Characterisation of *cis*-[$CoCl_2L$]$^+$ and Two Diastereoisomeric *trans*-[$CoCl_2L$]$^+$ Complexes and Studies of the Aquation Kinetics (L = C-*meso*-5,12-Dimethyl-1,4,8,11-tetra-azacyclotetradecane)

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The complex *cis*-[$CoCl_2L$]ClO_4 and two diastereoisomeric *trans*-[$CoCl_2L$]ClO_4 complexes have been isolated and characterised (α- and β-*trans* isomers; L = C-*meso*-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane). The two *trans* isomers differ in the configuration at the chiral secondary NH centres (in principle ten diastereoisomers are possible). The β-*trans* isomer is found in conjunction with the *cis* isomer and isomerisation of *cis*-[$CoCl_2L$]ClO_4 in hot dilute hydrochloric acid gives β-*trans*-[$CoCl_2L$]$^+$. The aquation kinetics of the three isomers have been studied over a temperature range and activation parameters determined. At 25 °C the values of $k_{aq.}$ are 2.4×10^{-5} s^{-1} (α-*trans*), 5.5×10^{-5} s^{-1} (β-*trans*), and 8.7×10^{-2} s^{-1} (*cis* isomer). Configurations for the complexes are considered in detail, and their reactivities in aquation discussed.

In a previous paper[1] we described the preparation of a variety of copper(II), nickel(II), and cobalt(III) complexes of the macrocyclic ligand C-*meso*-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane (1). The present paper describes the characterisation of *cis*-[$CoCl_2L$]ClO_4 and two diastereoisomeric *trans*-[$CoCl_2L$]ClO_4 complexes (designated α- and β-*trans*) and discusses the aquation kinetics. Owing to the presence of four chiral nitrogen centres in complexes of L, six racemic diastereoisomers and four *meso* diastereoisomers can in principle occur in *trans*-[$CoCl_2L$]$^+$ complexes.

Until recently little attention has been paid to the problem of chiral nitrogen centres in macrocyclic cobalt(III) complexes and their influence on aquation rates. Pioneering work in this area has been carried out by Cooksey and Tobe[2] who found that the *RRRR*(*SSSS*) diastereoisomer of *trans*-[$CoCl_2$(cyclam)]$^+$ is aquated 1.6×10^3 times faster than the *RSSR* diastereoisomer at 25 °C [cyclam = (2) = 1,4,8,11-tetra-azacyclotetradecane]. In addition, the *RSSR* diastereoisomer gives 100% *trans*-[CoCl(cyclam)(H_2O)]$^{2+}$ while the *RRRR*(*SSSS*) diastereoisomer gives initially a mixture of 75% *trans*- and 25% *cis*-[CoCl(cyclam)(H_2O)]$^{2+}$ which then isomerises to 100% *cis*-[CoCl(cyclam)(H_2O)]$^{2+}$. Aquation of *cis*-[$CoCl_2$(cyclam)]$^+$ takes place 1.45×10^4 times faster than that of the *RSSR* diastereoisomer of *trans*-[$CoCl_2$(cyclam)]$^+$ at 25 °C.[3]

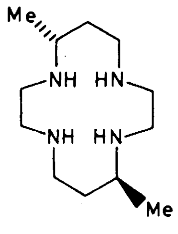
Less significant effects have been noted by Hung and Busch[4] in two diastereoisomeric complexes of *trans*-dichloro-(1,4,8,12-tetra-azacyclopentadecane)cobalt(III) ($k_{aq.} = 1.16 \times 10^{-3}$ and 9.92×10^{-3} s^{-1} at 25 °C).

Some of us[5] have shown that the two geometrical isomers of N-*rac*-*trans*-chloro(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)nitrocobalt(III) in which the chloride ligand lies *syn* or *anti* to the two chiral N–H groups differ by a factor of at least 10^3 in their aquation rates. The results can be rationalised in terms of the macrocycle folding towards or against the leaving group in the transition state of the reaction. It is therefore of considerable importance to extend these studies to other 14-membered macrocyclic ring systems.

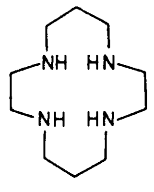
Experimental

The ligand C-*meso*-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane (L) was prepared as previously described.[1,6]

Preparation of Cobalt(III) *Complexes*.—Cobalt(II) chloride hexahydrate (0.92 g) and the ligand L (0.90 g) were dissolved in methanol (75 cm^3) to give a deep brown solution. This solution was aerated with a rapid stream of air for 2 h and then treated with concentrated HCl (3 cm^3). Aeration was continued until the solution volume was reduced to *ca.* 50 cm^3. Water (25 cm^3) was then added followed by $HClO_4$ (3 cm^3, 71%). A pale green complex was obtained immediately, and was filtered off, washed with ethanol then diethyl ether, and dried. This complex is the α isomer of *trans*-[$CoCl_2L$]ClO_4 (Found: C, 31.4; H, 6.1; N, 11.9. Calc. for $C_{12}H_{28}Cl_3CoN_4O_4$: C, 31.5; H, 6.2; N, 12.2%). The violet filtrate obtained from the above procedure was heated on a steam-bath for *ca.* 1 h, then cooled. The bright green complex obtained on cooling was filtered off, washed with ethanol then diethyl ether and dried. This complex is the β isomer of *trans*-[$CoCl_2L$]ClO_4 (Found: C, 31.8; H, 6.2; N, 12.1%).



(1) (=L)



(2)

The violet filtrate obtained was heated on a steam-bath to reduce its volume by half, then cooled to room temperature. A green complex with some associated violet material was filtered off and rejected. The clear violet filtrate was allowed to stand for *ca.* 4 h, when the violet-blue *cis*-[$CoCl_2L$]ClO_4 complex was deposited. This complex was filtered off, washed with ethanol then diethyl ether, and dried (Found: C, 31.7; H, 6.2; N, 12.2%).

Isomerisation of cis-[$CoCl_2L$]ClO_4 *to the* β-trans *Isomer*.—The complex *cis*-[$CoCl_2L$]ClO_4 (0.2 g) in dilute hydrochloric acid (30 cm^3) was heated on a steam-bath until a green suspension appeared. A few drops of $HClO_4$ (71%) were then added and heating was continued for a further 10 min. On cooling to room temperature, a green complex deposited, which was the β isomer of *trans*-[$CoCl_2L$]ClO_4. The complex was filtered off, washed with ethanol then diethyl ether, and dried (Found: C, 31.7; H, 6.2; N, 12.2%). The i.r. spectrum

Table 1. Visible spectra (sh = shoulder) of the dichloro-complexes in acetonitrile solvent

Complex	$\lambda_{max.}$/nm	ε/dm^3 mol^{-1} cm^{-1}
α-*trans*-$[CoCl_2L]ClO_4$	625	34
	455 (sh)	45
	390 (sh)	181
	318	1 795
β-*trans*-$[CoCl_2L]ClO_4$	625	28
	460 (sh)	29
	390	61
	317	1 100
cis-$[CoCl_2L]ClO_4$	576	97
	366 (sh)	437

of this complex (KBr disc) is identical in every respect with that of the previously prepared β-*trans* isomer. All the complexes are soluble in acetonitrile and dimethyl sulphoxide.

Kinetic Measurements.—The aquation kinetics were monitored spectrophotometrically with a Gilford 2400S spectrophotometer which was interfaced with an Apple II computing system. Aquation of the *cis* complex was monitored at 333 nm using 0.097 mol dm^{-3} HNO_3 as solvent. Aquation of the α-*trans* isomer was monitored at 260 nm (0.097 mol dm^{-3} $HClO_4$ as solvent) and that of the β-*trans* isomer at 325 nm with 0.097 mol dm^{-3} HNO_3 as solvent. Excellent first-order plots were obtained in all cases, consistent with a high degree of isomeric purity.

Routine and interval-scan electronic spectra were measured using a Perkin-Elmer 402 spectrophotometer. I.r. spectra were determined as discs in KBr using a Perkin-Elmer 457 instrument. ^1H N.m.r. spectra were obtained using $(CD_3)_2SO$ as solvent and tetramethylsilane as internal reference. Measurements were made with a Bruker WP80 instrument.

Results and Discussion

Aeration of methanolic solutions of cobalt(II) chloride and the ligand followed by addition of $HClO_4$ gives the α-*trans*-$[CoCl_2L]ClO_4$ isomer; later fractions give initially the β-*trans* isomer and finally the more soluble *cis* isomer.

The *cis*-$[CoCl_2L]ClO_4$ complex is violet-blue and has a *d–d* spectrum typical of a *cis*-$[CoCl_2(N_4)]^+$ chromophore (Table 1). Its i.r. spectrum has two ν(NH) bands at 3 220 and 3 140 cm^{-1} while only a single ν(NH) band occurs for the *trans* isomers near 3 200 cm^{-1}. Similar observations have been made with *cis* and *trans* isomers of $[CrCl_2L]^+$ (ref. 7) and $[RhCl_2(cyclam)]^+$ (ref. 8).

The α-*trans* and β-*trans* isomers are green with *d–d* spectra typical of *trans*-$[CoCl_2(N_4)]^+$ chromophores (Table 1). The α isomer has a strong sharp ν(NH) i.r. band at 3 195 cm^{-1}, while for the β isomer the ν(NH) band occurs at 3 190 cm^{-1} with indications of a shoulder on the high wavenumber side of the band. The two *trans* isomers can be distinguished by minor differences in their i.r. spectra in the fingerprint region of 1 400—800 cm^{-1} (Figure 1). Quite marked differences are seen in the 1 400—1 200 and the 950—800 cm^{-1} regions.

Isomerisation of *cis*-$[CoCl_2L]ClO_4$ in dilute hydrochloric acid gives the β-*trans* isomer as shown by complete coincidence of i.r. spectra and identical aquation rates for the β-*trans* isomer and the isomerised *cis* isomer.

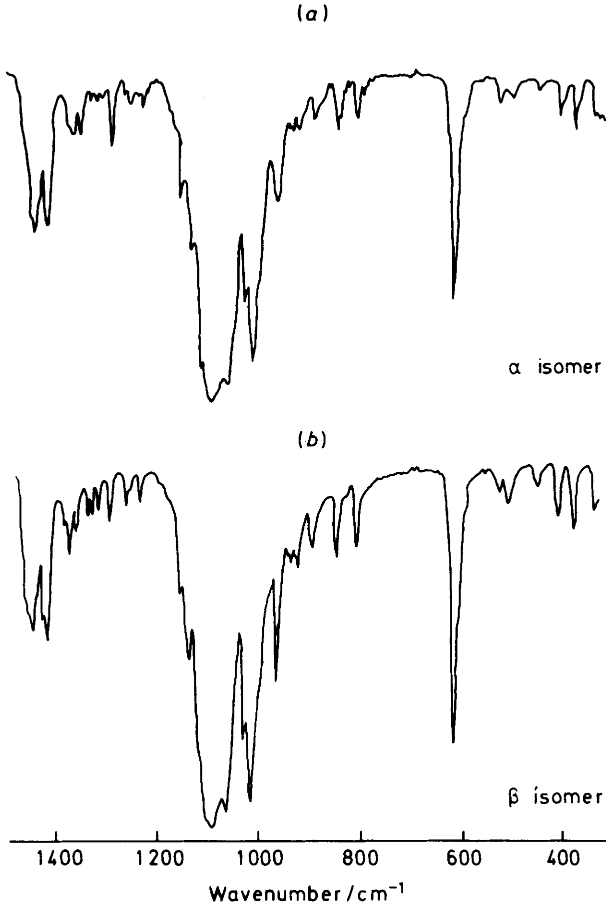
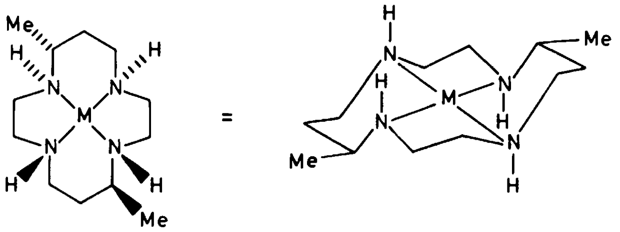


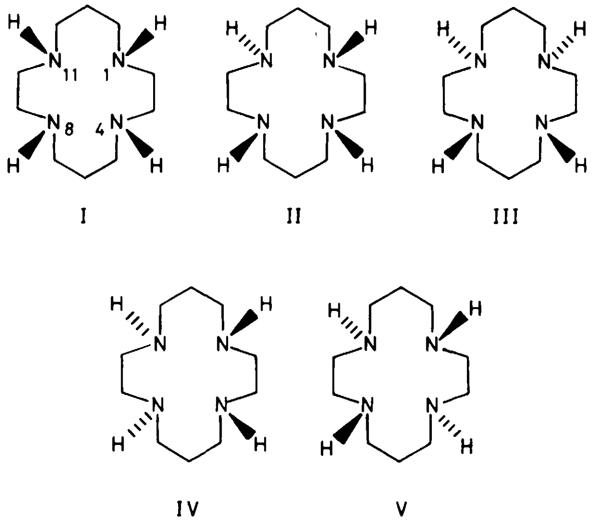
Figure. The i.r. spectra of the α-*trans* (*a*) and β-*trans* (*b*) diastereoisomers (KBr discs) of $[CoCl_2L]ClO_4$



(3)

^1H N.m.r. work using $(CD_3)_2SO$ as solvent establishes that both the α-*trans* and the β-*trans* diastereoisomers give single methyl doublets near δ 1.4 (Table 2); both complexes also show two distinct NH resonances near δ 6.6 and 5.5. The crystal structure of *trans*-$[CoL(N_3)_2]N_3$ has been determined [9] and the complex has been shown to have the configuration (3). This configuration, often referred to as the *trans* III form,[10] minimises hydrogen–hydrogen interactions in the chelate rings and is virtually free from torsional bond strain. In the *C-meso* ligand this configuration places the two methyl groups in equatorial positions. The ^1H n.m.r. spectrum of *trans*-$[CoL(N_3)_2]N_3$ in $(CD_3)_2SO$, with tetramethylsilane as internal standard, has a methyl doublet centred at δ 1.35 (J = 6.6 Hz) which can be assigned to the two equatorial groups.[1] Additional work with complexes of the *C-rac* ligand indicates that axial methyl groups in cobalt(III) complexes of this type give ^1H n.m.r. signals near δ 1.2.[11] As a result we can conclude that both the α-*trans* and the β-*trans* diastereoisomers have both methyl groups equatorial.

In 1,4,8,11-tetra-azacyclotetradecane (cyclam) complexes there are five possible configurations of the chiral nitrogen



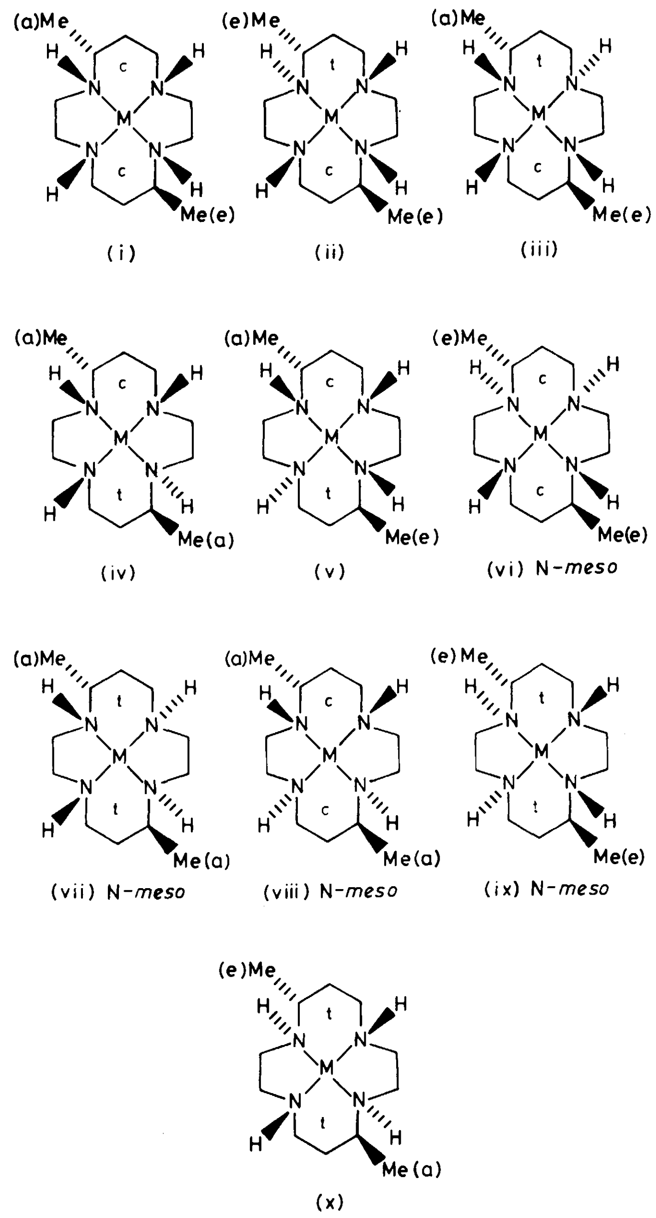
Scheme 1. Possible chiral nitrogen configurations in complexes of 1,4,8,11-tetra-azacyclotetradecane

Table 2. ^{1}H N.m.r. spectra of the α-*trans*- and β-*trans*-[$CoCl_2L$]ClO_4 complexes in $(CD_3)_2SO$ solvent

	δ/p.p.m.	
Complex	CH_3	NH
α-*trans*	1.41 (d, *J* = 7.3 Hz)	6.62 and 5.52
β-*trans*	1.40 (d, *J* = 7.3 Hz)	6.63 and 5.52

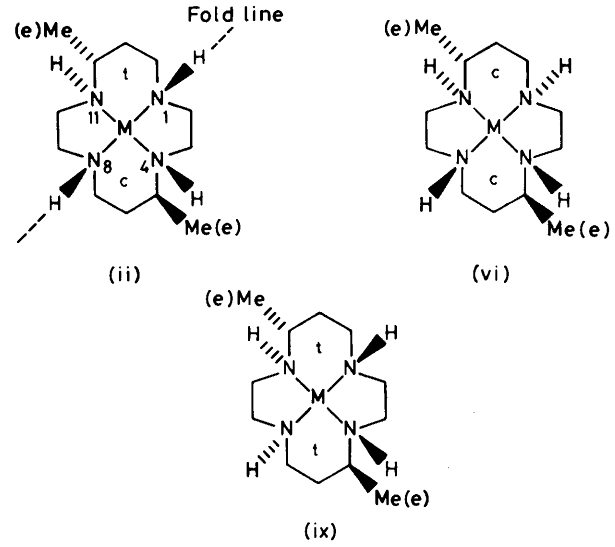
centres (Scheme 1). These are called the *trans* I, II, III, IV, and V configurations.[10] The additional two chiral carbon centres in the C-*meso* ligand gives the 10 possible diastereoisomers shown in Scheme 2. Four of these diastereoisomers are centrosymmetric [(vi)—(ix)] while the other six are racemates. An examination of molecular models establishes that in Scheme 2, diastereoisomers (ii), (vi), and (ix) have a diequatorial arrangement of the ring methyl groups, while diaxial arrangements occur with (iv), (vii), and (viii). The diastereoisomers (i), (iii), (v), and (x) have one axial and one equatorial methyl group. The α-*trans* and β-*trans* isomers must therefore belong to the set (ii), (vi), and (ix). The diastereoisomer (vi) has the *trans* III (*RSSR*) arrangement of the chiral nitrogen centres (Scheme 3). It is likely that (vi) is the structure of the α-*trans* isomer and (ii) represents the β-*trans* isomer. The β-*trans* isomer is found in conjunction with the *cis* isomer and isomerisation of the latter under acidic conditions (which should not allow inversion of the chiral nitrogen centres) gives the former. The *cis* isomer must be derived from (ii) as this configuration can fold across the N(1)–N(8) axis as indicated. Diastereoisomers (vi) and (ix) cannot fold to give *cis* complexes. Folding to give *cis* complexes cannot occur in 12-, 13-, and 14-membered tetra-aza ligands unless the secondary NH groups lying diagonally across the ring reside on the same side of the ring. It is noteworthy that a single nitrogen inversion in structure (ii) can give both (vi) and (ix).

In cobalt(III) complexes of cyclam, folding normally occurs *via* the *trans* V configuration (Scheme 1) which has two potential fold lines. This configuration is observed in the crystal structures of *cis*-[Co(cyclam)(en)]Cl_3·$3H_2O$ [12] (en = ethylenediamine) and *cis*-[$CoCl_2$(cyclam)]Cl.[13] Interestingly the *cis*-cobalt(III) complexes of cyclen (1,4,7,10-tetra-azacyclododecane), *cis*-[Co(cyclen)$(NO_2)_2$]Cl [14] and *cis*-[Co(cyclen)(CO_3)]ClO_4·H_2O,[15] have the nitrogen configuration II (Scheme 1) as shown in structure (4) with an N(1)–N(7) fold line similar to that observed with the present *cis*-[$CoCl_2L$]Cl complex.

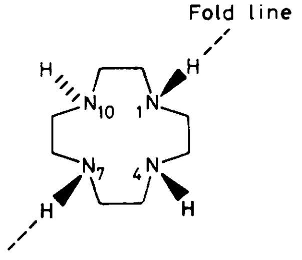


Scheme 2. Diastereoisomeric complexes of the C-*meso* ligand. a = Axial; e = equatorial; c = chair six-membered ring; t = twist-boat ring

Aquation Studies.—The kinetics of aquation of *cis*-[$CoCl_2L$]$^+$ and the α- and β-*trans*-[$CoCl_2L$]$^+$ complexes were studied over a temperature range (Tables 3 and 4). As has been previously observed in the *cis*- and *trans*-[$CoCl_2$(cyclam)]$^+$ complexes the *cis* isomer is aquated very rapidly.[3] The α-*trans*-[$CoCl_2L$]$^+$ is aquated some 4.4 times more rapidly than the β-*trans* isomer at 25 °C (Table 5), and the two *trans* isomers have substantial negative entropies of activation. In aquation reactions of cobalt(III) polyamine complexes proceeding *via* a dissociative mechanism it is generally observed [16–18] that stereochemical retention is associated with negative values of



Scheme 3. Structures of the diastereoisomers with two equatorial (e) methyl groups. Only diastereoisomer (ii) is capable of folding to give *cis* complexes



(4)

Table 3. Kinetics of aquation of the *trans*-dichloro-complexes *

Complex	θ_c/°C	$10^4k_{aq.}$/s^{-1}
α-*trans*	25.0	2.4
	31.0	4.0
	36.0	6.1
	41.5	10.95
$\Delta H^{\ddagger} = 68.5 \pm 3.7$ kJ mol^{-1}, $\Delta S^{\ddagger}_{298} = -84 \pm 12$ J K^{-1} mol^{-1}		
β-*trans*	25.0	0.55
	30.0	1.05
	35.5	1.7
	42.0	3.1
$\Delta H^{\ddagger} = 75.6 \pm 4.0$ kJ mol^{-1}, $\Delta S^{\ddagger}_{298} = -72 \pm 13$ J K^{-1} mol^{-1}		

* Values of the activation parameters were obtained by least-squares analysis of the Eyring plots. The solvent employed was 0.097 mol dm^{-3} $HClO_4$ (α isomer) and 0.097 mol dm^{-3} HNO_3 (β isomer). The quoted activation parameters give the following calculated values of $k_{aq.}$ at 25 °C: 2.3 × 10^{-4} (α-*trans* isomer) and 0.58 × 10^{-4} s^{-1} (β-*trans* isomer).

Table 4. Kinetics of aquation of *cis*-$[CoCl_2L]^+$ and $[CoCl(L)(H_2O)]^{2+}$ *

Complex	θ_c/°C	$10^3k_{aq.}$/s^{-1}
cis-$[CoCl_2L]^+$	6.5	5.3
	8.5	7.1
	11.5	11.8
	14.5	18.4
$\Delta H^{\ddagger} = 103 \pm 2$ kJ mol^{-1}, $\Delta S^{\ddagger}_{298} = 80 \pm 7$ J K^{-1} mol^{-1}		
$[CoCl(L)(H_2O)]^{2+}$	25.0	0.75
	28.5	1.2
	33.0	2.8
	35.5	4.0
$\Delta H^{\ddagger} = 123 \pm 6$ kJ mol^{-1}, $\Delta S^{\ddagger}_{298} = 106 \pm 20$ J K^{-1} mol^{-1}		

* For $[CoCl(L)(H_2O)]^{2+}$, the product of aquation of *cis*-$[CoCl_2L]^+$, the stereochemistry is not defined. The loss of the second halide ligand may lead to an equilibrium and values of $k_{aq.}$ may relate to the approach to equilibrium. The quoted activation parameters give the following calculated values of $k_{aq.}$ at 25 °C: 8.7 × 10^{-2} for *cis*-$[CoCl_2L]^+$ and 7.2 × 10^{-4} s^{-1} for $[CoCl(L)(H_2O)]^{2+}$.

Table 5. Relative rates at 25 °C and activation parameters for aquation of the dichloro-complexes

Isomer	$k_{aq.}{}^{25}$/s^{-1}	Relative rate	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}_{298}$/J K^{-1} mol^{-1}
α-*trans*	2.4 × 10^{-4}	4.4	69 ± 4	−84 ± 12
β-*trans*	0.55 × 10^{-4}	1.0	76 ± 4	−72 ± 13
cis	8.7 × 10^{-2}	1 613	103 ± 2	+80 ± 7

$\Delta S^{\ddagger}$ and stereochemical change with positive values. Substantial negative values of $\Delta S^{\ddagger}$ are observed for the α-*trans* and β-*trans* isomers indicating retention of configuration. In the case of the *cis* isomer the value of $\Delta S^{\ddagger}$ is +80 J K^{-1} mol^{-1}, consistent with stereochemical change. Stereochemical change in the aquation of *cis*-$[CoCl_2L]^+$ is observed experimentally as this isomer gives the β-*trans* isomer on heating in dilute hydrochloric acid where chiral nitrogen inversion will not occur. This isomerisation presumably involves the reaction (i) followed by the reverse anation reaction (ii). Tobe and co-

$$cis\text{-}[CoCl_2L]^+ \longrightarrow cis\text{-}[CoCl(L)(H_2O)]^{2+} + \beta\text{-}trans\text{-}[CoCl(L)(H_2O)]^{2+} + Cl^- \quad \text{(i)}$$

$$\beta\text{-}trans\text{-}[CoCl(L)(H_2O)]^{2+} + Cl^- \longrightarrow \beta\text{-}trans\text{-}[CoCl_2L]^+ \quad \text{(ii)}$$

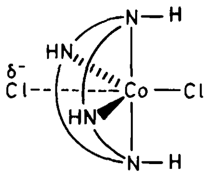
workers[2,3,19] have studied the aquation of *cis*-$[CoCl_2(cyclam)]^+$ and two diastereoisomers of *trans*-$[CoCl_2(cyclam)]^+$. One *trans* isomer, which is very labile in aquation, is obtained by isomerisation of *cis*-$[CoCl_2(cyclam)]Cl$ in ethanolic hydrochloric acid.[2] Crystallographic evidence [13] confirms that the *cis* complex has the nitrogen configuration V (Scheme 1) with two fold lines (*i.e.* *RRRR*), and this configuration is expected to be retained in the labile *trans* isomer. The unreactive *trans* isomer is believed to have the thermodynamically favourable nitrogen configuration III (Scheme 1) (*RSSR*) which does not allow ligand folding. The results suggest that the presence of fold lines in the macrocyclic ligand can lead, in some circumstances, to rapid aquation. Aquation is believed to be a dissociative process giving an intermediate of lower co-ordination number. This dissociative process in a macrocyclic complex is illustrated diagrammatically in structure (5). The shape of the intermediate is not a regular square pyramid, but a trigonal bipyramid or distorted square pyramid with the cobalt ion lying out of the macrocycle plane. The macrocycle folds towards the leaving group.

In the α-*trans*- and β-*trans*-$[CoCl_2L]^+$ complexes only the β-

Table 6. Aquation rates at 25 °C and activation parameters for *cis*- and *trans*-$[CoCl_2(cyclam)]^+$ complexes *

Isomer	Configuration	$k_{aq.}/s^{-1}$	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	% Steric change
cis	*RRRR*	1.6×10^{-2}	76.6	−25	0
trans	*RRRR*	1.75×10^{-3}	101.3	+42	25
trans	*RSSR*	1.10×10^{-6}	103	−12	0

* Data taken from ref. 2.



(5)

trans-isomer has a potential fold axis. Interestingly the β-*trans* isomer has $k_{aq.}^{25} = 5.5 \times 10^{-5}$ s^{-1} and is some four times *less* reactive than the α-*trans* isomer ($k_{aq.}^{25} = 2.4 \times 10^{-4}$ s^{-1}) which cannot fold. Both isomers are considerably less reactive than *trans*-$[CoCl_2(cyclam)]^+$ ($k_{aq.}^{25} = 1.75 \times 10^{-3}$ s^{-1})[2] (Table 6), which has two fold lines.

The apparently low reactivity of the β-*trans* isomer may be due to the fact that the macrocycle cannot fold towards the leaving Cl^- ligand. The theme of ligand folding is considered in more detail in the following paper which discusses the reactivity of dichlorocobalt(III) complexes of the *C*-*rac* ligand. In this case it was possible to characterise the *cis* isomer and three diastereoisomeric *trans* isomers thus providing considerably more experimental data.

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References

1 R. W. Hay and D. P. Piplani, *J. Chem. Soc., Dalton Trans.*, 1977, 1956.
2 C. J. Cooksey and M. L. Tobe, *Inorg. Chem.*, 1978, **17**, 1558.
3 C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 1968, 1549.
4 Y. Hung and D. H. Busch, *J. Am. Chem. Soc.*, 1977, **99**, 4977.
5 R. W. Hay, P. R. Norman, D. A. House, and C. K. Poon, *Inorg. Chim. Acta*, 1981, **48**, 81.
6 R. A. Kolinski and B. Korybut-Daszkiewicz, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1969, **17**, 13.
7 R. W. Hay, O. Bembi, and P. R. Norman, unpublished work.
8 E. J. Bounsall and S. R. Koprich, *Can. J. Chem.*, 1970, **48**, 1481.
9 R. J. Restivo, G. Ferguson, R. W. Hay, and D. P. Piplani, *J. Chem. Soc., Dalton Trans.*, 1978, 1131.
10 B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.
11 R. W. Hay, D. A. House, and R. Bembi, following paper.
12 T. F. Lai and C. K. Poon, *Inorg. Chem.*, 1976, **15**, 1562.
13 G. B. Robertson and P. O. Whimp, unpublished work, quoted by N. F. Curtis as ref. 24 in 'Coordination Chemistry of Macrocyclic Compounds,' ed. G. A. Melson, Plenum Press, New York, 1979.
14 Y. Iitaka, M. Shina, and E. Kimura, *Inorg. Chem.*, 1974, **13**, 2886.
15 J. H. Loehlin and E. B. Fleisher, *Acta Crystallogr., Sect. B*, 1976, **32**, 3036.
16 M. L. Tobe, *Inorg. Chem.*, 1968, **7**, 1260.
17 G. Jackson, *Inorg. Chim. Acta*, 1974, **10**, 51.
18 G. Jackson, *Inorg. Chem.*, 1978, **17**, 1348.
19 C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 1967, 2069.

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