

Structural and Mechanistic Studies of Co-ordination Compounds. Part XI.¹ Preparation and Acid Hydrolysis of some Octahedral cobalt(III) Complexes of *meso*-1,4,8,11-Tetra-aza-5,5,7,12,12,14-hexamethylcyclo-tetradecane and -tetradeca-1,7-diene

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

The preparation and characterization of *trans*-[CoL'(A)Br]⁺ (I; L' = *meso*-1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcyclo-tetradecane; A = N₃ and NCS) and *trans*-[CoL''(A)X]ⁿ⁺ (II; L'' = *meso*-1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcyclo-tetradeca-1,7-diene; A = OH₂, N₃, and NCS; X = Cl and Br) cations are described. The acid hydrolysis of the azido- and isothiocyanato-cations has been studied over a range of temperature. The ratio of the rate constant with bromide to that with chloride as leaving group, $k_{Br} : k_{Cl}$, at 25 °C is *ca.* 10 : 1 for complexes (I) but decreases to *ca.* 2 : 1 for (II), independent of the nature of the orienting ligands A. This observation is consistent with the proposition that the relative 'softness' of the central cobalt(III) ion increases in going from complexes (I) to (II).

THERE have been several studies on different aspects of vitamin B₁₂ model complexes.² We are interested³ in electronic effects of the corrin ring on the thermodynamic and kinetic stability of the B₁₂ series of com-

plexes towards ligand-substitution reactions. It is not sufficient to study the real systems alone since the electronic structure of the corrin ring is constant and hence its electronic effects on the lability of real complexes is not easily appreciated. We proposed^{3,4} to tackle the problem by examining systematic changes in the kinetics and mechanisms of substitution reactions of complexes of the type *trans*-[CoL(A)X]ⁿ⁺ (L = a macrocyclic quadridentate amine ligand, A a unidentate

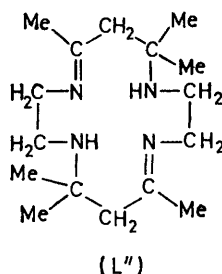
¹ Part X, W. K. Chau, W. K. Lee, and C. K. Poon, preceding paper.

² For example, see G. N. Schrauzer, 'Plenary Lectures 14th Internat. Conf. Co-ordination Chem., Toronto, 1972, ed. A. B. P. Lever, Butterworths, London, 1973, p. 545; D. H. Busch, K. Farmery, V. Goedken, V. Katavic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Adv. Chem. Ser.*, No. 100, 1970, 1; A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Perxeddi, E. Reisenhofer, L. Stefani, and G. M. Tazher, *Inorg. Chim. Acta Rev.*, 1970, **4**, 41; R. J. Guschl and T. L. Brown, *Inorg. Chem.*, 1973, **12**, 2815.

³ C. K. Poon, *Co-ordination Chem. Rev.*, 1973, **10**, 1.

⁴ C. K. Poon and W. K. Wan, *Proc. 14th Internat. Conf. Co-ordination Chem.*, Toronto, 1972, p. 209.

orienting ligand, and X a unidentate leaving group) with progressive degrees of unsaturation in the amine macrocycles. It is hoped that the knowledge obtained from the simpler systems can be extrapolated to give an understanding of the natural reactions in real systems. Based on a very limited amount of experimental data, it was rationalized³ that as the extent of unsaturation of the amine macrocycles increases the 'softness'⁵ of the central cobalt(III) ion progressively increases, with a corresponding increase in ligand lability. It was tentatively proposed³ that this gradual increase in 'softness' was a consequence of the enhanced polarizability of the central metal ion brought about by the increasing extent of electronic delocalization between the metal ion and the encircling macrocycle. This enhanced polarizability might also help to stabilize five-co-ordinate intermediates and increase the kinetic lability of these complexes. These propositions, however, require experimental justification. This paper



describes the preparation and acid hydrolysis of *trans*-[CoL'(A)Br]⁺, (I), and *trans*-[CoL''(A)X]⁺, (II) (L' = *meso*-1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcyclo-tetradecane and L'' = *meso*-1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcyclo-tetradeca-1,7-diene; A = NCS and N₃; X = Cl and Br). Corresponding rate data for *trans*-[CoL'(A)Cl]⁺ are known.¹ The choice of these macrocycles has the additional advantage in that steric effects arising from the geminal dimethyl groups of these macrocycles on the reactivity of the complexes are very nearly the same.¹ This effect has been estimated¹ by comparing the lability of corresponding L' and L''' systems (L''' = 1,4,8,11-tetra-azacyclo-tetradecane).

EXPERIMENTAL

trans-Dichloro(1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcyclo-tetradeca-1,7-diene)cobalt(III) Perchlorate.—The published method⁶ for the preparation of the stable *meso*-isomer of this salt could not be repeated and a modified method was used. An aqueous solution (200 cm³) of Na₃[Co(CO₃)₃].3H₂O⁷ (6 g, 16mm) and L'', 2HClO₄⁸ (8 g, 16mm) was heated on a steam-bath for 5 min.* The red solution was filtered, treated with concentrated HCl (30 cm³), and the resulting solution was set aside. Green crystals of the desired product slowly separated out. The yield was improved by addition of an excess of NaClO₄

* 1M = 1 mol dm⁻³.

⁵ R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.

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

in HClO₄ to the solution. The salt was recrystallized from hot methanol (yield 5 g) (Found: C, 37.4; H, 6.40; Cl, 21.2; N, 11.0. Calc. for C₁₆H₃₂Cl₃CoN₄O₄: C, 37.7; H, 6.35; Cl, 20.9; N, 11.0%).

trans-Dibromo(1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcyclo-tetradeca-1,7-diene)cobalt(III) Perchlorate.—This salt was similarly prepared by a modification of the published method⁶ using HBr (48%) instead of concentrated HCl. The solution was warmed for ca. 0.5 h before setting aside for crystallization (yield 40%) (Found: C, 31.8; H, 5.40; Br, 26.7; N, 9.45. Calc. for C₁₆H₃₂Br₂ClCoN₄O₄: C, 32.1; H, 5.40; Br, 26.7; N, 9.35%).

trans-Aqua-chloro(1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcyclo-tetradeca-1,7-diene)cobalt(III) Diperchlorate, (II; A = OH₂, X = Cl).—This salt was prepared by a slight modification of the published method.⁶ Perchloric acid (70%; 50 cm³) was added to a saturated solution of *trans*-[Co(L'')Cl₂][ClO₄] (4 g in 100 cm³) at ca. 50 °C. The resulting solution was cooled and green needle-shaped crystals began to separate. These were filtered off, washed with diethyl ether, and dried *in vacuo* (yield 3 g) (Found: C, 30.6; H, 5.80; Cl, 17.2; N, 8.90. Calc. for C₁₆H₃₄Cl₃CoN₄O₉: C, 30.6; H, 5.90; Cl, 17.0; N, 8.90%).

trans-Aqua-bromo(1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcyclo-tetradeca-1,7-diene)cobalt(III) Diperchlorate Dihydrate, (II; A = OH₂, X = Br).—This salt was similarly prepared by the action of HClO₄ (70%) on *trans*-[Co(L'')Br₂][ClO₄] (yield 2.5 g) (Found: C, 28.4; H, 5.55; Br, 12.0; N, 8.15. Calc. for C₁₆H₃₈BrCl₂CoN₄O₁₁: C, 28.6; H, 5.65; Br, 11.9; N, 8.35%).

trans-Chloro-isothiocyanato(1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcyclo-tetradeca-1,7-diene)cobalt(III) Perchlorate, (II; A = NCS, X = Cl).—The diperchlorate salt (II; A = OH₂, X = Cl) (3 g, 5mm) in the minimum amount of methanol was treated with a methanolic solution of NaNCS (5mm), which was also saturated with NaClO₄ (prepared by adding a suitable amount of KNCS to a methanolic solution of NaClO₄ and filtering off the insoluble KClO₄). Scratching the side of the container induced slow deposition of purple crystals which were filtered off and washed with several small portions of methanol to remove the unreacted starting salt, if any. The salt was recrystallized by adding diethyl ether to a saturated solution of it in absolute ethanol. The final product was filtered off, washed with diethyl ether, and dried *in vacuo* (yield 2.0 g, 75%) (Found: C, 38.3; H, 5.95; Cl, 13.4; N, 13.2. Calc. for C₁₇H₃₂Cl₂CoN₅O₄S: C, 38.3; H, 6.00; Cl, 13.4; N, 13.3%).

trans-Bromo-isothiocyanato(1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcyclo-tetradeca-1,7-diene)cobalt(III) Perchlorate, (II; A = NCS, X = Br).—This salt was prepared and recrystallized by essentially the same method as that described above by anating the diperchlorate of (II; A = OH₂, X = Br) with an equivalent amount of NaNCS in methanol (yield 70%) (Found: C, 35.2; H, 6.30; Br, 13.7; N, 12.4. Calc. for C₁₇H₃₂BrClCoN₅O₄S: C, 35.4; H, 6.25; Br, 13.9; N, 12.3%).

trans-Azido-chloro(1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcyclo-tetradeca-1,7-diene)cobalt(III) Perchlorate Monohydrate, (II; A = N₃, X = Cl).—A warm methanolic solution (25 cm³) of NaN₃ (0.4 g, 5mm) was added to the diperchlorate of (II; A = OH₂, X = Cl) (3 g, 5mm) dissolved in the minimum amount of methanol (20 cm³).

⁷ H. F. Bauer and W. C. Drinkard, *J. Amer. Chem. Soc.*, 1960, **82**, 5031.

⁸ N. F. Curtis and R. W. Hay, *Chem. Comm.*, 1966, 524.

Scratching the side of the container induced slow deposition of bluish purple crystals which were filtered off and washed with ethanol and diethyl ether. The salt was recrystallized by adding diethyl ether to an ethanolic solution of it (yield 2 g, 60%) (Found: C, 36.1; H, 6.00; Cl, 13.0; N, 18.2. Calc. for $C_{16}H_{34}Cl_2CoN_7O_5$: C, 36.0; H, 6.35; Cl, 13.3; N, 18.4%).

trans-Azidobromo(1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcycloctetradeca-1,7-diene)cobalt(III) Perchlorate, (II; A = N_3 , X = Br).—Hydrobromic acid (48%; 5 cm³) was added to a saturated aqueous solution (5 cm³) of *trans*-[Co(L'')(N₃)₂][ClO₄]⁶ (2.2 g, 4mm) and the solution was warmed for ca. 5 min. The resulting green solution was cooled with ice and excess of NaClO₄ was added to precipitate out the crude product which was shown to be contaminated with *trans*-[Co(L'')Br₂][ClO₄]. The salt was recrystallized several times (ca. 3 times) by adding diethyl ether to a saturated ethanolic solution of it until a constant visible spectrum was obtained (yield 0.6 g, 25%) (Found: C, 34.6; H, 6.00; Br, 14.3; N, 17.8. Calc. for $C_{16}H_{32}BrClCoN_7O_4$: C, 34.3; H, 5.70; Br, 14.3; N, 17.5%).

trans-Bromoisothiocyanato(1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcycloctetradecane)cobalt(III) Perchlorate, (I; A = NCS).—An aqueous solution (200 cm³) of *trans*-[Co(L'')Br₂]⁹ (3 g, 5mm) was maintained at 70 °C for 20 min. KNCS (0.5 g, 5mm) was added and the resulting solution maintained at this temperature for a further 10 min. The dark green solution was then filtered and the filtrate cooled and treated with excess of NaClO₄ to precipitate out the desired green product. This was recrystallized by adding diethyl ether to a saturated ethanolic solution of it. The recrystallized product was dried *in vacuo* at 50 °C (yield 1.4 g, 50%) (Found: C, 34.2; H, 5.55; Br, 13.2; N, 11.8. Calc. for $C_{17}H_{36}BrClCoN_5O_4S$: C, 34.3; H, 5.70; Br, 13.5; N, 11.8%).

trans-Azidobromo(1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcycloctetradecane)cobalt(III) Perchlorate, (I; A = N₃).—This salt was prepared by a similar method as that of the chloro-analogue¹ by treating *trans*-[CoL'(N₃)OH₂][ClO₄]₂¹ with LiBr in methanol (yield 50%) (Found: C, 33.7; H, 6.20; Br, 14.3; N, 17.5. Calc. for $C_{16}H_{36}BrClCoN_7O_4$: C, 34.1; H, 6.40; Br, 14.2; N, 17.4%).

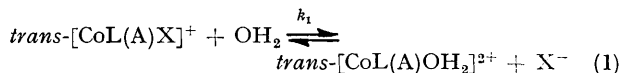
Kinetics.—The acid hydrolysis was followed spectrophotometrically *in situ* using either a Unicam SP 700 or 8000 recording spectrophotometer, separately equipped with a thermostatted cell holder, scale-expansion accessory, and external recorder Unicam AR25, in a conventional manner as described previously.¹⁰ The reaction temperature was maintained to ± 0.1 °C with a Haake Unitherm immersion circulator (model E52) (for temperatures about room temperature) and with a Townson and Mercer refrigerated unit (type 50A—105) (for temperatures below room temperature). For kinetic studies at temperatures below room temperature, the cell compartment of the spectrophotometer was constantly flushed with a stream of dry air to keep the optical windows free from water-vapour condensation. The extent of acid hydrolysis and the corresponding equilibrium constant were determined by allowing the reaction solution to stand at the desired temperature for 10 aquation half-lives. The solution was then passed down a cation-exchange column of Amberlite IR-100 resin in the acid form and the eluate containing

ionic halide titrated against standard silver(I) nitrate by Volhard's method.

RESULTS

The ambidentate thiocyanate ligand was shown to be N-bonded in the complexes by the absence of any peak assignable to $\nu(C-S)$ of the S-bonded form in the 680—750 cm⁻¹ region of the i.r. spectra.¹¹ On the other hand, bands characteristic of N-bonded $\nu(C-S)$ and $\nu(C-N)$ were present [at 840 and 2 085 (I), 832 and 2 110 (II; X = Cl), and 835 and 2 115 cm⁻¹ (II; X = Br)].

The acid hydrolysis of the complexes in dilute perchloric acid invariably involved replacement of the co-ordinated halide by water [equation (1); L = L' and L'', A = NCS



and N₃, X = Cl and Br]. This was confirmed by Volhard's titration and by the observation that the visible absorption spectra had their peaks slightly shifted to the blue as reactions proceeded. For the relatively slow reactions of the isothiocyanato-complexes, full spectral scan in the visible region revealed isosbestic points throughout the entire reactions [at 600 and 455 (I; X = Br), 582 (II; X = Cl), and 573 and 469 nm (II; X = Br)]. Addition of excess of the corresponding halide reversed the reaction, retracing the same set of isosbestic points. The same repeated spectral scan was not possible, however, for the relatively fast reactions of the azido-complexes. For (I; A = N₃), the final reaction spectrum was very similar to that of an authentic sample of *trans*-[CoL'(N₃)OH₂]²⁺.¹ Although the visible spectrum of *trans*-[CoL''(N₃)OH₂]²⁺ was not available, the spectra of the reaction products of complexes (II; A = N₃) were rather similar to that of *trans*-[CoL'(N₃)OH₂]²⁺. It seemed fair to assume that the behaviour of complexes (II; A = N₃) also followed equation (1). This was confirmed (to be described later) by linear semilogarithmic plots over three aquation half-lives.

TABLE I

First-order rate constants for acid hydrolysis of *trans*-[CoL'(A)Br]⁺, (I), at $I = 0.1M$

A	$\theta_c/^\circ\text{C}$	k s ⁻¹
NCS ^b	43.5	1.32×10^{-4}
	50.0	3.70×10^{-4}
	52.8	5.17×10^{-4}
	54.8	7.52×10^{-4}
	60.2	1.56×10^{-3}
N ₃ ^b	5.1	7.1×10^{-3}
	c	1.12×10^{-2}
	11.5	1.55×10^{-2}
	c	2.55×10^{-2}

^a Each entry represents an average of two or three different determinations at [Complex] = 0.5—1.5mm. ^b k was found to be independent of acid concentration over 0.01—0.1M-HClO₄. ^c At 0.01M-HClO₄.

Volhard's titration confirmed that acid hydrolysis of all the complexes was over 95% complete. First-order rate constants were obtained from gradients of semilogarithmic plots of $\log(D_\infty - D_t)$ against time, where D_∞ and D_t represent absorbances after 10 half-lives and at time t respectively, at wavelengths corresponding to the maximum change in absorbance [560 (I; A = NCS or N₃), 540

⁹ P. O. Whimp and N. F. Curtis, *J. Chem. Soc. (A)*, 1966, 867.

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

¹¹ K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Wiley, New York, 1970, p. 187.

(II; A = NCS, X = Cl or Br), 550 nm (II; A = N₃, X = Cl or Br)]. All these reactions were studied at constant ionic strength, 0.1M with NaClO₄, and over a range of temperature. Relevant data are collected in Tables 1 and 2.

TABLE 2

First-order rate constants for acid hydrolysis of *trans*-[CoL''(A)X]ⁿ⁺, (II), at I = 0.1M

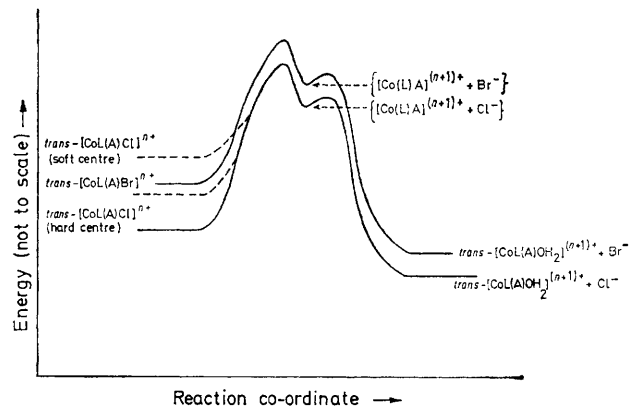
A	X	θ _c /°C	k*/s ⁻¹
NCS	Cl	50.6	5.2 × 10 ⁻⁵
		60.6	1.90 × 10 ⁻⁴
		64.8	3.11 × 10 ⁻⁴
		67.6	4.26 × 10 ⁻⁴
		69.4	5.18 × 10 ⁻⁴
	Br	42.0	5.04 × 10 ⁻⁵
		44.4	7.38 × 10 ⁻⁵
		47.5	1.19 × 10 ⁻⁴
		52.8	2.78 × 10 ⁻⁴
		56.5	4.84 × 10 ⁻⁴
N ₃	Cl	5.0	1.98 × 10 ⁻³
		9.3	3.28 × 10 ⁻³
		11.5	4.36 × 10 ⁻³
		19.0	1.09 × 10 ⁻²
		20.8	1.37 × 10 ⁻²
	Br	4.4	3.65 × 10 ⁻³
		7.6	5.80 × 10 ⁻³
		11.8	9.9 × 10 ⁻³
		17.5	2.20 × 10 ⁻²

* Each entry represents an average of two or three different determinations at [Complex] = 0.4—1.0mM, and 0.01—0.1M-HClO₄ for isothiocyanato-complexes and 0.01M-HClO₄ for azido-complexes.

DISCUSSION

Some of the rate constants extrapolated to 25.0 °C are collected in Table 3. It is clear from this Table that

as the central cobalt(III) ion becomes more polarizable on increasing the extent of electron delocalization between the central metal ion and the encircling macrocycles. On the other hand, the relative stability of their reaction intermediates {i.e. [Co(L)A]⁽ⁿ⁺¹⁾⁺ + X⁻ (X = Cl or Br)} remains constant and is equal to the difference in stability of the solvated Cl⁻ and Br⁻ ions



Variation of the energy profile for acid hydrolysis of a corresponding pair of *trans*-[CoL(A)X]ⁿ⁺ (X = Cl and Br) with the extent of unsaturation of the amine macrocycle L. The energy of *trans*-[CoL(A)Cl]ⁿ⁺ increases (---) relative to that of *trans*-[CoL(A)Br]ⁿ⁺ as the extent of electron delocalization between the cobalt(III) ion and the encircling macrocycle L increases

and is thus independent of the nature of the encircling macrocycles. This seems to imply that the difference in relative stability of the two corresponding transition states should also be nearly constant. Now, for L'

TABLE 3

First-order acid hydrolysis rate constants ^a of some complexes of the type *trans*-[CoL(A)X]ⁿ⁺ at 25.0 °C

L	A	k _{Cl} /s ⁻¹	k _{Br} /s ⁻¹	k _I /s ⁻¹	k _{Br} :k _{Cl}	k _I :k _{Br}
L'	Cl	9.3 × 10 ⁻⁴ ^b				
	Br		3.8 × 10 ⁻² ^c			
	NCS	7.0 × 10 ⁻⁷ ^d	6.1 × 10 ⁻⁶ ^e		8.7	
	N ₃	6.5 × 10 ⁻³ ^d	7.1 × 10 ⁻² ^e		10.9	
L''	Cl	3.6 × 10 ⁻² ^e				
	Br		5.1 × 10 ⁻² ^e			
	NCS	1.4 × 10 ⁻⁶ ^e	3.0 × 10 ⁻⁶ ^e		2.1	
	N ₃	2.1 × 10 ⁻² ^e	5.5 × 10 ⁻² ^e		2.6	
(Hdmg) ₂ ²⁻	NO ₂	1.0 × 10 ⁻⁴ ^f	1.2 × 10 ⁻⁴ ^f		1.2	
	I	6.0 × 10 ⁻⁵ ^g	7.2 × 10 ⁻⁵ ^g		1.2	
Corrin ²⁻ ^h	h		5.9 × 10 ² ^{i,j}	3.5 × 10 ^{4,k}		0.059

^a k_{Cl}, k_{Br}, and k_I Represent the rate constant with Cl⁻, Br⁻, and I⁻ as leaving group respectively. ^b Ref. 13. ^c Ref. 12. ^d Ref. 1. ^e This work, extrapolated from data at other temperatures. ^f A. V. Ablov and D. M. Palade, *Doklady Akad. Nauk S.S.S.R.*, 1962, **144**, 341. ^g D. N. Hague and J. Halpern, *Inorg. Chem.*, 1967, **6**, 2059. ^h *trans*-[CoL(A)X]ⁿ⁺ = Cobalamin. ⁱ D. Thusius, *J. Amer. Chem. Soc.*, 1971, **93**, 2629. ^j At 26.0 °C. ^k At 25.5 °C.

as the degree of unsaturation in the following macrocyclic (or pseudo-macrocyclic) amine ligands is increased, L' < L'' < (Hdmg)₂ < corrin, the 'softness' of the central cobalt(III) ion, as judged by the k_{Br}:k_{Cl} (or k_I:k_{Br}) ratio, is gradually increased [(Hdmg) = dimethylglyoximate(1-)]. This can be explained by assuming a dissociative mechanism for these reactions ³ as illustrated in the Figure. For a corresponding pair of [CoL(A)Cl]ⁿ⁺ and [CoL(A)Br]ⁿ⁺ complexes, the relative stability of the former to the latter will decrease

complexes, the cobalt(III) ion is essentially 'hard' and hence chloro-complexes are much more stable than corresponding bromo-complexes resulting in relative lability of the latter. This situation is reversed for 'soft' cobalamin complexes. In (Hdmg)₂ complexes, the difference in stability of halogeno-complexes in the ground state becomes comparable to that in the transition state and the reactivity of these complexes appears to be independent of the nature of the leaving halide groups.

The above discussion shows the danger of assessing the 'hard' and 'soft' character of cobalt(III) ion by considering kinetic ratios of corresponding pairs of $[\text{Co}(\text{L})\text{Br}_2]^{n+}$ and $[\text{Co}(\text{L})\text{Cl}_2]^{n+}$. In such a comparison not only are the leaving groups different, but the orienting ligands A are also different. Correlation of the relative stability of these complexes in the ground state and transition states is much more complicated. As the encircling macrocycle is varied, the relative stabilities of these halogeno-complexes will change both in the ground and transition states and it becomes much more difficult to estimate the relative importance of the changes in these two different states. For the same reason, comparison of the rate constants of corresponding complexes of the type $\text{trans-}[\text{CoL}(\text{A})\text{X}]^{n+}$ with the nature of L should be exercised with care. Unless a big change in rate constant is observed, it becomes dangerous to ascribe any small difference in rate constants, as in the present systems between corresponding pairs of L' and L'' complexes, to any particular effect.

¹² J. A. Kernohan and J. F. Endicott, *Inorg. Chem.*, 1970, **9**, 1504.

¹³ W. K. Chau and C. K. Poon, *J. Chem. Soc. (A)*, 1971, 3087.

However, it may be worthwhile to note that $\text{trans-}[\text{Co}(\text{L})\text{Cl}_2]^+$ is rather exceptional in that the L'' complex is distinctly more reactive than the corresponding L' complex by a factor of 39 at 25 °C^{12,13} (Table 3). If the earlier proposition,^{1,3,14,15} that the reactivity of these macrocyclic amine complexes $\text{trans-}[\text{CoL}(\text{A})\text{X}]^{n+}$, saturated or otherwise, depends to a large extent on the amount of negative charge donated to the central cobalt(III) ion by the orienting ligands A, is correct, the present observation suggests that the donating power of the chloride orienting ligand is much more susceptible to changes in the *cis*-macrocyclic ligand than that of azide and isothiocyanate. Work is now in progress to substantiate the above discussions experimentally.

We thank the Committee on Higher Degrees and Research Grants of the University of Hong Kong for support and the award of a Higher Degree Studentship (to W. K. L.).

[4/869 Received, 1st May, 1974]

¹⁴ D. P. Rillema, J. F. Endicott, and J. R. Barber, *J. Amer. Chem. Soc.*, 1973, **95**, 6987.

¹⁵ W. K. Lee and C. K. Poon, *Inorg. Chem.*, in the press.