Structural and Mechanistic Studies of Co-ordination Compounds. Part X.[1] Steric Effects in Aquation of some Octahedral Cobalt(III) Complexes of 1,4,8,11-Tetra-azacyclotetradecane and *meso*-1,4,8,11-Tetra-aza-5,5,7,12,12,14-hexamethylcyclotetradecane

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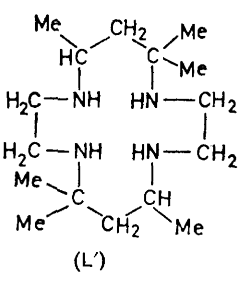
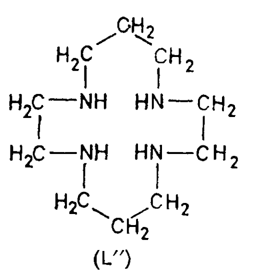
The preparation of a series of cations of the type *trans*-$[CoL'(A)Cl]^+$ are described (I; L′ = *meso*-1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcyclotetradecane; A = NO_2, N_3, NCS, and CN). The acid hydrolysis of these cations has been studied over a range of temperature. The lability of the relatively inert cations *trans*-$[CoL''(A)Cl]^+$ (II; L″ = 1,4,8,11-tetra-azacyclotetradecane; A = NCS and N_3) at 25·0 °C has been reassessed by following the thiocyanate-substitution reactions over a rather extended range of temperature. A comparison of the reaction rates of (I) with those of the corresponding complexes (II) shows that the former are more reactive by a factor of *ca.* 10^3 at 25·0 °C, depending only slightly on the different electronic-displacement properties of A. These results are consistent with a dissociative mechanism with basically a tetragonal-pyramidal intermediate. In the sterically congested complexes (I), a slight distortion of the intermediate from tetragonal-pyramidal geometry is evident. A linear Hammett relation with unit gradient exists over five logarithmic units between the reactions of these two series of complexes. This observation strongly indicates that the sensitivity of acid hydrolysis of these complexes to changes in the electronic structure of non-labile orienting ligands is independent of steric effects. This further suggests, together with the nearly constant rate increment as described previously, that electronic and steric effects independently affect the lability of cobalt(III) amine complexes.

PREVIOUSLY we showed that acid hydrolysis of *trans*-$[Co(L')Cl_2]^+$ was faster than that of *trans*-$[Co(L'')Cl_2]^+$ (L′ and L″ = *meso*-1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcyclotetradecane and 1,4,8,11-tetra-azacyclotetradecane respectively) by a factor of 850 at 25·0 °C.[2] In order to understand the influence of steric effects better, we have extended this kinetic study to a series of *trans*-$[CoL'(A)Cl]^+$ complexes, (I), containing a wide range of orienting ligand A of different electronic-displacement properties to see if this steric effect is dependent on the nature of A. The study is most significant for complexes containing electron-withdrawing orienting ligands, such as NO_2^- and CN^-, which have the potential to promote bimolecular reactions.[3]



(L′)



(L″)

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

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

[3] S. Ašperger and C. K. Ingold, *J. Chem. Soc.*, 1956, 2862.

This paper describes the preparation and aquation study of (I; A = NO_2, CN, N_3, and NCS). Rate data for the corresponding L″ complexes, (II), are known.[4-6]

When all known aquation rate data at 25·0 °C for complexes of the type *trans*-$[CoL(A)Cl]^+$ [L = *meso*-1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcyclotetradecane, 1,4,8,11-tetra-azacyclotetradecane, $(en)_2$ (en = ethylenediamine), and $(NH_3)_4$; A = NO_2, N_3, Cl, CN, and NCS] were plotted according to the Hammett equation[7] (see Discussion section), it was found that, with the exception of the rate constant for (II; A = NCS), all kinetic data nicely conformed to straight lines over five logarithmic units. A close re-examination of the conditions under which the aquation rate constants of (II; A = NCS) were obtained[6] suggested that the rate constant reported at 25·0 °C could be in error. The aquation reaction was only *ca.* 35% complete. Spectrophotometric determination of the forward aquation rate constant depended critically on correct estimation of the molar absorbance of *trans*-$[CoL''(NCS)OH_2]^{2+}$ at 556 nm and accurate determination of the aquation equilibrium constant at the reaction temperature.[6] An error in the determinations of these values would result in a rate constant different from the true value. The error introduced might not be too serious if one was interested in rate constants directly determined at the reaction temperatures, but it might be very serious for the estimated rate constant at 25·0 °C obtained by a relatively extended extrapolation of rate data determined at *ca.* 90 °C. In order to obtain a more reliable rate constant at 25·0 °C for comparison purposes in the present investigation of steric effects, we followed the thiocyanate-substitution reaction of (II; A = NCS) at lower temperatures. Since the substitution reaction goes to completion, a much more reliable rate constant can be obtained by the simpler semilogarithmic treatment of the changing absorbance with time. This paper also describes the thiocyanate-substitution reaction of (II; A = N_3) to check the reliability of using this reaction as a measure of the aquation reaction.

EXPERIMENTAL

Preparation of the Complexes.—trans-*Chloronitro*(1,4,8,11-*tetra-aza*-5,5,7,12,12,14-*hexamethylcyclotetradecane*)*cobalt*(III) *nitrate*, (I; A = NO_2): *method* (*a*). A filtered solution of *trans*-$[Co(L')Cl_2][NO_3]$ [2] (L′ = *meso*-1,4,8,11-tetra-aza-5,5,7,12,12,14-hexamethylcyclotetradecane) (2 g) in the minimum volume of hot dilute ammonia was treated with an equimolar amount of sodium nitrite. After *ca.* 5 min, the solution was rendered acidic by dropwise addition of concentrated hydrochloric acid. Addition of concentrated nitric acid to the final solution crystallized out the desired product, which was recrystallized by adding diethyl ether to a saturated solution of the complex in ethanol (yield 1·5 g) (Found: C, 39·3; H, 7·3; Cl, 7·2; N, 17·5. Calc. for $C_{16}H_{36}ClCoN_6O_5$: C, 39·4; H, 7·4; Cl, 7·3; N, 17·3%).

Method (*b*). An ethanolic solution of L′ [8] (2 g in 20 cm^3 of 95% ethanol) was added to a solution of $Na_3[Co(NO_2)_6]$ (3 g in 20 cm^3 water). The resulting mixture was digested over a steam-bath for 0·5 h until the solution turned reddish brown. On cooling, *trans*-$[CoL'(NO_2)_2][NO_2]$ precipitated out in high yield, and was treated, dropwise, with concentrated hydrochloric acid. When liberation of brown fumes had subsided, further concentrated hydrochloric acid (5 cm^3) was added to ensure complete conversion of the dinitro-complex to *trans*-$[CoL'(NO_2)Cl]Cl$. After allowing the solution to stand for 1 h, the solid was filtered off and converted to the nitrate salt by addition of concentrated nitric acid to a saturated aqueous solution of the chloride. The crude *product* was recrystallized from the ethanol–diethyl ether (yield 2·5 g). I.r. and visible spectra of the salt were identical with those of the sample prepared by method (*a*) (Found: Cl, 7·2%).

trans-*Chloroisothiocyanato*(1,4,8,11-*tetra-aza*-5,5,7,12,12,14-*hexamethylcyclotetradecane*)*cobalt*(III) *perchlorate*, (I; A = NCS). A suspension of *trans*-$[Co(L')Cl_2][NCS]$, prepared by addition of a strong aqueous solution of NH_4NCS to a strong aqueous solution of *trans*-$[Co(L')Cl_2]Cl,4H_2O$ [9] (2 g), in water (20 cm^3) was digested on a steam-bath for 15 min. The resulting purple solution was filtered and the filtrate cooled and treated with excess of $NaClO_4$. A greenish blue product separated out, and was recrystallized at least three times by adding $NaClO_4$ to a saturated solution of the crude product in cold water. The recrystallized pale blue *complex* was finally filtered off, washed with ethanol and diethyl ether, and dried *in vacuo* at 50 °C (yield 1 g) (Found: C, 37·9; H, 6·75; Cl, 13·5; N, 13·2. Calc. for $C_{17}H_{36}Cl_2CoN_5O_4S$: C, 38·1; H, 6·70; Cl, 13·2; N, 13·1%). That the thiocyanate ligand is *N*-bonded in this complex was confirmed by the presence of i.r. bands at 849 [ν(C–S)] and 2 130 cm^{-1} [ν(C–N)] and the absence of any band in the 680—750 cm^{-1} region assignable to ν(C–S) of the *S*-bonded form.[10]

trans-*Aqua-azido*(1,4,8,11-*tetra-aza*-5,5,7,12,12,14-*hexamethylcyclotetradecane*)*cobalt*(III) *perchlorate*. A hot aqueous solution (70 °C) of *trans*-$[Co(L')Cl_2]Cl,4H_2O$ [9] (2·7 g, 5mM; * in 150 cm^3) was maintained at this temperature for 1 h. NaN_3 (0·2 g, 5mM) was added and the resulting solution was maintained at the same temperature for a further 10 min. The filtered dark green solution was cooled and excess of $NaClO_4$ was added to precipitate the crude green product which was filtered off and washed with a small quantity of cold water. The crude product was dissolved in the minimum amount of hot ethanol and to the resulting cooled solution diethyl ether was added to reprecipitate the desired product. This was filtered off, washed with diethyl ether, and dried *in vacuo* at 50 °C (yield 1·6 g) (Found: C, 32·4; H, 6·25; Cl, 12·0; N, 16·1. Calc. for $C_{16}H_{38}Cl_2CoN_7O_9$: C, 31·9; H, 6·30; Cl, 11·8; N, 16·3%).

trans-*Azidochloro*(1,4,8,11-*tetra-aza*-5,5,7,12,12,14-*hexamethylcyclotetradecane*)*cobalt*(III) *perchlorate dihydrate*, (I; A = N_3). A mixture of LiCl (10 g) and *trans*-$[CoL'(N_3)OH_2][ClO_4]_2$ (3 g) in water–methanol (1 : 1; 100 cm^3) was heated on a steam-bath for 15 min, after which excess of $NaClO_4$ was added to the cooled solution to precipitate

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* 1M = 1 mol dm^{-3}.

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

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

[6] K. S. Mok, C. K. Poon, and H. W. Tong, *J.C.S. Dalton*, 1972, 1701.

[7] W. K. Lee and C. K. Poon, *Inorg. Chem.*, 1974, in the press.

[8] A. M. Tait and D. H. Busch, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 491.

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

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

a crude product which was contaminated with a small quantity of *trans*-[Co(L′)Cl_2][ClO_4]. The *product* was recrystallized at least three times by adding diethyl ether to a filtered saturated solution of it in ethanol (yield 2 g) (Found: C, 34·5; H, 6·80; Cl, 13·0; N, 17·3. Calc. for $C_{16}H_{40}Cl_2CoN_7O_6$: C, 34·8; H, 7·20; Cl, 12·9; N, 17·8%).

trans-*Aquosulphito*(1,4,8,11-*tetra-aza*-5,5,7,12,12,14-*hexamethylcyclotetradecane*)*cobalt*(III) *chloride.* An aqueous solution of Na_2SO_3 (0·62 g, 5mM; in 10 cm^3) was added with stirring to an aqueous solution of *trans*-[Co(L′)Cl_2]Cl,$4H_2O$ [9] (2·5 g, 5mM; in 30 cm^3). The colour of the solution gradually changed from green to red. The solution was set aside at room temperature for 3 h with occasional stirring. Purple crystals which formed were collected, washed with ethanol and diethyl ether, and air dried (yield 1·5 g) (Found: C, 40·5; H, 8·00; ionic Cl, 7·80; N, 11·7. Calc. for $C_{16}H_{38}ClCoN_4O_4S$: C, 40·3; H, 7·95; ionic Cl, 7·45; N, 11·8%).

trans-*Chlorocyano*(1,4,8,11-*tetra-aza*-5,5,7,12,12,14-*hexamethylcyclotetradecane*)*cobalt*(III) *nitrate monohydrate,* (I; A = CN).* NaCN (0·49 g, 10mM) was added to a boiling aqueous solution of *trans*-[CoL′(SO_3)OH_2]Cl (2·4 g, 5 mM; in 200 cm^3). The colour of the solution changed instantaneously from red to orange. Concentrated hydrochloric acid (10 cm^3) was added and the volume of the final solution was reduced to 50 cm^3 by means of a rotary evaporator. Concentrated nitric acid (10 cm^3) was added to the cooled solution, followed by ethanol and diethyl ether to precipitate the crude product. The *complex,* recrystallized from a hot mixed solvent of HCl and HNO_3 (3M in each acid), was collected, washed with ethanol and diethyl ether, and dried *in vacuo* at 78 °C (yield 0·5 g) (Found: C, 42·6; H, 7·80; Cl, 7·0; N, 17·6. Calc. for $C_{17}H_{38}ClCoN_6O_4$: C, 42·1; H, 7·85; Cl, 7·3; N, 17·3%).

The *perchlorate* salt of the complex was obtained by adding $HClO_4$ (or $NaClO_4$) to a saturated solution of the nitrate (Found: C, 39·9; H, 6·95; Cl, 14·2; N, 13·9. Calc. for $C_{17}H_{36}Cl_2CoN_5O_4$: C, 40·5; H, 7·15; Cl, 14·1; N, 13·9%).

Other complexes, *trans*-[CoL″(NCS)Cl][ClO_4] [6] and *trans*-[CoL″(N_3)Cl][ClO_4] (II; L″ = 1,4,8,11-tetra-azacyclotetradecane),[5] were prepared by methods described previously.

Kinetics.—All the reactions, aquation and thiocyanate substitution, were followed spectrophotometrically, either *in situ* [4] or by the sealed-tube method,[4] using either a Unicam SP 700 or 8000 recording spectrophotometer equipped with a scale-expansion accessory and an external recorder Unicam AR 25, in a conventional manner as described previously. Aquation equilibrium constants at a given reaction temperature were determined also conventionally [5] by measuring the amount of ionic chloride released at equilibrium. Reaction temperatures were maintained to ±0·1 °C using either a Haake Unitherm immersion circulator (model E52) (for temperatures above room temperature) or a Townson and Mercer refrigerated unit (type 50A—105) (for temperatures below room temperature).

RESULTS

The visible spectrophotometric change associated with acid hydrolysis of (I; A = NO_2, CN, N_3, and NCS) in 0·01M- (or 0·1M) nitric acid (or perchloric acid) was very similar to those of the corresponding complexes (II).[4-6] The absorption peaks shifted slightly to the blue with respect to those of the corresponding starting complexes. Volhard's titration confirmed that chloride was released in the course of the reaction. Addition of a large excess of chloride to the final solutions reversed the reaction. It is, therefore, clear that these reactions obey equation (1).

$$\underset{\text{(I)}}{trans\text{-}[\mathrm{CoL'(A)Cl}]} + \mathrm{H_2O} \overset{K}{\rightleftharpoons} trans\text{-}[\mathrm{CoL'(A)OH_2}]^{2+} + \mathrm{Cl^-} \quad (1)$$

Apart from the isothiocyanato-complex, aquation of all complexes (I) was over 95% complete at equilibrium. The first-order aquation rate constants were determined from gradients of standard semilogarithmic plots of log ($D_\infty - D_t$) against time, where D_∞ and D_t represent absorbances after 10 aquation half-lives and at time t respectively at a given wavelength which corresponded to the maximum change in absorbance [550 (NO_2), 450 (CN), and 560 nm (N_3)]. For all these reactions the ionic strength was maintained at 0·1M with either $NaNO_3$ or $NaClO_4$. For (I; A = NCS), the aquation was *ca.* 70% complete and standard expression (2) [11] for opposed first- and second-order reactions was used to calculate the aquation rate constant, k_1, where $c_0 = [(\mathrm{I})]_0$ and c_e and c_t are the concentrations of the complex [CoL′(NCS)(OH_2)] = [Cl^-] at equilibrium and time t. The concentration c_t of the aqua-complex at time t was determined from the observed absorbance at 560 nm using molar absorption coefficients for the starting and aqua-complexes (ε = 80 and 139 l mol^{-1} cm^{-1} respectively). All kinetic plots were linear to two half-lives. The data are collected in Table 1.

$$2{\cdot}303 \log \{[c_0c_e + c_t(c_0 - c_e)]/c_0(c_e - c_t)\} = k_1[(2c_0 - c_e)/c_e]t \quad (2)$$

TABLE 1

First-order rate constants and equilibrium constants for aquation of *trans*-[CoL′(A)Cl]$^+$, (I), at I = 0·1M

A	θ_c/°C	k_1 [a]/s^{-1}	10^3K [a]/mol l^{-1}
NCS [b]	74·0	$5{\cdot}4 \times 10^{-4}$	2·7
	64·8	$1{\cdot}8 \times 10^{-4}$	2·05
	60·6	$1{\cdot}1 \times 10^{-4}$	1·8
	53·5	$4{\cdot}2 \times 10^{-5}$	1·4
CN [c]	46·2	$7{\cdot}1 \times 10^{-3}$	
	41·5	$3{\cdot}5 \times 10^{-3}$	
	37·2	$2{\cdot}0 \times 10^{-3}$	
	31·5	$9{\cdot}0 \times 10^{-4}$	
N_3 [d]	31·6	$1{\cdot}4 \times 10^{-2}$	
	27·0	$8{\cdot}0 \times 10^{-3}$	
	23·2	$5{\cdot}4 \times 10^{-3}$	
	20·0	$3{\cdot}7 \times 10^{-3}$	
	17·7	$2{\cdot}8 \times 10^{-3}$	
NO_2 [e]	14·2	$9{\cdot}5 \times 10^{-3}$	
	12·2	$7{\cdot}0 \times 10^{-3}$	
	9·9	$5{\cdot}0 \times 10^{-3}$	
	8·9	$4{\cdot}3 \times 10^{-3}$	
	5·9	$2{\cdot}9 \times 10^{-3}$	

[a] Each entry represents an average of two or three different determinations. [b] [Complex] = 1·4—2·4mM, [$HClO_4$] = 0·01—0·1M. [c] [Complex] = 0·5—2·0mM, [HNO_3] = 0·1M. [d] [Complex] = 0·3—1·0mM, [$HClO_4$] = 0·01M. [e] [Complex] = 1·8—2·8mM, [HNO_3] = 0·01M.

The substitution reactions of (II; A = NCS and N_3)

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* **CAUTION**: the method is potentially hazardous and should only be carried out in a good fumehood.

[11] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanisms,' 2nd edn., Wiley, New York, 1961, p. 187.

in 0·01M-HNO_3 were followed spectrophotometrically at 530 nm. Here both reactions went to completion and first-order rate constants, k_1, were obtained from gradients of standard semilogarithmic plots of log ($D_\infty - D_t$) against time. These plots were linear to three half-lives and the rate constants were independent of thiocyanate concentration (0·01—0·05M) (Table 2). A plot of log k against $1/T$ for the reaction of (II; A = N_3) is shown in Figure 1.

TABLE 2

First-order rate constants for the following reaction in 0·01M-HNO_3: *trans*-$[CoL''(A)Cl]^+ + NCS^- \longrightarrow$ *trans*-$[CoL''(A)NCS]^+ + Cl^-$

A	θ_c/°C	k*/s^{-1}
NCS	89·3	$5·6 \times 10^{-5}$
	81·8	$2·1 \times 10^{-5}$
	77·6	$1·1 \times 10^{-5}$
	70·1	$3·7 \times 10^{-6}$
N_3	71·5	$8·4 \times 10^{-4}$
	60·8	$2·7 \times 10^{-4}$
	52·5	$1·1 \times 10^{-4}$
	45·8	$4·9 \times 10^{-5}$

* Each entry represents an average of two or three different determinations over a range of [NCS^-] between 0·01 and 0·05M and of [Complex] between 0·5 and 1·0mM.

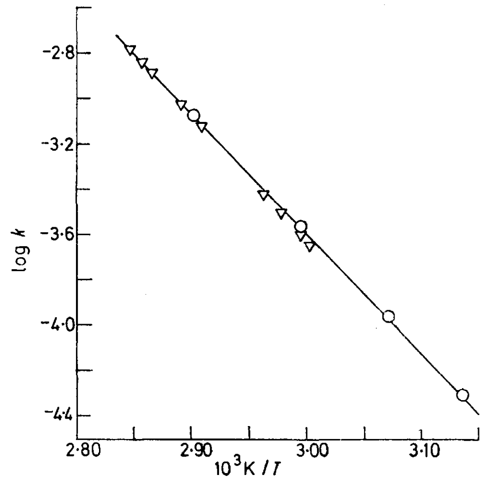

FIGURE 1 Temperature dependence of ligand-substitution reactions of (II; A = N_3) in 0·01M-HNO_3: (▽), acid hydrolysis; (○), thiocyanate substitution

Aquation rate data for the same cation determined previously[5] are also shown to demonstrate that thiocyanate-substitution reactions do give a good measure of aquation rate constants at the same temperature. From this combined set of data over a much wider range of temperature, a slightly improved rate constant of $3·6 \times 10^{-6}$ s^{-1} at 25·0 °C was obtained by extrapolation. The present study also confirms that the previous aquation study of (II; A = NCS) was indeed in error and the value of $1·1 \times 10^{-9}$ s^{-1} at 25·0 °C determined here is taken to supersede that reported previously.[6] For the same reason, the substitution reaction of (I; A = NCS) by thiocyanate was attempted to check the above aquation study. Unfortunately, *trans*-$[Co(L')(NCS)_2][NCS]$ precipitated, but not completely, during the course of the reaction and this made the kinetic study rather difficult. Fortunately, aquation of this cation was *ca.* 70% complete and so the correction introduced in equation (2) for the opposed anation is not too serious, at least at the beginning of the reaction, to make the observed rate constant differ greatly from the true value. In the present case, the rate constant at 25·0 °C was obtained by a much less extended extrapolation than was the case for the corresponding complex (II). Furthermore, the observation that the aquation rate constant determined here perfectly fitted various Hammett plots[7] (see Discussion section) strongly endorses the reliability of the value.

DISCUSSION

Some of the kinetic data relevant to the subsequent discussion are collected in Table 3. It is clear that the sterically more congested complexes (I) are more labile than (II) by a factor of *ca.* 10^3. This is consistent with a dissociative mechanism for aquation of these complexes. In view of steric constraints imposed on these macrocycles, it was demonstrated[12] that tetragonal-pyramidal intermediates were more favourable than the alternative trigonal bipyramidals. On the other hand, for these sterically congested complexes (I), a slight distortion from tetragonal-pyramidal-like geometry in the transition state may partially decrease non-bonded steric repulsion between the orienting ligand A and its geminal dimethyl neighbours. The observation that kinetic ratios (Table 3) for corresponding pairs of complexes do vary slightly with the nature of A supports the above conclusion. If both series of complexes generated tetragonal-pyramidal-like transition states, these ratios would be nearly the same, since the steric effect of the geminal dimethyl groups on releasing the outgoing chloride was quite independent of the nature of the *trans*-orienting ligands A when they were little disturbed in the course of the reaction. After all, as discussed later, sterics effect do not affect the electronic influence of these *trans*-orienting ligands on the lability of the complexes. In any case, the small variation in these kinetic ratios (less than a factor of three for five different orienting ligands of different π-character) implies that the distortion is rather small.

TABLE 3

First-order aquation rate constants of complexes (I) and (II) at 25·0 °C

	k_A/s^{-1}		$10^{-3}\frac{k_A(I)}{k_A(II)}$	log (k_A/k_{Cl}) *	
A	(I)	(II)		(II)	(I)
NO_2	$4·1 \times 10^{-2}$ [a]	$4·3 \times 10^{-5}$ [b]	0·95	1·59	1·64
N_3	$6·5 \times 10^{-3}$ [a]	$3·6 \times 10^{-6}$ [a]	1·8	0·52	0·84
Cl	$9·3 \times 10^{-4}$ [c]	$1·1 \times 10^{-6}$ [d]	0·85	0·00	0·00
CN	$3·4 \times 10^{-4}$ [a]	$4·8 \times 10^{-7}$ [d]	0·71	−0·36	−0·43
NCS	$7·0 \times 10^{-7}$ [a]	$1·1 \times 10^{-9}$ [a]	0·64	−3·00	−3·12

* For complexes (II), log (k_A/k_{Cl}) = σ_A.

[a] This work; obtained by extrapolation. [b] Ref. 4. [c] Ref. 2.
[d] C. K. Poon and M. L. Tobe, *J. Chem. Soc.* (*A*), 1967, 2069.

It has been suggested elsewhere[7] that the kinetic *cis*- and *trans*-influences in aquation of octahedral cobalt(III) amine complexes of the type *trans*-$[CoL(A)Cl]^{n+}$ [L = $(NH_3)_4$, $(en)_2$, L'', and L'; A = NO_2, N_3, Cl, CN, NCS, and NH_3] are well correlated quanti-

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

tatively with the Hammett equation.[13,14] It was proposed to take aquation of the series of L″ complexes as reference and define the labilizing constant, σ_A, of A by equation (3), where k_A and k_{Cl} are first-order aquation

$$\sigma_A = \log (k_A/k_{Cl})_{L''} \qquad (3)$$

rate constants of (II) and *trans*-$[Co(L'')Cl_2]^+$ respectively at 25·0 °C. A set of these σ_A values, together with corresponding values of $\log (k_A/k_{Cl})_{L'}$, are collected in Table 3. A plot of $\log (k_A/k_{Cl})_{L'}$ against σ_A (Figure 2) was linear over five logarithmic units according to the Hammett equation (4),[13,14] with the reaction constant $\rho_L = 1{\cdot}0$ being independent of the nature of A.

$$\log (k_A/k_{Cl})_{L'} = \rho_L\sigma_A \qquad (4)$$

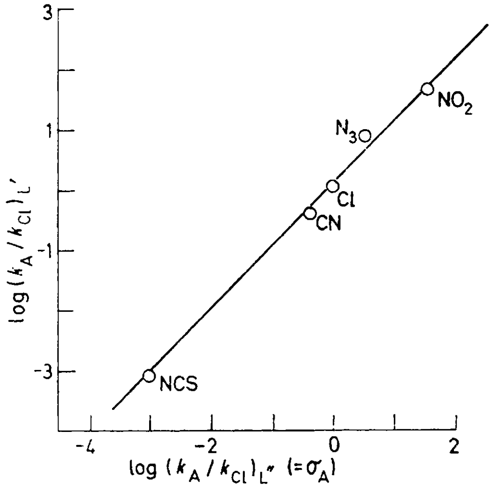

FIGURE 2 Hammett relation for acid hydrolysis of *trans*-$[CoL(A)Cl]^+$ at 25·0 °C (L = L′ and L″)

Since L″ and L′ are very similar in their ligand field and nephelauxetic effects, but differ greatly in steric effect at the axial reaction site in their cobalt(III) complexes,[2] the observation of $\rho_L = 1{\cdot}0$ implies that both series of complexes respond in exactly the same manner both qualitatively and quantitatively to changes in the nature of A of greatly different π-character. In other words, *the electronic influence of a* trans-*orienting ligand is unaffected by steric effects and these two effects independently affect the lability of these complexes towards ligand-substitution reactions.*

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[4/868 *Received*, 1*st May*, 1974]

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[13] L. P. Hammett, *Trans. Faraday Soc.*, 1938, **34**, 156.

[14] L. P. Hammett, ' Physical Organic Chemistry,' 2nd edn., McGraw-Hill, New York, 1970, p. 355.