Structural and Mechanistic Studies of Co-ordination Compounds. Part 22.[1] Preparation and Ligand-substitution Kinetics of some *trans*-Dihalogeno- and *trans*-Halogenoisothiocyanato-cobalt(III) Complexes of 2,12-Dimethyl- and 2,7,12-Trimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene

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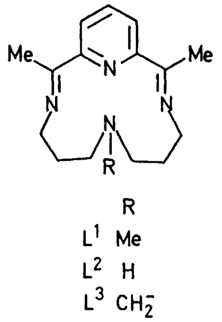
Complexes *trans*-$[CoL^1(NCS)X]^+$ {L^1 = 2,7,12-trimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),-2,11,13,15-pentaene; X = NCS, Cl, or Br} have been prepared and characterized. The kinetics of thiocyanate-substitution reactions of *trans*-$[CoLX_2]^+$ {L = L^1 or L^2 (2,12-dimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene); X = Cl or Br} have been studied over a range of temperature. The rate constants for the replacement of the first chloride from the dichloro-complexes are virtually independent of the nature of L [$k_{Cl} = 1.1 \times 10^{-2}$ (L^1) and 2.9×10^{-2} s^{-1} at 25.0 °C (L^2)] whereas those for the replacement of the second halide are much faster for L^2 ($k_{Cl} = 7.6 \times 10^{-4}$ and $k_{Br} = 9.1 \times 10^{-4}$ s^{-1} at 25.0 °C) than for L^1 ($k_{Cl} = 2.8 \times 10^{-6}$ and $k_{Br} = 4.5 \times 10^{-6}$ s^{-1} at 25.0 °C) by two orders of magnitude. This observation seems to indicate that the first step of substitution involves the release of the halide farther away from the N–R group of the L^1 (R = Me) and L^2 (R = H) macrocycles. The role played by the amine proton in promoting the rates of substitution of the second halide in the L^2 complexes is discussed. The hydrolysis of *trans*-$[CoL^1(NCS)X]^+$ involves concurrent release of both isothiocyanate and halide. This, coupled with a relatively low value of k_{Br}/k_{Cl}, is taken to indicate that the cobalt(III) ion in these L^1 and L^2 complexes is much softer than that in complexes of saturated macrocyclic amines.

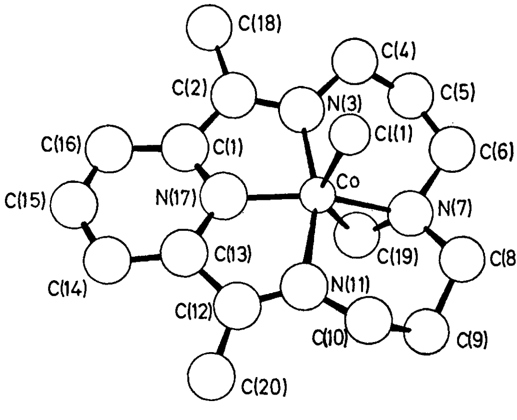
It was reported previously [2] that the rate of hydrolysis of the first halide from *trans*-$[CoL^1X_2]^+$ (X = Cl or Br) was too fast to be followed by conventional techniques and that the release of the second halide led to the formation of a distorted species $[CoL^3(OH_2)]^{2+}$ {L^3 = 2,12-dimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaen-7-ylmethyl}, according to equations (1) and (2). It was proposed that *trans*-$[CoL^1(OH_2)X]^{2+}$ had the isomeric structure in which the axial aqua-ligand was farther away from the *N*-methyl group of the macrocycle according to Scheme 1.



$$trans\text{-}[CoL^1X_2]^+ + H_2O \xrightarrow{\text{fast}} trans\text{-}[CoL^1(OH_2)X]^{2+} + X^- \quad (1)$$

$$trans\text{-}[CoL^1(OH_2)X]^{2+} \xrightarrow{\text{slow}} trans\text{-}[CoL^3(OH_2)]^{2+} + H^+ + X^- \quad (2)$$

Attempts to prepare the complexes *trans*-$[CoL^1(OH_2)X]^{2+}$ in crystalline form suitable for *X*-ray analysis have not been successful. Since the environment about the axial ligands X lying farther away from the N–R groups of corresponding *trans*-$[CoLX_2]^+$ complexes (L = L^1, R = Me; L^2, R = H) is very similar whereas that about the other axial ligands X on the same side of the N–R group is quite different, it seems feasible to deduce the structure of the aquahalogeno-complexes by comparing the kinetic behaviour of the substitution reactions of *trans*-$[CoLX_2]^+$ (L = L^1 or L^2, X = Cl or Br). In the course of the study of the thiocyanate-substitution reactions of *trans*-$[CoL^1X_2]^+$ at low temperatures it was found that the release of the first halide was not as fast as previously alleged.[2] The main reason for the failure in following reaction (1) previously was due partly to the low solubility of these complexes so that it took a relatively long time to get the complexes in solution. It is also due partly to the small spectral difference between the dihalogeno- and aquahalogeno-complexes such that by the time the complexes were dissolved the hydrolysis reactions would have proceeded to such an extent that no further noticeable spectral change was detected.



The $[Co(L^3)Cl]^+$ cation,[2] showing that C(19) together with Co and N(7) form a localized three-membered ring

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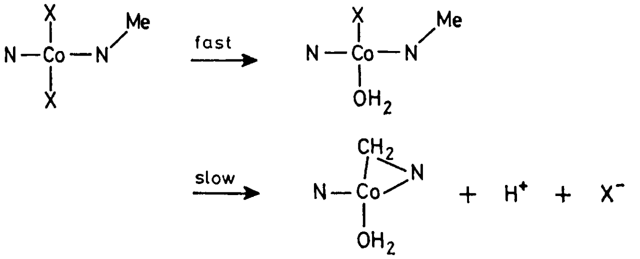
[1] Part 21, C. K. Poon and D. A. Isabirye, *J.C.S. Dalton*, 1978, 740.

[2] C. K. Poon, W. K. Wan, and S. S. T. Liao, *J.C.S. Dalton*, 1977, 1247.

However, the spectral change associated with the thiocyanate-substitution reactions of these complexes is substantially much greater and this enables the reactions to be followed spectrophotometrically. In order to understand these thiocyanate-substitution reactions better we have successfully prepared *trans*-$[\mathrm{CoL^1(NCS)X}]^+$ (X = Cl or Br). This paper also reports the kinetic behaviour of these isothiocyanato-complexes.



SCHEME 1 For simplicity, N—Co—$\overset{\mathrm{R}}{\mathrm{N}}$ represents a side view of the macrocyclic cobalt(III), CoL, units (L^1, R = Me; L^2, R = H)

EXPERIMENTAL

Preparation of Complexes.—trans-*Di-isothiocyanato*-{2,7,12-*trimethyl*-3,7,11,17-*tetra-azabicyclo*[11.3.1]*heptadeca*-1(17),2,11,13,15-*pentaene*}*cobalt*(III) *perchlorate monohydrate*, *trans*-$[\mathrm{CoL^1(NCS)_2}][\mathrm{ClO_4}]\cdot\mathrm{H_2O}$. The complex *trans*-$[\mathrm{CoCl_2L^1}][\mathrm{ClO_4}]$ [2] (0.5 g) in a minimum of warm water was added with stirring to a warm aqueous solution of $[\mathrm{NH_4}][\mathrm{NCS}]$ (0.5 g in 20 cm^3, *ca.* 60 °C). The resulting dark red solution was stirred and maintained at *ca.* 60 °C for 1 h. Sodium perchlorate was added to the cooled solution to precipitate out a crude product which was collected and recrystallized from ethanol–diethyl ether. The final product was dried *in vacuo* at *ca.* 54 °C (yield 40%) (Found: C, 39.8; H, 4.9; Cl, 6.3; N, 13.7. Calc. for $C_{18}H_{26}ClCoN_6O_5S_2$: C, 40.3; H, 4.9; Cl, 6.5; N, 13.8%).

trans-*Chloroisothiocyanato*{2,7,12-*trimethyl*-3,7,11,17-*tetra-azabicyclo*[11.3.1]*heptadeca*-1(17),2,11,13,15-*pentaene*}-*cobalt*(III) *perchlorate monohydrate*, *trans*-$[\mathrm{CoCl(L^1)(NCS)}][\mathrm{ClO_4}]\cdot\mathrm{H_2O}$. This complex was prepared by dissolving *trans*-$[\mathrm{CoCl_2L^1}][\mathrm{ClO_4}]$ in warm ethanol–water (1 : 1). The solution appeared slightly reddish. A stoicheiometric amount of $[\mathrm{NH_4}][\mathrm{NCS}]$ (0.05 g) dissolved in ethanol was added and a deep red solution resulted. Ethanol (10 cm^3) was added followed by diethyl ether until the solution became cloudy. Crystallization was induced by scratching the beaker with a glass rod and a brownish red solid precipitated out, which was collected, and recrystallized from ethanol–diethyl ether (yield 30%) (Found: C, 37.5; H, 4.5; Cl, 12.8; N, 12.8. Calc. for $C_{17}H_{26}Cl_2CoN_5O_5S$: C, 37.6; H, 4.8; Cl, 12.9; N, 12.9%).

trans-*Bromoisothiocyanato*{2,7,12-*trimethyl*-3,7,11,17-*tetra-azabicyclo*[11.3.1]*heptadeca*-1(17),2,11,13,15-*pentaene*}-*cobalt*(III) *perchlorate*, *trans*-$[\mathrm{CoBr(L^1)(NCS)}][\mathrm{ClO_4}]$. The preparation was very similar to that of *trans*-$[\mathrm{CoCl(L^1)(NCS)}][\mathrm{ClO_4}]\cdot\mathrm{H_2O}$ except that *trans*-$[\mathrm{CoBr_2L^1}][\mathrm{ClO_4}]$ (0.3 g) was used as the starting material and 0.04 g of $[\mathrm{NH_4}][\mathrm{NCS}]$ was added. The product isolated was crimson-red (yield 30%) (Found: C, 35.7; H, 4.5; Br, 14.1; Cl, 6.3; N, 15.6. Calc. for $C_{17}H_{26}BrClCoN_5O_5S$: C, 35.9; H, 4.2; Br, 14.0; Cl, 6.2; N, 15.3%).

Other complexes, *trans*-$[\mathrm{CoL^1X_2}]^+$ (ref. 2) and *trans*-$[\mathrm{CoL^2X_2}]^+$ (ref. 3) (X = Cl or Br) were prepared by published methods.

Kinetics.—The kinetics of thiocyanate-substitution reactions of *trans*-$[\mathrm{CoL^1(NCS)X}]^+$ (X = Cl or Br) and of chloride-substitution reactions of *trans*-$[\mathrm{CoCl(L^1)(NCS)}]^+$ were followed *in situ* in a conventional manner using a Unicam SP 8000 recording spectrophotometer, equipped with a thermostatted cell holder and a Weyfringe ADCP-2 digital printer. The reaction temperature was maintained to ±0.1 °C using a Haake model E52 Unitherm immersion circulator. The thiocyanate-substitution reactions of the much less soluble *trans*-$[\mathrm{CoLX_2}]^+$ (L = L^1 or L^2; X = Cl or Br) in reaction media containing excess of thiocyanate were similarly followed except that the reaction solution was prepared by adding with shaking a small quantity of the complex to the thermostatted reaction solution. The solution was rapidly filtered into a thermostatted flask and the filtrate immediately transferred to an optical cell housed in the thermostatted cell holder of the Unicam SP 8000 spectrophotometer. The complex concentration for each run was obtained by comparing the spectrum of the final reaction solution with the known spectrum of the corresponding *trans*-$[\mathrm{CoL(NCS)_2}]^+$ into which the substrate would be eventually transformed.

Acid hydrolysis of *trans*-$[\mathrm{CoCl(L^1)(NCS)}]^+$, which leads to a concurrent release of both chloride and thiocyanate, was followed by withdrawing known quantities of the reaction solution at different time intervals and passing them through an ice-jacketed column of cation-exchange resin (Amberlite IR-120) in the acid form. The effluent and washings were combined and made up to a known volume. The amount of chloride in the solution was then analysed by an Orion chloride-selective electrode using an Orion double-junction $\mathrm{K[NO_3]}$ reference electrode and an Orion model 701 pH–mV meter. The amount of thiocyanate in the same eluted solution was determined by a colorimetric method [4] using a freshly prepared iron(III) nitrate solution to give a red colouration with thiocyanate.

Physical Measurements.—Visible and u.v. absorption spectra were recorded with a Unicam SP 8000 recording spectrophotometer. Infrared spectra of Nujol mulls were obtained with a Perkin-Elmer 577 spectrophotometer.

RESULTS

The thiocyanate-substitution reactions of the L^1 complexes in dilute nitric acid (0.01 mol dm^{-3}) could be distinctly identified to consist of two consecutive steps. The first step was very fast and had to be followed at sufficiently low temperatures. The visible spectra of the starting dihalogeno-complexes rapidly changed with peaks gradually developing at 510 (X = Cl) and 500 nm (Br) and isosbestic points maintained at 552 and 462 nm (X = Cl) and 548 and 468 nm (Br). The molar absorption coefficients at these isosbestic points were identical to those of authentic samples of *trans*-$[\mathrm{CoL^1(NCS)X}]^+$. At a later stage of the reactions the temperature was increased. The absorption spectra then began to deviate from the isosbestic points and a new set of isosbestic points was maintained until the end of the reactions [at 564 and 430 nm (X = Cl) and at 574 and 418 nm (Br)]. The final spectra were identical to that of an

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[3] K. M. Long and D. H. Busch, *Inorg. Chem.*, 1970, **9**, 505.

[4] R. Belcher and A. J. Nutten, 'Quantitative Inorganic Analysis,' Butterworths, London, 1970.

authentic sample of *trans*-$[CoL^1(NCS)_2]^+$ with $\lambda_{max.}$ at 507 nm. These reactions can be represented by equations (3) and (4) (X = Cl or Br). Since reaction (4) was some 10^4

$$trans\text{-}[CoL^1X_2]^+ + [NCS]^- \longrightarrow trans\text{-}[CoL^1(NCS)X]^+ + X^- \quad (3)$$

$$trans\text{-}[CoL^1(NCS)X]^+ + [NCS]^- \longrightarrow trans\text{-}[CoL^1(NCS)_2]^+ + X^- \quad (4)$$

times slower than (3), the kinetics of both reactions could be separately followed spectrophotometrically over two different temperature ranges at a fixed wavelength [at 500 and 507 nm for reactions (3) and (4) respectively]. The rate constants obtained [by the Guggenheim method [5] for reaction (3) and from standard semilogarithmic plots of $\ln(D_\infty - D_t)$ against time for reaction (4)] in both cases were found to be independent of the wavelength chosen for the kinetic runs, and of the complex (0.001—0.002 mol dm^{-3}), acid (0.01—0.1 mol dm^{-3}), and thiocyanate concentrations (0.1—1.0 mol dm^{-3}). Most of the kinetic runs were then carried out at 0.01 mol dm^{-3} nitric acid containing 0.1 mol dm^{-3} thiocyanate. The kinetic data are collected in Table 1.

The thiocyanate-substitution reactions of *trans*-$[CoL^2X_2]^+$ (X = Cl or Br) were very similar to those of the L^1 analogues for which two consecutive steps could be identified. The first step was relatively fast and had to be examined at low temperatures for the dichloro-complex, but for the dibromo-complex the reaction was just too fast to be followed accurately by conventional methods. The spectral change associated with the first step for *trans*-$[CoCl_2L^2]^+$ gradually increased in absorbance in the visible region without any isosbestic point. After some time the spectra began to intersect one another indicating the onset of the second step which was *ca.* 100 times slower than the first. An isosbestic point at 590 nm was maintained until the end of the reaction. The spectral change associated with the second step for *trans*-$[CoBr_2L^2]^+$ was very similar to that of the dichloro-analogue with an isosbestic point maintained at 585 nm. Again, reactions were followed at a single wavelength (510 nm for the first step and at 500 nm for the second step) in both cases. The rate constants, being independent of the same complex, acid, and thiocyanate concentration ranges as the L^1 analogues, are also collected in Table 1.

The acid hydrolysis of *trans*-$[CoCl(L^1)(NCS)]^+$ in dilute HNO_3 (0.01 mol dm^{-3}) was rather extraordinary. The spectral change in the visible region resembled that of the formation of the intensely coloured $[CoL^3(OH_2)]^+$,[2] but isosbestic points at 568 and 435 nm were maintained only for a relatively short time. Both ionic thiocyanate and chloride were detected in the course of the reaction. Although the entire quantity of co-ordinated chloride was released, only about slightly less than half the calculated amount of thiocyanate was released at the end of the reaction. In order to follow spectrophotometrically the release of chloride alone excess of thiocyanate was added to the reaction solution to suppress the release of co-ordinated thiocyanate. Here, the spectral change was identical to that of the second step of the thiocyanate-substitution reaction of *trans*-$[CoCl_2L^1]^+$ described above, with isosbestic points at 564 and 430 nm and the final spectrum identical to that of *trans*-$[CoL^1(NCS)_2]^+$. The rate constants (k_{Cl}) determined at two different temperatures were also identical to those determined above [8.2×10^{-5} (55.0) and 1.3×10^{-4} s^{-1} (59.2 °C)]. These observations strongly suggest that the isomeric structure of this authentic *trans*-$[CoCl(L^1)(NCS)]^+$ is the same as that of the intermediate *trans*-$[CoCl(L^1)(NCS)]^+$ produced under kinetic conditions in the thiocyanate-substitution reactions of *trans*-$[CoCl_2L^1]^+$ (see Discussion section). The same is true for the isomeric structure of authentic *trans*-$[CoBr(L^1)(NCS)]^+$. In order to follow the release of thiocyanate from *trans*-$[CoCl(L^1)(NCS)]^+$ excess of chloride was added to suppress the release of the co-ordinated chloride. The visible spectrum slowly changed with isosbestic points maintained at 584 and 432 nm (ε 415 and 1 150 dm^3 mol^{-1} cm^{-1} respectively) and an intense absorption peak developed at 515 nm. This is consistent with the formation of $[CoCl(L^3)]^+$,[2] the molar absorption coefficients of which at 584 and 432 nm are 430 and 1 175 dm^3 mol^{-1} cm^{-1} respectively. At a later stage of the reaction, as observed previously,[2] the intensity of the absorption peak began to decrease and the spectrum deviated from the isosbestic points. This reaction, which was retarded by acid in a rather complicated manner, had not been investigated further. The release of thiocyanate was only followed at 55.0 °C and the rate constant (k_{NCS}), obtained by the Guggenheim method using spectrophotometric data over 1.5 half-lives before the isosbestic points started deviating, was 6.3×10^{-5} s^{-1}. In the absence of added thiocyanate, however, the rate constant for the release of chloride, $k_{Cl'}$, followed by detecting the amount of chloride released as a function of time, was much larger than k_{Cl}. In fact $k_{Cl'}$

TABLE 1

First-order rate constants for the reaction *trans*-$[CoA(L)X]^+ + [NCS]^- \longrightarrow$ *trans*-$[CoA(L)(NCS)]^+ + X^-$

L	A	X	$\frac{\theta_c}{°C}$	$\frac{k_{obs.}}{s^{-1}}$
L^1	Cl	Cl	5.0	$7.1_0 \times 10^{-4}$
			7.9	$1.1_7 \times 10^{-3}$
			11.8	$1.8_7 \times 10^{-3}$
			14.1	$2.7_0 \times 10^{-3}$
			15.2	$3.0_5 \times 10^{-3}$
	Br	Br	5.0	$1.7_0 \times 10^{-3}$
			6.8	$2.4_0 \times 10^{-3}$
			7.9	$2.9_0 \times 10^{-3}$
			11.8	$4.6_3 \times 10^{-3}$
			14.1	$7.0_0 \times 10^{-3}$
	NCS	Cl	45.2	$3.1_0 \times 10^{-5}$
			49.5	$5.1_7 \times 10^{-5}$
			55.0	$8.4_0 \times 10^{-5}$
			59.2	$1.3_7 \times 10^{-4}$
			66.1	$2.7_4 \times 10^{-4}$
	NCS	Br	48.0	$5.8_0 \times 10^{-5}$
			51.8	$8.3_5 \times 10^{-5}$
			56.7	$1.3_2 \times 10^{-4}$
			63.4	$2.6_2 \times 10^{-4}$
			67.5	$3.7_1 \times 10^{-4}$
L^2	Cl	Cl	4.0	$1.1_0 \times 10^{-3}$
			7.3	$1.8_0 \times 10^{-3}$
			9.2	$2.6_0 \times 10^{-3}$
			11.0	$3.2_5 \times 10^{-3}$
			13.2	$5.0_0 \times 10^{-3}$
	NCS	Cl	21.4	$5.0_0 \times 10^{-4}$
			27.8	$1.0_6 \times 10^{-3}$
			34.6	$1.9_6 \times 10^{-3}$
			39.6	$3.3_8 \times 10^{-3}$
			43.5	$4.5_5 \times 10^{-3}$
	NCS	Br	18.6	$4.1_5 \times 10^{-4}$
			21.2	$5.6_3 \times 10^{-4}$
			26.5	$1.0_6 \times 10^{-3}$
			32.2	$2.1_2 \times 10^{-3}$
			37.7	$3.8_3 \times 10^{-3}$

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

(1.46×10^{-4} s^{-1} at 55.0 °C) was equal to the sum of k_{Cl} (8.2×10^{-5} s^{-1}) and k_{NCS} (6.3×10^{-5} s^{-1}) at the same temperature.

DISCUSSION

In the preparation of *trans*-[CoL^1(NCS)X]$^+$ it is important to first allow the starting *trans*-[CoL^{1}X$_2$]$^+$ (X = Cl or Br) to aquate almost completely to *trans*-[CoL^1(OH$_2$)X]$^{2+}$ before the addition of thiocyanate, otherwise *trans*-[CoL^{1}X$_2$][NCS] precipitates. Warming a suspension of *trans*-[CoL^{1}X$_2$][NCS] produces a mixture of products which are relatively difficult to separate. However, care should be taken not to allow the *trans*-[CoL^{1}X$_2$]$^+$ to stand in the warm solvent for too long, otherwise the solution becomes deep red due to the formation of the relatively stable [CoL^3(OH$_2$)]$^{2+}$.

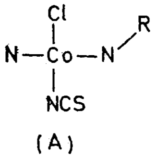
TABLE 2

Some first-order rate constants [a] at 25.0 °C for the acid hydrolysis or thiocyanate-substitution reactions of complexes *trans*-[CoA(L)X]$^+$

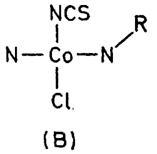
L	k_{Cl_2}/s^{-1}	k_{Br_2}/s^{-1}	$k_{(NCS)Cl}$/s^{-1}	$k_{(NCS)Br}$/s^{-1}	$k_{(NCS)Br}/k_{(NCS)Cl}$
L^1	1.1×10^{-2} [b,c]	3.1×10^{-2} [b,c]	2.8×10^{-6} [b,c]	4.5×10^{-6} [b,c]	1.6
L^2	2.9×10^{-2} [b,c]		7.6×10^{-4} [b,c]	9.1×10^{-4} [b,c]	1.2
L^4	2.1×10^{-2} [d]	1.2×10^{-1} [d]	1.8×10^{-6} [c,e]	2.2×10^{-6} [c,e]	1.2
L^5	2.3×10^{-4} [d]	7.8×10^{-2} [d]	4.4×10^{-7} [c,e]	5.7×10^{-7} [c,e]	1.3
L^6	3.6×10^{-2} [f]	5.1×10^{-2} [f]	1.4×10^{-6} [g]	3.0×10^{-6} [g]	2.1
L^7	9.3×10^{-4} [h]	3.8×10^{-2} [f]	7.0×10^{-7} [i]	6.1×10^{-6} [g]	8.7
L^8	1.1×10^{-6} [j]	2.2×10^{-5} [k]	1.1×10^{-9} [i]	1.3×10^{-8} [e]	11.8

[a] k_{AX} represents the rate constant of *trans*-[CoA(L)X]$^+$ for a given macrocyclic ligand L; data presented are for acid hydrolysis unless specified. [b] This work. [c] Thiocyanate-substitution reaction. [d] D. P. Rillema, J. F. Endicott, and J. R. Barber, *J. Amer. Chem. Soc.*, 1973, **95**, 6987. [e] Ref. 10. [f] J. A. Kernohan and J. F. Endicott, *Inorg. Chem.*, 1970, **9**, 1504. [g] Ref. 15. [h] W. K. Chau and C. K. Poon, *J. Chem. Soc. (A)*, 1971, 3087. [i] Ref. 12. [j] C. K. Poon and M. L. Tobe, *J. Chem. Soc. (A)*, 1967, 2069. [k] C. L. Wong, unpublished work.

The assignment of a *trans* configuration to the new complexes was made tentatively on the basis that these were all prepared from the corresponding *trans*-[CoL^{1}X$_2$]$^+$. It is well known that the hydrolysis of *trans*-[CoL^{1}X$_2$]$^+$ and, in general, of virtually all the *trans*-(macrocyclic amine)cobalt(III) complexes, are stereoretentive.[2,6] The ambidentate thiocyanate ligand in these *trans*-[CoL^1-(NCS)X]$^+$ complexes was clearly shown to be *N*-bonded by the presence of an i.r. band of medium intensity at 842, 844, and 843 cm^{-1} for X = NCS, Cl, and Br respectively, assignable to ν(C–S) of an *N*-bonded thiocyanate.[7] The assignment of a *trans* configuration to [CoL^1-(NCS)X]$^+$, however, does not fully characterize the complexes. As pointed out earlier,[2] these *trans* complexes can assume two different geometrical isomers (A) and (B). We have not been able to decide by conventional spectroscopic and n.m.r. techniques which isomer is involved. The complexes have been shown to be isomerically pure by both physical and kinetic methods. First, repeated recrystallization did not affect their absorption spectra. Secondly, chromatography also demonstrated that only one coloured band developed and was eluted using either Dowex 50W-X8 (20—50 mesh) and Sephadex C-25 cation exchangers or Sephadex G-10 resin. Thirdly, the kinetics of thiocyanate-substitution reactions of these two complexes gave linear semilogarithmic plots to three half-lives indicating that only one isomer was reacting. That the final absorption spectrum was identical to that of *trans*-[CoL^1(NCS)$_2$]$^+$ ruled out the possibility of the presence of a second 'inert' isomer in the reacting solution. Unfortunately, attempts to grow single crystals of these two halogeno-isothiocyanato-complexes suitable for *X*-ray analysis were unsuccessful. However, a decision on the isomeric structure of these two complexes still appears possible from the present kinetic observation.



(A)



(B)

The rate constants, extrapolated to 25.0 °C by the Eyring equation, for the thiocyanate-substitution reactions of *trans*-[CoLX$_2$]$^+$ (L = L^1 or L^2; X = Cl or Br) are collected in Table 2. It is obvious, at least for the dichloro-system, that the rate constants for the first steps are virtually independent of the nature of L whereas those of the second steps are greatly different with the L^2 complexes much more reactive by two orders of magnitude. It has been well established [6,8,9] that all ligand-substitution reactions of octahedral cobalt(III) amine complexes are dissociative and that substitution reactions by any nucleophile invariably go through the corresponding aqua-species. It seems, therefore, reasonable to assume that the isomeric structure of *trans*-[CoL(OH$_2$)X]$^{2+}$ formed from acid hydrolysis is the same as that of the corresponding *trans*-[CoL(NCS)X]$^+$ formed from thiocyanate substitution of *trans*-[CoLX$_2$]$^+$ and that the intermediates (or transition states) of these reactions assume a square-pyramidal form which may have either structure (C) or (D). If structure (D) is the actual reaction intermediate the solvation changes associated with the release of X to attain this intermediate and hence the reaction rates would be expected to be very similar for

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

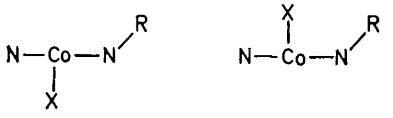
[7] K. Nakamoto, 'Infrared Spectra of Inorganic Compounds,' 2nd edn., Wiley, New York, 1970, p. 187.

[8] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1966.

[9] M. L. Tobe, 'Inorganic Reaction Mechanism,' Nelson, London, 1972.

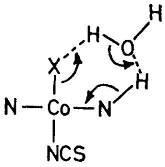
[10] C. K. Poon and C. L. Wong, *Inorg. Chem.*, 1976, **15**, 1573.

the corresponding pairs of L^1 and L^2 complexes. The above discussion assumes that these two macrocyclic ligands have similar electronic effects on the reactivities of the complexes. As for the release of the second halide, effectively from *trans*-$[CoL(NCS)X]^+$ of structure (A), the situation would be quite different. Simple molecular models suggest that there is no serious non-bonded steric repulsion between X and the N–R group of either L^1 or L^2. The much faster reaction of the L^2 complexes might be satisfactorily explained in terms of the momentary formation of a labilizing amido-group and also of a much more effective solvation of the leaving halide involving the acidic amine proton as follows:

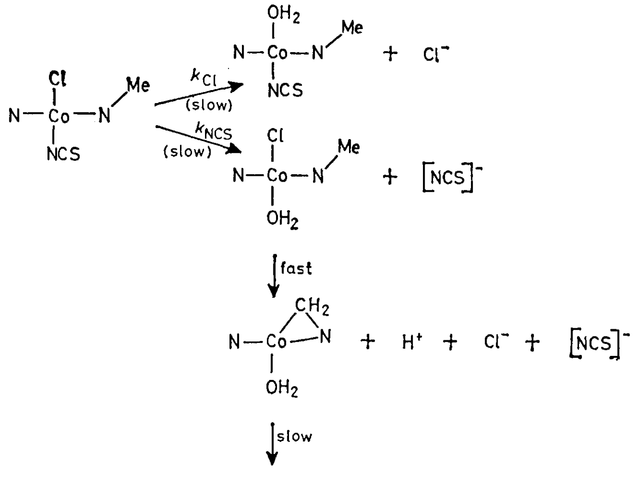


(C) (D)

L = L^1, R = Me; L^2, R = H

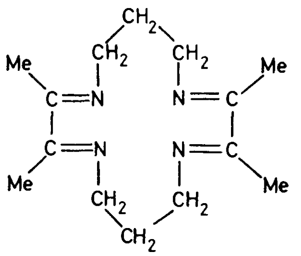


The above explanation seems reasonable in view of the ease of formation of the $[CoL^3(OH_2)]^{2+}$ complex from *trans*-$[CoCl(L^1)(OH_2)]^{2+}$ which suggests that even the proton in the N–Me group can be dissociated in acidic solution. The present kinetic results, therefore, strongly support the earlier conclusion [2] that the acid hydrolysis of *trans*-$[CoCl_2L^1]^+$ indeed follows Scheme 1.

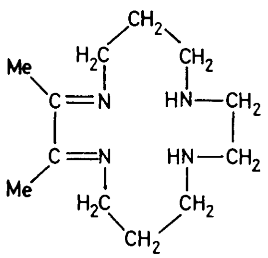


Scheme 2

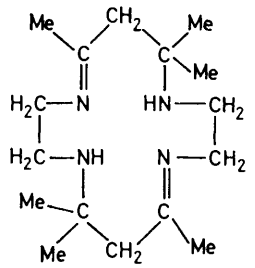
Accepting that *trans*-$[CoCl(L^1)(NCS)]^+$ has structure (A) and noting [2] that reaction (2) (6.8×10^{-3} s^{-1} at 55.0 °C) was some two orders of magnitude faster than k_{Cl} and k_{NCS} and that this reaction was not retarded by additional excess of chloride,[2] the behaviour of *trans*-$[CoCl(L^1)(NCS)]^+$ with $k_{Cl'} = k_{Cl} + k_{NCS}$ can now be explained by Scheme 2.



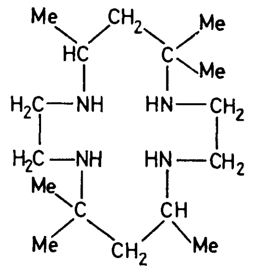
L^4



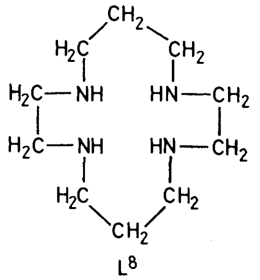
L^5



L^6



L^7



L^8

The observed concurrent release of isothiocyanate and chloride from *trans*-$[CoCl(L^1)(NCS)]^+$, together with low values of k_{Br}/k_{Cl} (Table 2) for the unsaturated macrocyclic amines L^1, L^2, L^4, L^5, and L^6 (L^4 = 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene, L^5 = 2,3-dimethyl-1,4,8,11-tetra-azacyclotetradeca-1,3-diene, and L^6 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene) systems relative to those of saturated amines L^7 and L^8 (L^7 = C-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane, L^8 = 1,4,8,11-tetra-azacyclotetradecane), support the conclusion [6] that the increasing extent of electronic delocalization between the metal ion and the encircling macrocycle increases the 'soft' character of the central metal ion. In complexes of the saturated macrocycles L^8 (ref. 11) and L^7,[12] as well as in other bis(ethylenediamine) [13,14] and tetra-ammine complexes,[11] preferential or concurrent release of the co-

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

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

[13] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1956, 1691.

[14] S. C. Chan, C. L. Chik, and B. Hui, *J. Chem. Soc. (A)*, 1967, 607.

ordinated isothiocyanate ligand with halide has never been observed. It seems reasonable to expect that the relative stability of the bonding of a ' hard ' *N*-bonded thiocyanate to the central cobalt(III) ion would decrease with increasing ' softness ' of the metal ion. Excluding L^6 and L^7 complexes the reactivity of which is seriously affected by steric effects, a comparison of the first-order rate constants (Table 2) of related series of complexes shows that the reactivities do increase with increasing ' softness ' of the central metal ion [6] in the order $L = L^8 < L^5 < L^4 \sim L^2 \sim L^1$. The exceptionally fast reactions of *trans*-$[CoL^2(NCS)X]^+$ have been explained previously in terms of the specific role played by the acidic amine proton in promoting the reactivities of these two complexes. It is not immediately clear why this ' internal conjugate-base mechanism ' is not found in the analogous reactions of complexes containing L^5, L^6, L^7, and L^8 which also possess suitably orientated amine protons. One possible explanation is that the cobalt(III) ion in these four macrocyclic systems is much less ' polarizable,' as reflected by the non-concurrent release of thiocyanate with halide in the hydrolysis of their *trans*-$[CoL(NCS)X]^+$ complex,[10,12,15] than that in the L^2 system, thus rendering the amine proton insufficiently acidic to take part in the proposed mechanism.

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[7/2059 *Received, 23rd November,* 1977]

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