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Aquation Rates of the Two *trans*-R,R(S,S)-chloro(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)nitrocobalt(III) Complexes and Comments of the Aquation Rates of Macrocyclic Complexes of Cobalt(III)

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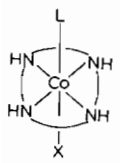
*The two geometrical isomers of N-*rac-trans-*[CoCl(Me$_6$[14]diene)NO$_2$]$^+$ (Me$_6$[14]diene = 5,7,7,12,13,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) have been isolated, in which the chloride ligand lies* syn *or* anti *to the two chiral N–H groups. The* syn*-isomer (isomer 1) aquates slowly in 0.1* M *HNO$_3$ with k_{aq} = 4.8 × 10^{-4} s^{-1} at 25 °C ($\Delta H^{\ddagger}$ = 75.3 kJ mol^{-1}, $\Delta S^{\ddagger}_{298}$ = −55 JK^{-1} mol^{-1}), while the* anti*-isomer (isomer 2) aquates very rapidly ($t_{1/2}$ < 10 s) at 25 °C. These results can be rationalised in terms of the macrocycle folding towards or against the leaving groups in the transition state of the reaction. Steric compression by the* gem*-dimethyl groups also facilitates rapid hydrolysis of the* anti*-isomer.*

Introduction

In macrocyclic cobalt(III) complexes of type (I), a number of different effects can be distinguished in acid aquation reactions. These effects may be summarised under the headings, (a) labilising effect of the ligand L and (b) labilising effect of the macrocycle. The labilising effect of the macrocycle is dependent upon (1) steric effects of alkyl substituents [1, 2], (2) the degree of unsaturation in the macrocycle ligand [1], (3) ring size and ring strain [3] and (4) the configuration of chiral nitrogen centres of the macrocycle. In addition specific leaving



(I)

group effects are observed, which are dependent upon the degree of unsaturation in the macrocycle. For 'hard' saturated macrocycles k_{Br}/k_{Cl} ratios are *ca.* 8, but approach unity as the unsaturation of the macrocycle increases [1].

Although considerable attention has been paid to many of the above points, less attention has been devoted to the problem of chiral nitrogen centres and this problem has been largely ignored in many kinetic studies. Cooksey and Tobe [4] have found that the R,R,R,R (S,S,S,S) isomer of [$CoCl_2$(cyclam)]$^+$ aquates 1.6 × 10^3 times faster than the R,S,S,R-complex at 25 °C. In addition the R,S,S,R-isomer gives 100% *trans*-[CoCl(cyclam)H_2O]$^{2+}$ while the R,R,R,R(S,S,S,S)-isomer 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]$^{2+}$. This case is the first example of stereochemical change in the aquation of a 14-membered macrocyclic complex, these reactions are normally fully stereoretentive. Less significant effects have been noted by Hung and Busch [3] for the two NH-isomers of *trans*-[$CoCl_2$([15]ane-N_4)]$^+$ (k_{aq} = 1.16 × 10^{-3} s^{-1} and k_{aq} = 9.92 × 10^{-3} s^{-1} at 25 °C). The present paper* discusses the aquation rates and stereochemistry of the two isomers of *trans*-R,R(S,S)-[CoCl(Me$_6$[14]diene)NO_2]$^+$.

Experimental

The ligand 5,7,7,12,14-,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene dihydrobromide

*Abbreviations used throughout this paper are Me$_6$[14]-diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene; Me$_2$[14]diene = 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene; [13]aneN$_4$ = 1,4,7,10-tetraazacyclotridecane; [14]aneN$_4$ = 1,4,8,11-tetra-azacyclotetradecane (cyclam); [15]ane N$_4$ = 1,4,8,12-tetra-azacyclopentadecane; [16]aneN$_4$ = 1,5,9,13-tetra-azacyclohexadecane.

dihydrate was synthesised as previously described [5]. The perchlorate salt was prepared by dissolving the dihydrobromide salt in water and adding a concentrated aqueous solution of sodium perchlorate. The perchlorate salt immediately crystallised.

N-*racemic*-$[CoCl_2(Me_6[14]diene)]ClO_4$ was prepared as described in the literature (isomer *a*) [6]. Isomer 1 of $[CoCl(Me_6[14]dieneNO_2]^+$ was prepared as described by Hay and Lawrance [7]. *Anal.* Calcd. for $[CoCl(Me_6[14]diene)NO_2]ClO_4$, $C_{16}H_{32}N_5Cl_2O_6Co$: C, 36.9; H, 6.2; N, 13.5. Found: C, 36.7; H, 6.3; N, 13.6%.

Isomer 2 of $[CoCl(Me_6[14]diene)NO_2]^+$ was prepared essentially as described by Poon and Wong [8]. *Anal.* Calcd. for $[CoCl(Me_6[14]diene)NO_2]ClO_4 \cdot HCl$, $C_{16}H_{33}N_5Cl_3O_6Co$: C, 34.5; H, 5.9; N, 12.9. Found: C, 33.5; H, 5.9; N, 12.6%.

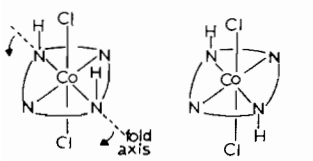
Kinetics

The kinetics of aquation if isomer 1 were studied using 0.1 *M* and 0.01 *M* nitric acid solutions as solvent. The kinetics were monitored using a Gilford 2400S spectrophotmeter by using the decrease in absorbance at 320 nm. Plots of log $(A_t - A_\infty)$ were linear for several half lives and values of k_{aq} were obtained from the slopes of these plots. Identical rate constants were obtained for both solvents, $k_{aq} = 4.83 \times 10^{-4}$ s^{-1} (0.1 *M* HNO_3) and $k_{aq} = 4.91 \times 10^{-4}$ s^{-1} (0.01 *M* HNO_3) at 25 °C.

^1H NMR spectra were determined using a Perkin-Elmer R32 instrument at 90 MHz using d_6-DMSO solvent and TMS as internal reference. Infrared spectra were obtained as KBr discs using a Perkin-Elmer 457 spectrometer. Routine UV-visible spectral measurements, including interval scan spectra, were made with a Perkin-Elmer 402 instrument.

Results and Discussion

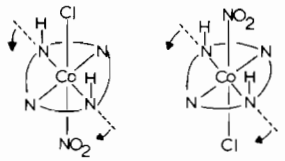
Sadasivan, Kernohan and Endicott [6] first isolated and characterised the two NH-isomers of *trans*-$[CoCl_2(Me_6[14]diene)]^+$. Their so called isomer *a* was prepared by treating *cis*-$[Co(Me_6[14]diene)CO_3]^+$ with concentrated hydrochloric acid. This isomer must have the N-racemic configuration (II), as it was prepared from the folded *cis*-carbonato complex in acidic solution. Only the N-*racemic* diastereoisomer can fold along the axis shown. The N-*meso* diastereoisomer(III) (isomer *b*) cannot fold to give *cis*-complexes and this diastereoisomer was prepared by aerial oxidation of a mixture of the ligand dihydroperchlorate and cobalt(II) acetate in methanol, followed by treatment with hydrochloric acid.



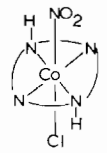
N-racemic R,R(S,S) (II)

N-meso R,S (III)

If one of the chloro-ligands is replaced by a nitro-group, three geometrical isomers of *trans*-$[CoCl(Me_6[14]diene)NO_2]^+$ are possible and these are shown in (IV–VI). Two isomers (IV) and (V) can arise from



(IV) (V)



(VI)

the N-*racemic* diastereoisomer, and a single isomer (VI) from the N-*meso* diastereoisomer. Hay and Lawrance [7] isolated one isomer of $[CoCl(Me_6[14]diene)NO_2]^+$ (isomer 1) by reacting the N-*racemic*-dichloro-complex with one equivalent of sodium nitrite in methanol solution. This isomer aquates slowly with $k_{aq} = 4.8 \times 10^{-4}$ s^{-1} at 25 °C in 0.1 *M* HNO_3. Subsequently, Poon and Wong [8] described the preparation of a second isomer (isomer 2) by the reaction of cold concentrated hydrochloric acid with *trans*-$[Co(Me_6[14]diene)(NO_2)_2]^+$ (prepared from the N-*racemic* dichloro-complex by treatment with sodium nitrite). This isomer was reported to undergo rapid aquation ($t_{1/2} < 10$ s) in 0.1 *M* HNO_3 at 25 °C. Treatment of these two isomers with 12 *M* HCl gives 100% N-*racemic* $[CoCl_2(Me_6[14]diene]^+$, as shown by ^1H NMR spectra and infrared spectroscopy, thus both isomers have the N-*racemic* chiral nitrogen configuration. The marked difference in the reactivities of the two complexes can be rationalised in terms of the position of the leaving group with respect to the chiral NH groups (Scheme 1). The complexes (IV) and (V) can readily fold in the direction shown by the arrows. *If folding occurs towards the leaving group (e.g.* Cl^-*) rapid aquation occurs* while slower aquation takes place if the chloride ligand lies on the same side of the macrocycle as the chiral N–H groups. Isomer 1 is (IV) and isomer 2 is (V)*.

*It seems appropriate to distinguish these two isomers as the *syn*-isomer in which Cl lies *cis* to the two chiral N–H groups and *anti*- in which the Cl lies *trans* to the two chiral N–H groups.

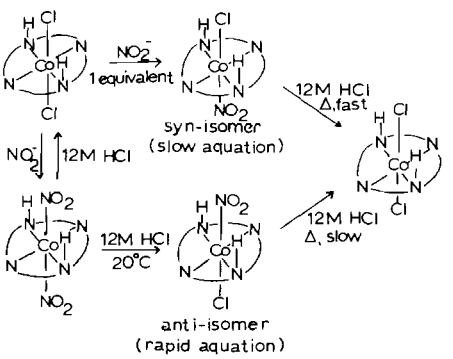
TABLE I. Temperature Dependence of k_{aq} for *trans*-R,R-(S,S)-*syn*-[CoCl(Me$_6$[14]diene)NO$_2$]$^+$ in 0.1 *M* HNO$_3$.[a,b]

Temp. (°C)	k_{aq} (s^{-1})
25	4.8×10^{-4}
35	15.4×10^{-4}
45	34.5×10^{-4}

[a] $\Delta H^{\ddagger} = 75.3$ kJ mol^{-1}; $\Delta S^{\ddagger}_{298} = -55$ JK^{-1} mol^{-1}. [b] For *trans*-[CoCl(cyclam)NO$_2$]$^+$, $k_{aq} = 4.3 \times 10^{-4}$ s^{-1} at 25 °C with $\Delta H^{\ddagger} = 86.2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -37$ JK^{-1} mol^{-1}. The complex presumably has the R,S,S,R chiral nitrogen configuration (ref. 18). For *trans*-[CoCl(en)$_2$NO$_2$]$^+$, $k_{aq} = 1 \times 10^{-3}$ s^{-1} at 25 °C with $\Delta H^{\ddagger} = 87.4$ kJ mol^{-1} and $\Delta S^{\ddagger} = 8.4$ JK^{-1} mol^{-1} (refs. 18, 19).

Steric considerations (see later) are also consistent with this assignment. These same effects are also seen in the relative reactivities of the nitro-groups in the complexes. Isomer 2 reacts *slowly* with 12 *M* HCl, while isomer 1 reacts *rapidly* to give the N-*racemic* dichloro-complex. The reasons for the different preparative routes giving different isomers can also be immediately rationalised on this basis (Scheme 1).

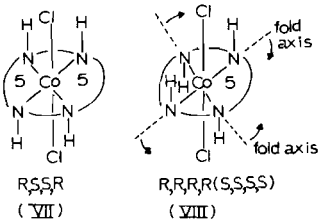
The temperature dependence of the aquation of the *syn*-isomer was studied over the temperature range 24–45 °C, and the rate constants obtained are summarised in Table I. The activation parameters are $\Delta H^{\ddagger} = 75.3$ kJ mol^{-1} and $\Delta S^{\ddagger}_{298} = -55$ JK^{-1} mol^{-1}. It is known that the steric environments on the two sides of the macrocyclic plane of the N-*rac* diastereoisomer are quite different with the two axial methyls of the *gem*-dimethyl groups pointing towards the axial site opposite the chiral N–H groups [9]. Steric compression in a dissociative type process arising from the *gem*-dimethyl groups would only facilitate the removal of the chloride ligand from the *anti* isomer (V), but not from the *syn*-isomer (IV). In a previous paper [7], one of us has discussed the aquation of the complex *cis*-[CoCl(Me$_2$[14]diene)NO$_2$]$^+$. The chloro-nitro complex was prepared by reacting



Scheme 1. Interconversion of isomers.

the dichloro-complex with one equivalent of sodium nitrite in methanol solution. The initial dichloro-complex was prepared via a folded carbonato intermediate and must thus have the N-*racemic* chiral nitrogen stereochemistry [10]. The resulting chloro-nitro complex is therefore expected to have the *syn* configuration shown in (IV). As the ligand lacks *gem*-dimethyl groups, neither the *syn*- nor the *anti*-isomers will be subject to steric effects. At 25 °C, $k_{aq} = 4.36 \times 10^{-4}$ s^{-1} with $\Delta H^{\ddagger} = 77.4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -50$ JK^{-1} mol^{-1}. These parameters are very comparable with those of the *syn* isomer of *trans*-[CoCl(Me$_6$[14]diene)NO$_2$]$^+$ where $k_{aq} = 4.8 \times 10^{-4}$ s^{-1} at 25 °C, $\Delta H^{\ddagger} = 75.3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -55$ JK^{-1} mol^{-1}. The similarity of the kinetic parameters confirms that steric considerations for the *syn* isomers are indeed of little importance. For the *anti* isomer of [CoCl(Me$_6$[14]diene)NO$_2$]$^+$ both ground state steric compression, and the ability to fold in the transition state may be responsible for the enhanced reactivity in aquation.

The ability of the macrocycle to fold appears to have important consequences regarding the rates of aquation of acidocomplexes and the stereochemistry of the final product obtained. Thus the R,S,S,R- and the R,R,R,R(S,S,S,S)-diastereoisomers of *trans*-[CoCl$_2$(cyclam)]$^+$ are shown in (VII) and (VIII) respectively. Neither of these complexes are subject to steric compression by ring substituents.



Both diastereoisomers have *equivalent* axial sites however, the R,S,S,R diastereoisomer cannot fold ($k_{aq} = 1.1 \times 10^{-6}$ s^{-1} at 25 °C) while the R,R,R,R(S,S,S,S) diastereoisomer has two possible fold axes and thus undergoes rapid aquation ($k_{aq} = 1.75 \times 10^{-3}$ s^{-1} at 25 °C). Significantly, the R,S,S,R diastereoisomer gives 100% *trans*-[CoCl(cyclam)OH$_2$]$^+$ while the R,R,R,R(S,S,S,S) diastereoisomer gives initially a mixture of 75% *trans*- and 25% *cis*-[CoCl(cyclam)-OH$_2$] which subsequently isomerises to 100% *cis*-isomer. Fortunately the R,S,S,R-configuration is the most thermodynamically stable arrangement for saturated 14-membered ring macrocycles leading to gauche five membered rings and chair six membered rings. The configuration has equivalent axial sites and no fold axes and as a result many potential complexities have been inadvertently avoided in many previous kinetic investigations.

TABLE II. Aquation Rates at 25 °C and Activation Parameters for *cis*- and *trans*-dichloro-amine Complexes of Cobalt(III), $[CoCl_2(N_4)]^+$.

N_4	Isomeric form	k_{aq} (s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})	% steric change	Ref.
trien	*cis*-α	1.5×10^{-4}	90.0	−25	0	15
$(en)_2$	*cis*	2.4×10^{-4}	90.0	−17 to +70	25	16
cyclen	*cis*	4.5×10^{-3}	78.2	−21	0	17
cyclam	*cis* R,R,R,R	1.6×10^{-2}	76.6	−25	0	4
cyclam	*trans* R,R,R,R	1.75×10^{-3}	101.3	+42	25	4
cyclam	*trans* R,S,S,R	1.10×10^{-6}	103	−12	0	4
[13]aneN$_4$	*trans*	6.76×10^{-4}	81.6[a]	−29[a]	0	4
[15]aneN$_4$	*trans* I	1.16×10^{-3}	72.4[a]	−59[a]	0	4
[15]aneN$_4$	*trans* II	9.92×10^{-3}	61.5[a]	−75[a]	0	4
[16]aneN$_4$	*trans* I	2.5	–	–	0	4
[16]aneN$_4$	*trans* II	3.0	–	–	0	4

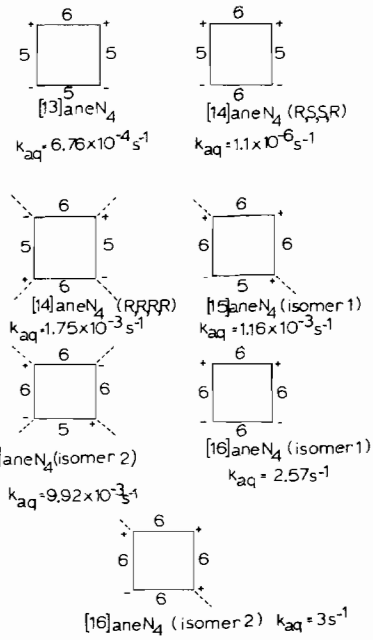
[a]These activation parameters have been recalculated (ref. 4) from ref. 3.

For aquation reactions of cobalt(III) polyamine complexes proceeding via a dissociative mechanism, it is generally observed [11–13] that stereochemical retention is associated with negative values of $\Delta S^{\ddagger}$ and stereochemical change with positive$\Delta S^{\ddagger}$ values. While it is generally accepted that stereochemical change is associated with a trigonal bipyramidal intermediate we do not believe that the absence of stereochemical change is necessarily associated with a square pyramidal intermediate. Distortion by the non-replaced ligands towards a trigonal bypyramidal intermediate can satisfactorily account for the variation in aquation rates for a series of closely related complexes which react with stereochemical retention of configuration [14].

It is noteworthy that for the series of complexes *cis*-$[CoCl_2L]^+$ where L = α-trien, $(en)_2$, cyclen and cyclam, the aquation rates at 25 °C vary by a factor of 10^2. Of these, only *cis*-$[CoCl_2(en)_2]^+$ shows some 25% stereochemical change (with a possibly positive $\Delta S^{\ddagger}$ value) and hence a trigonal bipyramidal transition state is most probable, Table II.

For the other complexes, the nature of the ligands makes stereochemical change less likely (and negative $\Delta S^{\ddagger}$ values are observed). Nevertheless, the flexibility of the polyamine in allowing distortion towards a trigonal bipyramidal intermediate can account for the observed reactivity order of α-trien < cyclen < cyclam. We hesitate to suggest a trigonal bipyramidal intermediate for the *cis*-ethylenediamine complex and a square pyramidal intermediate for the *cis*-α-trien, *cis*-cyclen and *cis*-cyclam complexes on the basis of this evidence.

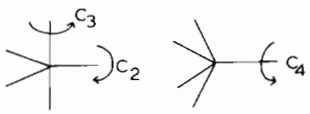
The *cis*-$[CoCl_2(cyclam)]^+$ complex is some 15,000 times more labile in aquation than the *trans*-R,S,S,R-$[CoCl_2(cyclam)]^+$, but only some 10 times more labile than the *trans*-R,R,R,R(S,S,S,S) isomer. It appears that the flexible *trans*-complexes and *cis*-complexes proceed via a similar intermediate which requires a certain degree of folding to achieve the transition state. Thirteen and fourteen membered rings *cannot* fold against the chiral nitrogens (*i.e.* the N–H bonds must lie on the same side of the macrocycle plane for folding to occur). Fifteen- and sixteen-membered rings *can* fold against the



Scheme 2. Configurations of the macrocyclic ligands in the *trans*-complexes. For the 15- and 16-membered rings, folding can also occur against the nitrogens, (+ represents a hydrogen above the ligand plane and − one below it).

nitrogens. As a result a very rapid aquation occurs with $[CoCl_2([16]aneN_4]^+$ as the ring is very flexible and can readily distort, Scheme 2. Hung and Busch [3] have recently shown that there is a good linear correlation between ln k_{aq} at 25 °C and H, the calculated minimised conformational strain energy. Ground state strain energies can only be related to reactivity if a constant proportion (or all) of the strain energy is released in the transition state of the reaction. The calculated strain energies increase in the order $[14]aneN_4 < [15]aneN_4 < [16]aneN_4$. We believe that the greater flexibility of the larger macrocycles and their ability to fold is the prime cause of their higher reactivity.

The idealised geometries for five coordinate systems are the trigonal bipyramid (D_{3h}) (IX) and the tetragonal pyramid (C_{4v}) (X). If the trigonal bipyramid is viewed along the C_2 axis and the tetragonal



D_{3h} (IX) C_{4v} (X)

bipyramid along the C_4 axis, the two geometries are extremely similar. Indeed, $(CH_3)_2NPF_4$ undergoes rapid interconversion at room temperature and the ion $Ni(CN)_5^{3-}$ appears in both C_{4v} and D_{3h} symmetries in the same crystal lattice. For complexes containing polydentate ligands, the potential for ligand distortion will define the stereochemistry of the intermediate. Hammond's Postulate establishes that the structure of the transition state leading to the five-coordinate intermediate in D reactions of cobalt(III) complexes must more closely resemble the intermediate than the ground state. A more flexible ligand geometry should therefore provide a lower energy pathway to the transition state.

Acknowledgements

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