Polyazamacrocycles. Part 7.† Kinetics of Aquation of *trans*-Dichloro and *trans*-Chloro (Nitro) Complexes of Cobalt(III) with Tetra-aza Macrocycles

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Kinetic studies on the aquation of *trans*-$[CoLCl_2]^+$ and *trans*-$[CoL(NO_2)Cl]^+$ (L = tetra-aza macrocycle) complexes show large variation in rates. The dependence of aquation rates on conformational strain energy is true only for a limited number of compounds. The rate enhancements can be rationalised in terms of the ability of the macrocycle to fold across a fold axis. The large-ringed macrocyclic complexes *trans*-$[CoL^6Cl_2]^+$ (L^6 = 1,4,8,11-tetra-azacyclohexadecane) and *trans*-$[CoL^7Cl_2]^+$ (L^7 = 1,4,8,11-tetra-azacycloheptadecane) aquate at much lower rates due to curtailed folding ability. The N ··· N bite distances also suggest a lower aquation rate for these complexes. The complexes of 2,5,5,7,9,12,12,14-octamethyl- and 5,7,12,14-tetraethyl-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane aquate with low rates lying in a narrow range. No specific trends can be identified in these complexes. These studies also show that very large aquation rate enhancements in cobalt(III) complexes of 14-membered macrocycles are possible only if *gem*-dialkyl groups are present.

The effect of an axially located orientating group Y on the rate of aquation of an outgoing group X in *trans*-$[CoL(X)Y]^+$ complexes is now well understood.[1–5] Studies with a given set of groups X and Y have shown that the rate of aquation is also influenced by the structure of the macrocycle.[6–9] In these studies the observed variation in aquation rates have been accounted for on the basis of (*i*) minimised conformational strain energy of the macrocycle,[6] (*ii*) ability of the macrocycle to fold,[7] and (*iii*) the presence of *gem*-dialkyl groups.[8] Each approach attempts to account for the wide variations in aquation rates of these complexes, but no comprehensive picture is available. In an effort to get more information on these reactions, we have studied the aquation of several *trans*-dichloro- and *trans*-chloronitro-cobalt(III) complexes of tetra-aza macrocycles. The results of these studies show that the accountability of variations in aquation rates on the basis of minimised conformational strain energy has very limited scope. In comparison, approaches (*ii*) and (*iii*) provide a better qualitative picture of why aquation rates vary with a change in the macrocyclic structure.

Table 1. Analytical data for the complexes with calculated values in parentheses

L (isomer)	Analysis (%) C	H	N
(*a*) $[CoLCl_2]ClO_4$ complexes			
$Me_8[14]aneN_4(A\alpha)$	40.00	7.45	10.25
	(39.90)	(7.45)	(10.25)
$(A\beta)$	39.80	7.50	10.25
$(B\alpha)$	40.00	7.35	10.45
$(B\beta)$	39.80	7.35	10.45
$(C\alpha)$	39.80	7.40	10.40
C-*meso-cis*-$Me_6[14]aneN_4$ (A)	37.45	7.10	11.00
	(37.40)	(7.05)	(10.90)
(B)	37.40	7.00	10.90
C-*rac-cis*-$Me_6[14]aneN_4$ (A)	37.35	7.10	10.90
C-*meso*-$Me_2Et_4[14]aneN_4$ (A)	42.20	7.75	9.85
	(42.15)	(7.80)	(9.85)
(B)	42.10	7.75	9.80
C-*rac*-$Me_2Et_4[14]aneN_4$ (A)	42.00	7.85	9.75
(B)	42.05	7.85	9.75
(*b*) $[CoL(NO_2)Cl]ClO_4$ complexes			
$Me_2[14]dieneN_4$ (*anti*)	31.10	5.25	15.00
(*syn*)	31.10	5.20	15.15
	(31.05)	(5.20)	(15.10)
$Me_2Ph_2[14]$-4,11-dieneN_4 (*anti*)	46.85	5.20	11.50
	(46.75)	(5.25)	(11.35)
(*syn*)	46.85	5.15	11.45

Experimental

The cobalt(III) complexes *trans*-$[CoLCl_2]ClO_4$ were prepared as described.[10–13] 7,14-Dimethyl-5,12-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene ($Me_2Ph_2$4,11-[14]diene) (L^1) was prepared by the method of Hideg and Lloyd.[14] The complex *trans*-$[Co(RS\text{-}L^1)Cl_2]ClO_4$ was prepared as follows. The ligand (0.1 mol) and cobalt(II) acetate tetrahydrate (0.1 mol) were dissolved in 50% methanol (200 cm^3) and aerated for 24 h. To the brown solution, concentrated HCl (15 cm^3) was added and the solution heated until it turned green. To this 70% $HClO_4$ (2 cm^3) was added and the solution concentrated on a steam-bath till crystallisation set in. After allowing the solution to stand for 2 h, the green complex was filtered off and washed with ethanol. This complex (5 g) was then suspended in water (20 cm^3) along with Na_2CO_3 (2 g) and heated until it completely dissolved and the solution turned deep red. The solution was quickly filtered and allowed to stand for a few hours after adding $NaClO_4$ (2 g). The red crystalline carbonato complex was filtered off, washed with Pr^iOH, and dissolved in 5 mol dm^{-3} HCl (10 cm^3). It was then heated until it turned green. After adding 70% $HClO_4$ (1 cm^3), the solution was concentrated to half its volume and cooled. The green complex was filtered off, washed with ethanol, then diethyl ether, and dried in vacuum. This complex was then used to prepare its *syn*- and *anti*-*trans*-$[Co(RS\text{-}L^1)(NO_2)Cl]ClO_4$ derivatives by following procedures similar to the ones described.[8] The same procedure was adopted for the preparation of the *syn*- and *anti*-*trans*-$[Co(Me_2[14]4,11\text{-diene-}RS)(NO_2)Cl]ClO_4$.

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† Part 6, R. Bembi, T. G. Roy, and A. K. Jhanji, *Transition Met. Chem. (Weinheim Ger.)*, 1989, **14**, 463.

The aquation kinetics of these complexes was followed spectrophotometrically on a Shimadzu UV2100 spectrophotometer at 25 °C. The kinetic runs were initiated by injecting a solution (0.1 cm^3) of the complex in acetonitrile into thermostatted 0.1 mol dm^{-3} HNO_3 (2.9 cm^3). The solution was rapidly stirred with a plumper before starting monitoring of the run. The aquation reactions were monitored by following the absorbance changes at suitable wavelengths in the range 290—330 nm. The values of $k_{obs.}$ were calculated from the spectrophotometric data on an IBM compatible PC/AT using a least-squares fitting program. All results reported herein are the mean of at least triplicate runs, each showing a correlation coefficient of at least 0.999, followed over a minimum of three half-lives.

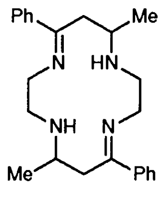
Results and Discussion

In order to facilitate comparison of aquation rates of cobalt(III) tetra-azamacrocyclic complexes of the type *trans*-$[CoLCl_2]^+$, the aquation rate of the complex of the *R,R,S,S* isomer* of cyclam (L^2) may be taken as the base value. This isomer is incapable of folding, exerts no steric effects, has the least-minimised conformational strain energy, and aquates[7] with $k_{aq}{}^{25} = 1.1 \times 10^{-6}$ s^{-1}.

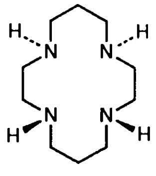
The minimised conformation strain energy has been shown to increase[6] in the order [14]aneN$_4$ < [15]aneN$_4$ < [16]aneN$_4$, and a plot of ln $k_{aq}{}^{25}$ against conformational strain energy of the macrocycles shown to be linear.[6] Some recent calculations on the minimised strain energies of conformational isomers of tetramethylcyclam[15] (L^3) show that for their six-co-ordinate complexes the strain energy increases from isomer A (149.5 kJ mol^{-1}) to isomer D (186.2 kJ mol^{-1}). It is also known that the conformational strain energy increases with the introduction of methyl substituents on the carbon chain.[6,16]

Taking these strain-energy enhancements as a rough guide, similar enhancements would be expected for the conformational isomers of six-co-ordinate complexes of *C*-*meso* and *C*-*rac*-Me_2[14]aneN$_4$ (L^4). The rates reported[17,18] for these complexes are much lower than might be expected on the basis of the reported linear plot.[6] The linear dependence of ln k_{aq} on strain energy would be justified only if a constant proportion of the strain energy is released in achieving the transition state. In arriving at this conclusion, a five-co-ordinate square-pyramidal intermediate has been assumed.[6] This would also result in retention of stereochemistry during aquation. We now know of several complexes[7,16,18] which aquate with a stereochemical change.

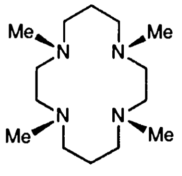
When viewed along the C_2 axis, the trigonal bipyramid(D_{3h}) and tetragonal(C_{4v}) geometries appear very similar. It has thus been suggested that distortion of the non-replaced ligands towards a trigonal-bipyramidal intermediate in a dissociative aquation pathway would account for both retention and inversion of configuration. The aquation rate would then be determined by the ease with which the distorted trigonal-bipyramidal intermediate is achieved and this is the main driving foce behind the reaction.[19] It has been further noted that those complexes which aquate with retention of configuration show a negative value of $\Delta S^‡$ while those showing a positive $\Delta S^‡$ aquate with inversion of configuration.[20] The greater flexibility of the macrocyclic structure would contribute towards the ease with which the distorted trigonal-bipyramidal structure is achieved. The folding of the macrocycle could exert steric compression on the leaving group. For folding, the 13- and 14-membered macrocycles need a fold axis in which the diagonally placed chiral NH groups lie on the same side of the N$_4$ plane. The 15-, 16-, and larger-membered macrocycles can fold[8] even against the NH groups due to their greater flexibility, unless restricted otherwise.



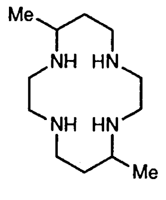
Me_2Ph_2[14]4,11-dieneN$_4$
(L^1)



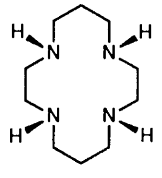
cyclam (*R, R, S, S*)
(L^2)



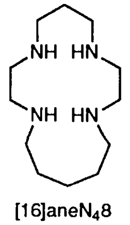
tetramethyl cyclam
(L^3)



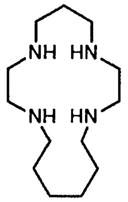
Me_2[14]aneN$_4$
(L^4)



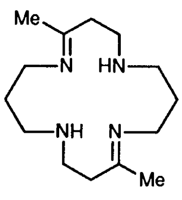
cyclam (*R, S, R, S*)
(L^5)



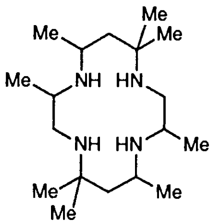
[16]aneN$_4$8
(L^6)



[17]aneN$_4$9
(L^7)



Me_2[16]1,9-dieneN$_4$
(L^8)



Me_8[14]aneN$_4$
(L^9)

The complex *trans*-$[CoL^2Cl_2]^+$ aquates with $k_{aq}{}^{25}$ = 1.1 × 10^{-6} s^{-1} ($\Delta H^‡$ = 103 kJ mol^{-1}, $\Delta S^‡$ = -12 J K^{-1} mol^{-1}) and *trans*-$[CoL^5Cl_2]^+$ aquates[7] with $k_{aq}{}^{25}$ = 1.75 × 10^{-3} s^{-1} ($\Delta H^‡$ = 101.3 kJ mol^{-1}, $\Delta S^‡$ = +42 J K^{-1} mol^{-1}). The *R,R,S,S* isomer (*trans*-III form) has no fold axis and cannot fold while the *R,S,R,S* isomer has a fold axis and hence can fold. This folding and consequent steric compression of the outgoing group can account for the *ca.* 10^3-fold rate enhancement. The larger ringed macrocycles have a better folding ability and hence show larger aquation rates, with some exceptions (Table 2). The complex *trans*-$[CoL^6Cl_2]^+$ aquates[11] with $k_{aq}{}^{25}$ = 3.9 × 10^{-3} s^{-1} ($\Delta H^‡$ = 47 kJ mol^{-1}; $\Delta S^‡$ = -133 J K^{-1} mol^{-1}) and *trans*-$[CoL^7Cl_2]^+$ aquates[11] with $k_{aq}{}^{25}$ = 1.5 × 10^{-3} s^{-1} ($\Delta H^‡$ = 19.6 kJ mol^{-1}, $\Delta S^‡$ = -233 J K^{-1} mol^{-1}). These rates are much lower than those exhibited by other large-ringed macrocyclic complexes. In the case of both these macrocycles, the folding ability is largely curtailed due to the bulky eight- and nine-membered chelate rings which lie on one side of the N$_4$ plane. *X*-Ray studies[21] on the nickel(II) complexes of analogous macrocycles carrying eight- and nine-membered chelate rings reveal them to be highly unsymmetrical. They have a highly distorted skeletal structure with the large chelate rings lying on one side of the N$_4$ plane. The skeletal structure is very difficult to twist and hence should be incapable of facile folding, even in solution. Both these complexes show very high negative entropy values, which means that they aquate with retention of

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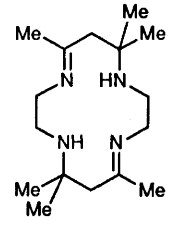
* This isomer, commonly referred to as the *trans*-III form, was called *R,S,S,R* by Tobe[7] and later on by many other workers. Hay has pointed out that this isomer is in *gauche*-chair–*gauche*-chair form and is actually *R,R,S,S*. Likewise the isomer having the hydrogens of all the four NH groups lying on one side of the N$_4$ plane is to be called *R,S,R,S*.

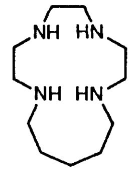
Table 2. Aquation data for *trans*-[CoLCl$_2$]$^+$ complexes at 25 °C

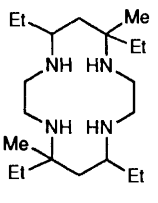
L (isomer)	10^3k_{aq}/s^{-1}	Ref.
cyclam (*R,R,S,S*)	0.0011	7
cyclam (*R,S,R,S*)	1.75	7
C-*meso*-Me$_2$[14]aneN$_4$ (α)	0.24	17
(β)	0.055	17
Me$_6$[14]4,11-dieneN$_4$	36	20
C-*rac*-Me$_2$[14]aneN$_4$ (B)	4.5	18
(C)	0.65	18
(D)	0.9	18
[13]aneN$_4$	0.676	6
[15]aneN$_4$ (isomer I)	1.16	6
(isomer II)	9.92	6
[16]aneN$_4$ (isomer I)	257	6
Me$_2$[16]1,9-dieneN$_4$	59.8	10
[16]aneN$_4$8	3.9	10
[17]aneN$_4$9	1.5	10
C-*meso*-Me$_2$[16]aneN$_4$	>100	10
C-*rac*-Me$_2$[16]aneN$_4$	>100	10
Me$_8$[14]aneN$_4$ (Aα)	0.47	This work
(Aβ)	0.62	This work
(Bα)	0.56	This work
(Bβ)	0.58	This work
(Cα)	0.87	This work
C-*meso-cis*-Me$_4$[14]aneN$_4$ (A)	0.20	This work
(B)	0.53	This work
C-*rac-cis*-Me$_6$[14]aneN$_4$ (A)	0.26	This work
C-*meso*-Me$_2$Et$_4$[14]aneN$_4$ (A)	0.10	This work
(B)	0.74	This work
C-*rac*-Me$_2$Et$_4$[14]aneN$_4$ (A)	0.30	This work
(B)	0.19	This work

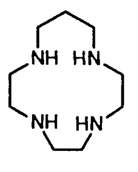
Table 3. Aquation data for *trans*-[CoL(NO$_2$)Cl]$^+$ complexes at 25 °C

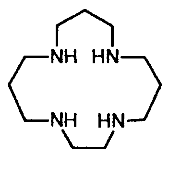
L (isomer)	10^3k_{aq}/s^{-1}	Ref.
Me$_6$[14]4,11-dieneN$_4$ (*anti*)	>100	8
(*syn*)	0.48	8
Me$_2$[14]4,11-dieneN$_4$ (*anti*)	0.43	This work
(*syn*)	0.44	This work
Me$_2$Ph$_2$[14]4,11-dieneN$_4$ (*anti*)	3.4	This work
(*syn*)	2.8	This work

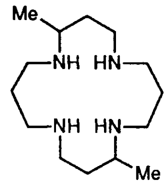

Me$_6$[14]4,11-dieneN$_4$
(L^{10})

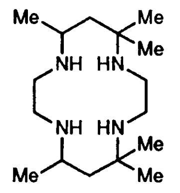

[15]aneN$_4$8
(L^{11})

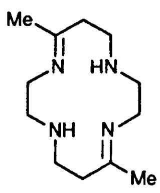

Me$_2$Et$_4$[14]aneN$_4$
(L^{12})


[13]aneN$_4$
(L^{13})


[15]aneN$_4$
(L^{14})


Me$_2$[16]aneN$_4$
(L^{15})


cis-Me$_6$[14]aneN$_4$
(L^{16})


Me$_2$[14]4,11-dieneN$_4$
(L^{17})

configuration. Those complexes which exhibit high reactivity coupled with a facile folding ability show positive entropy values[22] as in the case of the cyclam(*R,S,R,S*) isomer and Me$_2$[16]4,11-dieneN$_4$[11] (L^8) (k_{aq}^{25} = 59.8 × 10^{-3} s^{-1}, $\Delta H^‡$ = 84.5 kJ mol^{-1}, $\Delta S^‡$ = +14.8 J K^{-1} mol^{-1}).

The aquation rates of several alkyl-substituted 14-membered macrocycles have also been determined (Table 2). It may be noted that all these complexes aquate with rates lying within a narrow range. No specific trends can be identified. For example, in spite of the presence of a fold axis, Me$_8$[14]anes (L^9) are incapable of efficient folding due to the steric constraints imposed by the large number of methyl substituents. The *trans*-[CoL^{9}Cl$_2$]$^+$ complexes* aquate,[23] with rates lying in a very narrow range of (0.47—0.87) × 10^{-3} s^{-1}. Several other complexes of alkyl-substituted 14-membered macrocycles also aquate with similar rates (Table 2).

Hay and co-workers,[8,24] and Poon and Wong[25] studied the aquation of *syn*- and *anti*-[Co(*RS*-L^{10})(NO$_2$)Cl]ClO$_4$. They noticed that the *syn* isomer aquates with k_{aq}^{25} = 4.8 × 10^{-4} s^{-1} and the *anti* isomer has an aquation rate of >0.1 s^{-1}. The large acceleration in the latter case was thought to be due to the steric compression exerted by the *gem*-dimethyl groups in the folded form of the macrocycle. In the *anti* form the macrocycle folds towards the leaving chloride. In this form the chloride lies *anti* to the NH groups and the macrocycle folds in a direction away from the one in which the chiral NH groups are placed. In order to confirm that the *gem*-dimethyl groups exert steric compresson on the leaving groups in a macrocycle capable of folding, the aquation rates of two other *syn* and *anti* systems having a fold axis has been determined (Table 3). These macrocyclic systems do not carry any *gem*-dialkyl groups. These complexes aquate with rates similar to those shown by other cobalt(III) complexes. The steric effect of the *gem*-dialkyl groups is also evident in the higher aquation rate[26] of *trans*-[CoL^{10}Cl$_2$]$^+$ (k_{aq}^{25} = 36 × 10^{-3} s^{-1}).

House and co-workers[19] have suggested that the steric constraint to achieving the transition state in the aquation reactions could also be the N ··· N distance along the octahedral edge for the largest chelate ring in the complex. This distance corresponds to the so called 'bite distance'. According to them, the rate of aquation increases as the bite distance increases. On the basis of some published crystal structures of cobalt(III) complexes, they have shown that this distance for the chelate ring of ethylenediamine is 2.68 Å (five-membered ring), for propylenediamine is 2.83 Å (six-membered ring), and butylenediamine is 2.82 Å (seven-membered ring). It would thus be expected that the rate would increase as the chelate ring size increases. For larger rings the N ··· N distance would decrease due to considerable twisting in the chelate rings and the nitrogens are no longer forced to adopt a distance constrained by the ring size. The maximum bite distance is perhaps achieved with propylenediamine and butylenediamine. The crystal structure of [NiL^{11}]$^+$, which contains an eight-membered

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* The complete stereochemistry of the Me$_8$[14]anes and their cobalt(III) complexes has been worked out on the basis of their ^{1}H n.m.r. spectra.[12,23]

chelate ring, has been published.[21] On the basis of this the bite distance for the eight-membered chelate ring is 2.69 Å. This decreased bite distance would then predict a low aquation rate for *trans*-$[CoL^6Cl_2]^+$ in accord with our experimental results. However, even this concept of dependence of aquation rates on bite distances cannot be generalised. For example, the *X*-ray crystal structures[12,26] of $[Ni(C\alpha\text{-}L^9)][ClO_4]_2$ and *trans*-$[Co(A\alpha\text{-}L^9)Cl_2]ClO_4$ show bite distances for the six-membered chelate rings of 2.75 and 2.83 Å respectively. On this basis, *trans*-$[Co(A\alpha\text{-}L^9)Cl_2]ClO_4$ and other complexes of $Me_8[14]$anes would be predicted to show high aquation rates, which is in fact not the case.

Acknowledgements

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