 ± 4	2.1
L^2	3.1×10^{-4} [f]	73.6 ± 1.3	-63 ± 8	2.3×10^{-4} [f]	92.4 ± 1.3	-4 ± 4	1.3

[a] Obtained from least-squares plots of $\ln(k/T)$ against $1/T$. [b] C. K. Lui and C. K. Poon, *J.C.S. Dalton*, 1972, 216. [c] K. S. Mok and C. K. Poon, *Inorg. Chem.*, 1971, **10**, 225. [d] Ref. 9. [e] Ref. 6. [f] This work.

could not be reconciled with our observation that the release of the co-ordinated chloride was complete as soon as the complex *trans*-[CoCl(L^5)(NO_2)][ClO_4] was dissolved in ice-cold dilute nitric acid. We confirmed this by immediately passing the complex solution down an ice-cooled cation-exchange resin column of Amberlite IR-120 in the acid form and titrating the amount of ionic chloride in the effluent and washings by Volhard's method. A consideration of the steric effects arising from the six methyl groups in L^4 and L^5 macrocycles [3,9] [L^4 = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (teta)] on the aquation of their cobalt(III) complexes (Table 3) suggests that the aquation rate constant of *trans*-[CoCl(L^5)(NO_2)]$^+$ would probably be of the order of 10^{-2} s^{-1} at 25 °C.

DISCUSSION

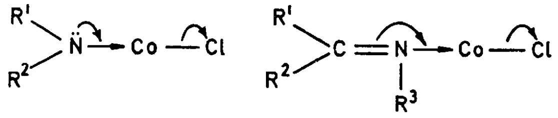
It is clear from Table 2 that as the extent of unsaturation in the amine macrocycle L is gradually increased from L^3 through L^1 to L^2, the kinetic quotient k_{Br}/k_{Cl} for the aquation of *trans*-[CoX(L)(NO_2)]$^+$ (X = Br and Cl) indeed decreases indicating a gradual increase in the polarizability or ' softness ' of the central cobalt(III) ion in these systems. However, these nitro-complexes behave quite differently from other complexes of the same type. For a given orientating ligand A, such as Cl,[7] N_3,[4] and NCS,[5] of complexes of the type *trans*-[CoCl(L)A]$^+$, the aquation rate constants increase in the ratio $1 : 10^2 : 10^3$ when L is changed from L^3 through L^1 to L^2. However, for the nitro-series, the three complexes have similar aquation rate constants. The same trend is observed for the bromonitro-series of complexes but the difference is less dramatic. It is interesting to note, as shown in Table 3, that as the extent of unsaturation in the amine macrocycle increases the order of the labilizing power of A gradually changes * (L^3 and L^4, $NO_2 > N_3 > Cl > NCS$; L^1, $N_3 \geqslant NO_2 \geqslant Cl > NCS$; L^2, $Cl \geqslant N_3 > NO_2 > NCS$). This change in the labilizing order of A is reflected more clearly by considering the following changes in k_{Cl}/k_{NO_2} and k_{NO_2}/k_{NCS}, where k_{Cl}, k_{NO_2}, and k_{NCS} represent the first-order aquation rate constants of *trans*-[CoCl(L)A]$^+$ with A = Cl, NO_2, and NCS respectively. It is clear that the former kinetic quotient increases [L^3 (2.6×10^{-2}), L^4 (2.2×10^{-2}), L^1 (4.3×10^{-1}), and L^2 (9.1×10)] whereas the latter decreases [L^3 (3.9×10^4), L^4 (5.9×10^4), L^1 (1.2×10^3), and L^2 (1.3×10^2)] systematically with the extent of unsaturation in L. Extrapolating these changes in the kinetic quotients to a more unsaturated macrocyclic system, it seems that the labilizing order of A is changing steadily with the extent of unsaturation in the amine macrocycle towards that for the base hydrolysis of the saturated macrocyclic L^3 system [$Cl > N_3 > NCS \geqslant NO_2$; k_{Cl}/k_{NO_2} (1.1×10^2); k_{NO_2}/k_{NCS} (6.8×10^{-1}); Table 3]. Since the π conjugation in the amine macrocycle can act either as an electron sink or an electron pool depending on the electronic demand at the reaction site, the above observation seems to indicate, as shown schematically below, that the source of labilization of macrocyclic π conjugation is rather similar to that of an amido-group on the hydrolysis of cobalt(III) complexes.

TABLE 3

Some aquation and base-hydrolysis rate constants of complexes of the type *trans*-[CoCl(L)A]$^+$ at 25.0 °C

	k_1 [a]/s^{-1}					k_2 [a] for L^3
A	L^3	L^4	L^5	L^1	L^2	dm^3 mol^{-1} s^{-1}
NO_2	4.3×10^{-5} [b]	4.1×10^{-2} [c]	5.5×10^{-4} [d]	5.3×10^{-4} [e]	2.3×10^{-4} [e]	6.1×10^2 [f]
N_3	3.6×10^{-6} [c]	6.5×10^{-3} [c]	2.1×10^{-2} [g]	1.6×10^{-3} [h]	8.8×10^{-3} [h]	2.8×10^3 [i]
Cl	1.1×10^{-6} [j]	9.3×10^{-4} [k]	3.6×10^{-2} [l]	2.3×10^{-4} [m]	2.1×10^{-2} [m]	6.7×10^4 [j]
NCS	1.1×10^{-9} [c]	7.0×10^{-7} [c]	1.4×10^{-6} [g]	4.4×10^{-7} [n]	1.8×10^{-6} [n]	9.0×10^2 [o]

[a] k_1 and k_2 represent the first-order aquation and second-order base-hydrolysis rate constants respectively. [b] K. S. Mok and C. K. Poon, *Inorg. Chem.*, 1971, **10**, 225. [c] Ref. 9. [d] Ref. 6; this rate constant could not be reproduced by us (see text). [e] This work. [f] C. K. Lui and C. K. Poon, *J.C.S. Dalton*, 1972, 216. [g] Ref. 3. [h] Ref. 4. [i] C. K. Poon and H. W. Tong, *J.C.S. Dalton*, 1974, 1. [j] C. K. Poon and M. L. Tobe, *J. Chem. Soc.* (*A*), 1967, 2069. [k] W. K. Chau and C. K. Poon, *J. Chem. Soc.* (*A*), 1971, 3087. [l] J. A. Kernohan and J. F. Endicott, *Inorg. Chem.*, 1970, **9**, 1504. [m] Ref. 7. [n] Ref. 5. [o] K. S. Mok, C. K. Poon, and H. W. Tong, *J.C.S. Dalton*, 1972, 1701.



The electronic donating power of an amido-group may be much greater than that of a conjugated amine group which, in turn, may be greater than that of a saturated amine, resulting in the following order of kinetic lability of cobalt(III) complexes: base hydrolysis of complexes of macrocyclic amines > aquation of complexes of conjugative unsaturated macrocyclic amines > aquation of complexes of saturated macrocyclic amines. Thus, following the same argument [10] used to explain the low reactivity of [CoCl(en)$_2$(NO_2)]$^+$ (en = ethylenediamine) to base hydrolysis, the relatively low reactivity of nitro-complexes of L^1 and L^2 to acid hydrolysis may now be interpreted in terms of a co-operative π-conjugative effect. The electronic charge that the π-conjugated system of the macrocyclic amine places on the cobalt(III)

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* The labilizing order for L^5 series of complexes is not presented here because of the uncertainty of the aquation rate constant of the nitro-complex.

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

[10] F. Basolo and R. G. Pearson, ' Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, p. 186.

ion may be effectively removed by the nitro-group. This may have the effect of removing the labilizing power of the unsaturated macrocyclic system to promote hydrolysis reactions. Hence, it is not surprising to observe here that the aquation rate constants of *trans*-$[CoX(L)(NO_2)]^+$ are nearly independent of the nature of L (L = L^1, L^2, and L^3).

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

[6/841 *Received, 3rd May,* 1976]