Structural and Mechanistic Studies of Co-ordination Compounds. Part 17.[1] Preparation and Acid Hydrolysis of Some Cobalt(III) Complexes containing the Quadridentate Macrocycle 2,7,12-Trimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene: An Extraordinary Hydrolysis Reaction

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The preparation and characterization of *trans*-$[Co(HL^1)X_2]^+$ and $[Co(L^1)X]^+$ {HL^1 = 2,7,12-trimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene, L^1 = 2,12-dimethyl-3,7,11,17-tetra-azabicyclo-[11.3.1]heptadeca-1(17),2,11,13,15-pentaen-7-ylmethyl, X = Cl or Br} are described. The acid hydrolysis for the release of the first halide from *trans*-$[Co(HL^1)X_2]^+$ is too fast to be followed by conventional techniques. The rates of release of the second halide from the corresponding aquahalogeno-complexes have been studied over a range of temperature. The immediate reaction product, $[Co(L^1)(OH_2)]^{2+}$, for these two reactions has been shown by *X*-ray diffraction analysis on its chloro-analogue, $[Co(L^1)Cl][ClO_4]\cdot H_2O$, to be a distorted octahedral complex in which the *N*-methyl carbon, after losing one proton, is σ-bonded to the central cobalt(III) ion forming a localized three-membered ring. The mechanisms for these reactions are discussed. The observation that the kinetic ratio $k_{Cl}:k_{Br}$ is equal to 2.3 indicates that the softness of the central cobalt(III) ion is enhanced in this HL^1 system as compared to that in other complexes of saturated macrocyclic amines.

In the course of our study[1-5] of the systematic changes in the kinetics and mechanisms of ligand-substitution reactions of complexes of the type *trans*-$[CoLAX]^{n+}$ (A = unidentate orientating ligand, X = Cl^- or Br^-) with different degrees of unsaturation in the quadridentate amine macrocycle L, it was noticed[2] that as the extent of the unsaturation increased the soft character of the central cobalt(III)

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[1] Part 16, C. K. Poon and C. L. Wong, *J.C.S. Dalton*, 1977, 523.

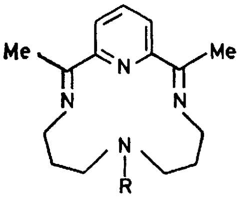
[2] C. K. Poon, *Co-ordination Chem. Rev.*, 1973, **10**, 1.

[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.

ion progressively increased. This enhanced softness of the central metal ion, brought about by the increasing extent of electronic delocalization between the metal ion and the encircling macrocycle of increasing degree of unsaturation, might help stabilize five-coordinate intermediates and increase the specific rates of ligand-substitution reactions of these complexes. These proposals,[2] however, require more experimental justification. This paper describes the preparation and acid hydrolysis of *trans*-$[Co(HL^1)X_2]^+$ {HL^1 = 2,7,12-trimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene, X = Cl or Br}.



HL^1 R = Me
L^1 R = CH_2^-
HL^2 R = H

A preliminary study [6] of the acid hydrolysis of *trans*-$[Co(HL^1)Cl_2]^+$ showed that the rate of release of the first chloride was too fast to be followed by any conventional technique. The release of the second chloride from the corresponding *trans*-$[Co(HL^1)(OH_2)Cl]^{2+}$ was first thought [6] to involve the formation of a stable five-coordinate complex $[Co(HL^1)(OH_2)]^{3+}$. In order to substantiate the argument, the crystal and molecular structure of the chloro-analogue of the so-called five-coordinate complex was analysed by *X*-ray diffraction studies.[7] To our surprise, the structure was rather extraordinary in that the *N*-methyl carbon, presumably on losing a proton, was directly bonded to the central cobalt(III) ion.[7] This paper also describes the preparation of $[Co(L^1)X]^+$ (X = Cl or Br). Possible mechanisms for the hydrolysis reactions are discussed.

EXPERIMENTAL

Preparation of Complexes.—{2,7,12-*Trimethyl*-3,7,11,17-*tetra-azabicyclo*[11.3.1]*heptadeca*-1(17),2,11,13,15-*pentaene*}-*cobalt*(II) *perchlorate monohydrate*. This complex was prepared in a similar manner to that for $[Co(HL^2)][ClO_4]_2{\cdot}H_2O$ [8] {HL^2 = 2,12-dimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]-heptadeca-1(17),2,11,13,15-pentaene}, by mixing an ethanolic solution of 2,6-diacetylpyridine (8.5 g, 0.05 mol, in 80 cm³) and an aqueous solution of $CoCl_2{\cdot}6H_2O$ (12 g, 0.05 mol, in 100 cm³) and the mixture was warmed to *ca.* 70 °C. Bis(3-aminopropyl)-*N*-methylamine (7.3 g, 0.05 mol) was added, followed immediately by glacial acetic acid (5 cm³) and the solution was maintained at *ca.* 70 °C for 5 h. The resulting reddish brown solution was concentrated in a rotary evaporator to remove as much ethanol as possible. Sodium perchlorate was then added and the reddish brown crystals were separated out, washed with 95% ethanol and then diethyl ether, and dried in air. The complex was recrystallized by dissolving it in the minimum amount of hot water. The solution was filtered and to the filtrate perchloric acid was added (70%, *ca.* 5 cm³ per 100 cm³ filtrate) followed by a saturated sodium perchlorate solution to induce crystallization (yield 14 g) (Found: C, 35.0; H, 4.6; Cl, 12.6; N, 9.9. Calc. for $C_{16}H_{26}Cl_2CoN_4O_9$: C, 35.0; H, 4.7; Cl, 13.0; N, 10.2%).

trans-*Dichloro*{2,7,12-*trimethyl*-3,7,11,17-*tetra-azabicyclo*-[11.3.1]*heptadeca*-1(17),2,11,13,15-*pentaene*}*cobalt*(III) *perchlorate*. This complex was prepared by bubbling chlorine gas (dried over calcium chloride) into a warm methanolic solution of $[Co(HL^1)][ClO_4]_2{\cdot}H_2O$ (5.5 g, 0.01 mol, in 50 cm³) for 20 min during which time the colour of the solution changed from reddish brown to dull green. The solution was then flushed with dry air for *ca.* 0.5 h to remove as much of the dissolved chlorine as possible. The dark green product which separated out was filtered off, washed with ice-cold methanol until the washings were neutral to litmus, and then dried in air. The crude product was recrystallized by dissolving it in the minimum amount of dimethyl sulphoxide and four times this quantity of ethanol was added followed by diethyl ether to induce crystallization (yield 1 g) (Found: C, 38.5; H, 4.9; Cl, 21.5; N, 11.2. Calc. for $C_{16}H_{24}Cl_3CoN_4O_4$: C, 38.3; H, 4.8; Cl, 21.3; N, 11.1%).

trans-*Dibromo*{2,7,12-*trimethyl*-3,7,11,17-*tetra-azabicyclo*-[11.3.1]*heptadeca*-1(17),2,11,13,15-*pentaene*}*cobalt*(III) *perchlorate* was similarly prepared and recrystallized except that here a dilute methanolic bromine solution (20%) was added dropwise to a hot saturated methanolic solution of $[Co(HL^1)][ClO_4]_2{\cdot}H_2O$ (5.5 g, 0.01 mol in 50 cm³) (yield 2.0 g) (Found: C, 32.6; H, 4.1; Br, 27.4; Cl, 6.0; N, 9.2. Calc. for $C_{16}H_{24}Br_2ClCoN_4O_4$: C, 32.5; H, 4.1; Br, 27.1; Cl, 6.0; N, 9.5%).

Chloro{2,12-*dimethyl*-3,7,11,17-*tetra-azabicyclo*[11.3.1]-*heptadeca*-1(17),2,11,13,15-*pentaen*-7-*ylmethyl*}*cobalt*(III) *perchlorate monohydrate*. This complex was prepared by suspending *trans*-$[Co(HL^1)Cl_2][ClO_4]$ in methanol (3 g in 100 cm³). On warming, the green dichloro-complex gradually dissolved to give a deep red solution. The volume of the solution was then reduced to about a quarter of its original volume and dark red needle-shaped crystals separated out on cooling. The crystals were collected, washed with a little cold methanol, and dried in air. The complex could be recrystallized from methanol (yield 1.6 g) (Found: C, 39.6; H, 5.2; Cl, 15.0; N, 11.6. Calc. for $C_{16}H_{25}Cl_2CoN_4O_5$: C, 39.8; H, 5.2; Cl, 14.7; N, 11.6%). A tabular-shaped crystal suitable for *X*-ray analysis was obtained by slow evaporation of an aqueous solution of the complex.

Bromo{2,12-*dimethyl*-3,7,11,17-*tetra-azabicyclo*[11.3.1]-*heptadeca*-1(17),2,11,13,15-*pentaen*-7-*ylmethyl*}*cobalt*(III) *perchlorate* was similarly prepared with similar yield starting with *trans*-$[Co(HL^1)Br_2][ClO_4]$. The complex was dried *in vacuo* at 80 °C for 24 h (Found: C, 37.7; H, 4.4; Br, 15.9; Cl, 7.0; N, 10.9. Calc. for $C_{16}H_{23}BrClCoN_4O_4$: C, 37.7; H, 4.5; Br, 15.7; Cl, 7.0; N, 11.1%).

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. The reaction temperature was maintained to ±0.1 °C with a Haake model E52 Unitherm immersion circulator.

Physical Measurements.—Visible and u.v. absorption

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[6] C. K. Poon and W. K. Wan, *Proc. 14th Internat. Conf. Coordination Chem.*, Toronto, 1972, p. 209.

[7] R. Bau, unpublished work.

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

spectra were recorded on a Unicam SP 8000 spectrophotometer. Infrared spectra of Nujol mulls were obtained with a Perkin–Elmer 337 spectrophotometer.

RESULTS

When *trans*-$[Co(HL^1)X_2][ClO_4]$ (X = Cl or Br) was dissolved in dilute nitric acid (0.01—0.10 mol dm^{-3}) the visible absorption spectrum slowly changed with isosbestic points maintained at 618 and 336 nm for the chloro- and at 614 and 343 nm for the bromo-complex. The absorption peaks developed at 575 and 385 nm were *ca*. 8 times as intense as those of the initial spectra. The final spectrum [$\lambda_{max.}$ 515 and 385 nm, log ε 3.37 and 3.39 respectively (ε in dm^3 cm^{-1} mol^{-1})] was very similar to that of $[CoL^1(OH_2)]^{2+}$ in the same acid medium * ($\lambda_{max.}$ 515 and 385 nm, log ε 3.40 and 3.42 respectively). A Volhard titration of ionic halide under kinetic conditions suggested that the release of the first co-ordinated halide was virtually complete as soon as the complexes were completely dissolved in the solvent and that the observed spectral change corresponded to the release of the second halide, as confirmed by titrating the amount of halide released in the course of the reaction. These observations suggest that the above spectrophotometric change corresponds to the release of halide from *trans*-$[Co(HL^1)(OH_2)X]^{2+}$ to give the species $[CoL^1(OH_2)]^{2+}$. This is reasonable because the initial spectrum has the general shape and intensity corresponding to those of normal six-co-ordinate tetra-aminecobalt(III) complexes. In view of the stereoretentive nature of all the substitution reactions of *trans*-quadridentate macrocyclic amine–cobalt(III) systems,[2] it seems reasonable to assume that *trans*-$[Co(HL^1)X_2]^+$ aquates with retention of configuration.

TABLE 1

First-order rate constants for the release of X^- from *trans*-$[Co(HL^1)(OH_2)X]^{2+}$ (X = Cl or Br) at $I = 0.1$ mol dm^{-3} maintained with $Na[NO_3]$

X	θ_c/°C	[H+]/mol dm^{-3}	10^4k [a]/s^{-1}
Cl	19.1	0.01	1.60
	19.1	0.05	1.55
	19.1	0.10	1.50
	23.8 [b]	0.10	2.60
	23.8 [b]	0.10	2.45
	23.8 [b]	0.10	2.60
	23.8 [b]	0.10	2.55
	24.9	0.01	2.90
	24.9	0.01	3.00
	24.9	0.01	2.95
	28.7	0.01	5.00
	28.7	0.01	4.90
	28.7	0.01	4.90
	34.5	0.01	8.60
	34.5	0.01	8.70
	34.5	0.01	8.70
	36.8	0.01	10.5
	36.8	0.05	11.0
	36.8	0.10	11.0
Br	28.4	0.01	10.0
	28.4	0.01	10.0
	29.2	0.01	11.0
	29.2	0.05	10.0
	29.2	0.10	12.0
	31.8	0.01	14.5
	31.8	0.01	15.0
	31.8	0.05	15.0
	31.8	0.10	14.0
	37.5	0.01	28.5
	37.5	0.10	28.0
	42.2	0.05	46.0
	42.2	0.10	46.0

[a] Activation parameters for these reactions were obtained from standard plots of log(k/T) against $1/T$: X = Cl, $\Delta H^‡ = 19.6 \pm 0.3$ kcal mol^{-1}, $\Delta S^‡ = -9 \pm 2$ cal K^{-1} mol^{-1}; X = Br, $\Delta H^‡ = 20.3 \pm 0.2$ kcal mol^{-1}, $\Delta S^‡ = -5 \pm 1$ cal K^{-1} mol^{-1}; 1 cal = 4.184 J. [b] The temperature appeared wrongly as 25.8 °C in ref. 6.

At a later stage of the reaction the intensity of the absorption peaks began to decrease very slowly and the rate was retarded by acid in a rather complicated manner. No effort, however, has yet been made to explore this reaction further.

The release of halide from *trans*-$[Co(HL^1)(OH_2)X]^{2+}$ was followed spectrophotometrically at 520 nm and the first-order rate constants were determined by Guggenheim's method. The data are collected in Table 1.

The formation of $[CoL^1(OH_2)]^{2+}$ was prevented when the hydrolysis of these dihalogeno-complexes was carried out in the presence of excess of thiocyanate ion. Here the changing spectra of *trans*-$[Co(HL^1)Cl_2]^+$ maintained an isosbestic point at 578 nm with the peak intensity increasing slowly with time. The initial spectrum was different from that of the starting dichloro-complex. A comparison of the absorption spectrum of the final stable reaction product ($\lambda_{max.}$ 525 nm, ε 830 dm^3 cm^{-1} mol^{-1}) with the known spectrum of *trans*-$[Co(HL^2)(NCS)_2]^+$ ($\lambda_{max.}$ 525 nm, ε 775 dm^3 cm^{-1} mol^{-1}) [9] suggested that the final reaction product was *trans*-$[Co(HL^1)(NCS)_2]^+$. Attempts to isolate this di-isothiocyanato-complex in a pure crystalline state were not successful. The relatively low intensity of these changing spectra suggested that the reaction did not involve formation of the distorted species $[CoL^1(OH_2)]^{2+}$, or of its chloro- and thiocyanato-analogues. The observed reaction, however, is consistent with the following scheme:

$$\textit{trans}\text{-}[Co(HL^1)Cl_2]^+ + [NCS]^- \xrightarrow{\text{fast}} \textit{trans}\text{-}[Co(HL^1)(NCS)Cl]^+ + Cl^- \quad (1)$$

$$\textit{trans}\text{-}[Co(HL^1)(NCS)Cl]^+ + [NCS]^- \xrightarrow{\text{slow}} \textit{trans}\text{-}[Co(HL^1)(NCS)_2]^+ + Cl^- \quad (2)$$

DISCUSSION

(1) *The Molecular Structure of* $[Co(L^1)Cl][ClO_4]\cdot H_2O$.[7, †] —The *X*-ray evidence shows that N(3), N(7), N(11), N(14), and C(19) (of CH_2) of the macrocyclic ligand L^1 are within bonding distances of the cobalt atom [Co–N(3) 1.921(8), Co–N(7) 1.942(8), Co–N(11) 1.924(8), Co–N(14) 1.824(7), Co–C(19) 1.950(10) Å (Figure)]. Geometrically speaking, the complex can be described as a distorted six-co-ordinated species in which σ bonds are formed between Co^{III} and a $N\text{–}CH_2^-$ group.

As for the structure of $[CoL^1(OH_2)]^{2+}$, it seems likely that the metal–macrocycle skeleton is the same as that of $[Co(L^1)Cl]^+$. These two complex cations have similarly intense visible absorption spectra indicating

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[*] The reversible acid hydrolysis of $[Co(L^1)X]^+$ (X = Cl and Br) is very fast giving $[Co(L^1)(OH_2)]^{2+}$ in aqueous acidic solution; S. S. T. Liao, unpublished work.

[†] Crystals are monoclinic (space group $P2_1/c$), with a = 7.157 (5), b = 20.341 (13), c = 14.199 (7) Å, β = 101.11(3)°; U = 2 028.4 $Å^3$, Z = 4; D_c = 1.581 g cm^{-3}. Data were collected with Mo-K_α radiation up to 2θ 48°, and the structure was solved by heavy-atom methods. At the present stage of analysis, the agreement factor R is 9.6% for 2 035 non-zero reflections. Further crystallographic work is continuing.

[9] K. M. Long, Ph.D. Thesis, The Ohio State University, 1967.

that they are both seriously distorted from an octahedral structure and, furthermore, they are easily interconvertible by chloride anation or aquation (see footnote * on p. 1249).

(2) *Mechanisms for the Conversion of trans-*[Co(HL^1)(OH$_2$)X]$^{2+}$ (X = Cl *or* Br) *into trans-*[CoL^1(OH$_2$)]$^{2+}$ *with the Release of* X$^-$.—The acid hydrolysis of *trans*-[Co(HL^1)X$_2$]$^+$ (X = Cl or Br) is divided into three distinct steps, (3)—(5). Since the third step shows a rather complicated acid-dependent path, the present discussion is confined to the first and second steps.

$$trans\text{-}[\mathrm{Co(HL^1)X_2}]^+ + \mathrm{H_2O} \xrightarrow{\text{fast}} trans\text{-}[\mathrm{Co(HL^1)(OH_2)X}]^{2+} + \mathrm{X} \quad (3)$$

$$trans\text{-}[\mathrm{Co(HL^1)(OH_2)X}]^{2+} \xrightarrow{\text{slow}} [\mathrm{CoL^1(OH_2)}]^{2+} + \mathrm{H^+} + \mathrm{X^-} \quad (4)$$

$$[\mathrm{CoL^1(OH_2)}]^{2+} + \mathrm{H^+} + \mathrm{H_2O} \longrightarrow \text{further reactions (very slow)} \quad (5)$$

The observation that reaction (3) is much faster than (4) is consistent with the general behaviour of most tetra-aminecobalt(III) systems in which the reactivity of dihalogeno-complexes is much greater than that of the aquahalogeno-analogues.[10] Since these complexes are unsymmetrical with respect to the macrocyclic plane, these hydrolysis reactions (3) and (4) must occur *via* one of the following two alternatives. Route 2 requires slow formation of [Co(L^1)X]$^+$ followed by a fast hydrolysis to [CoL^1(OH$_2$)]$^{2+}$ in order to be consistent with the concomitant release of the second halide and the observed spectral change as the reaction proceeds. On the other hand, rapid formation of [Co(L^1)X]$^+$ followed by slow hydrolysis to [CoL^1(OH$_2$)]$^{2+}$ would require a rapid initial increase in absorbance of the absorption spectrum to that of [Co(L^1)X]$^+$ followed by a slow spectral change, but without substantial absorbance change, to the product. Independent kinetic study of the hydrolysis of [Co(L^1)X]$^+$ (X = Cl or Br) (see footnote * on p. 1249) shows that these two complexes are indeed kinetically much more labile than *trans*-[Co(HL^1)(OH$_2$)X]$^{2+}$. Therefore, the present kinetic results cannot differentiate between these two alternative reaction routes.

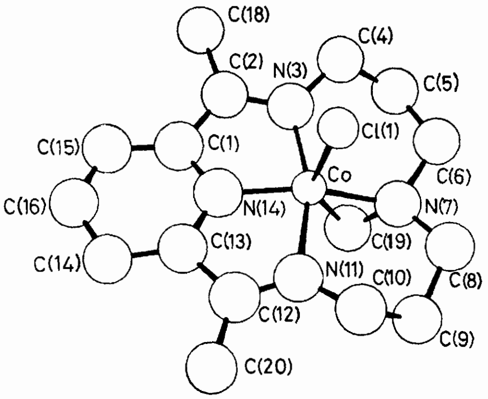
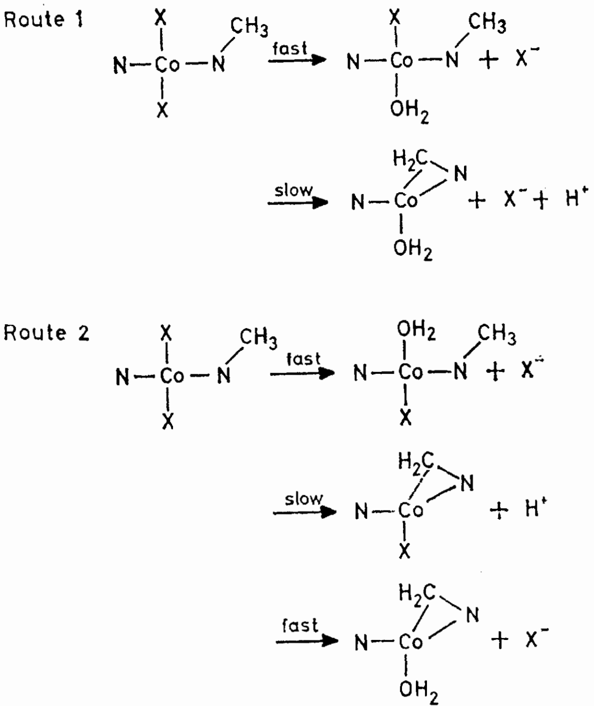
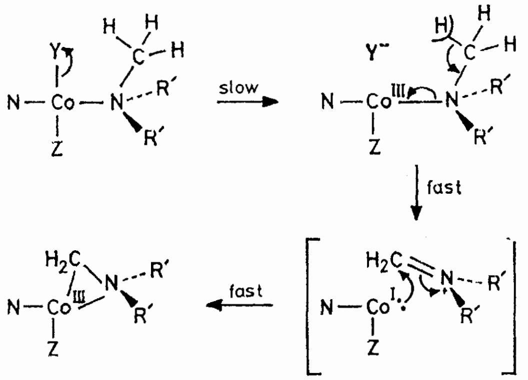


FIGURE The [Co(L^1)Cl]$^+$ cation,[7] showing that C(19) together with Co and N(7) form a localized three-membered ring



For simplicity, $\mathrm{N{-}Co{-}\overset{CH_3}{N}}$ represents a side view of the macrocycle-cobalt(III), Co(HL^1), unit

On the basis of either reaction route, it seems feasible that the formation of [CoL^1(OH$_2$)]$^{2+}$ from [Co(HL^1)(OH$_2$)X]$^{2+}$ {or, in general, the formation of [Co(L^1)Z]$^{n+}$ from *trans*-[Co(HL^1)(Y)Z]$^{2+}$} occurs *via* the following intimate mechanism. Since the *N*-methyl nitrogen is rigidly linked to other parts of the macrocycle, a molecular model shows that the formation of a H$_2$C=$\overset{+}{\mathrm{N}}$R$'_2$ double bond (*i.e.* sp^2 hybridization on N) forces the carbon to lie in the plane defined by the NR$'_2$ group hence bringing it within the bonding distance of the



R′ refers to the linkage of N to other parts of the macro-cycle. The complex *trans*-[Co(HL^1)(OH$_2$)X]$^{2+}$ is represented in the scheme as *trans*-[Co(HL^1)(Y)Z]$^{2+}$ to avoid giving preference to either isomer of the aquahalogeno-complex at this stage.

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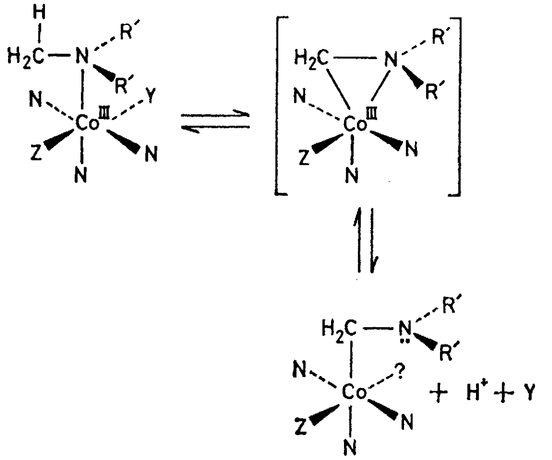
[10] F. Basolo and R. G. Pearson, ' Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967.

central cobalt atom. This mechanism for the formation of $[Co(L^1)Z]^{n+}$ is rather reminiscent of the type of mechanism suggested for many so-called 'isomerase' reactions brought about by coenzyme B_{12}.[11] The complex $[Co(L^1)Z]^{n+}$ could be looked on as the intermediate in the following 'isomerase' reaction:



At the right-hand side of the above scheme the nitrogen atom is still held within the bonding distance of the cobalt(III) by its linkages to other parts of the macrocycle, and can hence easily donate its lone-pair electrons back to cobalt and form the relatively stable $[Co(L^1)Z]^{n+}$. This must occur faster than the rate of its protonation by the acidic proton in solution in order to account for the observed relative stability of this intermediate.

On the basis of this mechanism, the key step is the deprotonation of the $N-CH_3$ group. It seems reasonable to assume that this deprotonation step would be most efficient for the isomer where $Z = OH_2$ (hence $Y = Cl^-$ or Br^-; *i.e.* route 1) than for the other isomer where $Z = Cl^-$ or Br^- (hence $Y = OH_2$; *i.e.* route 2) since the cobalt(III) centre in the former five-co-ordinate transition state $\{[Co(HL^1)(OH_2)]^{3+} \cdots X^-\}$ or intermediate $\{[Co(HL^1)(OH_2)]^{3+}\}$ would be more electron deficient. This idea, although speculative, is supported by the observation that the hydrolysis of *trans*-$[Co(HL^1)Cl_2]^+$ in the presence of excess of thiocyanate does not give the distorted $[CoL^1(NCS)]^+$ species. In this case, $Z = [NCS]^-$ and the cobalt(III) centre in the corresponding five-co-ordinate transition state (or intermediate) may not be sufficiently electron deficient to induce the deprotonation step. In other words, it seems likely that the hydrolysis of *trans*-$[Co(HL^1)X_2]^+$ (X = Cl or Br) involves the release of the halide which is relatively remote from the *N*-methyl group (*i.e.* route **1**). At this stage, the reason behind this preferential lability of this halide over the other is not obvious. A molecular model, however, suggests that there is not a great difference in steric effect between the two halide leaving groups. If there is, the one facing the *N*-methyl group is less sterically affected than the other one which faces the two propylene chains of the macrocycle. This may well be the reason for the difference in lability of the two leaving halide ligands, but this cannot be confirmed without suitable crystallographic data on *trans*-$[Co(HL^1)X_2]^+$.

Finally, as compiled in Table 2, the present kinetic results for *trans*-$[Co(HL^1)(OH_2)X]^{2+}$ fit the proposal[2] that as the degree of unsaturation of the following macrocyclic (or pseudo-macrocyclic) amine ligands in the immediate surroundings of the cobalt(III) centre is increased, $L^3 \sim L^4 < L^5 \sim HL^1 < 2Hdmg^- <$ corrin,* the softness of the central metal ion, as judged by the $k_{Br} : k_{Cl}$ (or $k_I : k_{Br}$) ratio, is gradually increased.

TABLE 2

First-order acid-hydrolysis rate constants of some complexes of the type *trans*-$[CoLAX]^{n+}$ at 25.0 °C[a]

L	A	$\frac{k_{Cl}}{s^{-1}}$	$\frac{k_{Br}}{s^{-1}}$	$\frac{k_I}{s^{-1}}$	$k_{Br} : k_{Cl}$	$k_I : k_{Br}$
L^3	$[NO_2]^-$	4.3×10^{-5} [b]	5.5×10^{-4} [c]		13	
	$[CN]^-$	4.8×10^{-7} [b]	2.8×10^{-6} [d]		5.8	
	$[N_3]^-$	3.6×10^{-6} [c]	3.8×10^{-5} [f]		11	
	$[NCS]^-$	1.1×10^{-9} [e]	1.3×10^{-8} [g]		12	
L^4	$[NCS]^-$	7.0×10^{-7} [c]	6.1×10^{-6} [h]		8.7	
	$[N_3]^-$	6.5×10^{-3} [c]	7.1×10^{-2} [h]		11	
L^5	$[NCS]^-$	1.4×10^{-6} [h]	3.0×10^{-6} [h]		2.1	
	$[N_3]^-$	2.1×10^{-2} [h]	5.5×10^{-2} [h]		2.6	
HL^1	OH_2	3.0×10^{-4} [i]	6.8×10^{-4} [i]		2.3	
2 $Hdmg^-$	$[NO_2]^-$	1.0×10^{-4} [j]	1.2×10^{-4} [j]		1.2	
	I^-	6.0×10^{-5} [k]	7.2×10^{-5} [k]		1.2	
$corrin^{2-}$	bzm [l]		5.9×10^2 [m,n]	3.5×10 [m,o]		0.059

[a] k_{Cl}, k_{Br}, and k_I represent the rate constant with Cl^-, Br^-, and I^- as leaving group respectively. [b] K. S. Mok and C. K. Poon, *Inorg. Chem.*, 1971, **10**, 225. [c] C. K. Lui and C. K. Poon, *J.C.S. Dalton*, 1972, 216. [d] C. K. Poon and H. W. Tong, *J.C.S. Dalton*, 1974, 1. [e] W. K. Chau, W. K. Lee, and C. K. Poon, *J.C.S. Dalton*, 1974, 2419. [f] Ref. 4. [g] Ref. 5. [h] Ref. 3. [i] This work, extrapolated from data at other temperatures. [j] A. V. Ablov and D. M. Palade, *Doklady Akad. Nauk S.S.S.R.*, 1962, **144**, 341. [k] D. N. Hague and J. Halpern, *Inorg. Chem.*, 1967, **6**, 2059. [l] bzm = Benzimidazole. [m] D. Thusius, *J. Amer. Chem. Soc.*, 1971, **93**, 2629. [n] At 26.0 °C. [o] At 25.5 °C.

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* L^3 = 1,4,8,11-Tetra-azacyclotetradecane, L^4 = *meso*-5,7,7,12-14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane, L^5 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-1,7-diene, and $Hdmg^-$ = dimethylglyoximate(1−).

[11] R. H. Prince and D. A. Stotter, *J. Inorg. Nuclear Chem.*, 1973, **35**, 321 and refs. therein.