Kinetics of Aquation and Base Hydrolysis of the Macrocyclic Complex *trans*-Chloro(5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)-nitrocobalt(III) Perchlorate

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The macrocyclic complex *trans*-$[Co(dtcd)(NO_2)Cl][ClO_4]$ (dtcd = 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene) has been prepared and its hydrolysis kinetics investigated. At 25 °C and 0.1 M-HNO_3 the aquation occurs with $k_{aq} = 4.4 \times 10^{-4}\ s^{-1}$ to give the *trans*-$[Co(dtcd)(NO_2)(OH_2)]^{2+}$ cation. The activation parameters are $\Delta H^{\ddagger} = 77.4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -49.8$ J K^{-1} mol^{-1} at 298 K. Hydrolysis of the chloride in the pH range 7.7—8.9 follows the rate expression $k_{obs.} = k_{aq} + k_2[OH^-]$. At 25 °C ($I$ = 0.1 M $Na[ClO_4]$) $k_2 = 2.5 \times 10^2$ l mol^{-1} s^{-1} and the activation parameters for base hydrolysis are $\Delta H^{\ddagger} = 69$ kJ mol^{-1} and $\Delta S^{\ddagger} = +24.5$ J K^{-1} mol^{-1}. Base hydrolysis of the nitro-group has been studied at 25 °C and 0.1 M–NaOH and $k = 2.1$ l mol^{-1} s^{-1}. Slow decomposition of the complex occurs, possibly as a result of hydrolysis of the imine linkages; however, this decomposition ($k_{obs.} = 2.2 \times 10^{-3}\ s^{-1}$) is much slower than nitro-hydrolysis. The analogous complex *trans*-$[Co(htcd)(NO_2)Cl][ClO_4]$ (htcd = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene) exhibits similar kinetic behaviour for base hydrolysis of the chloride. At 25 °C (I = 0.1 M), $k_2 = 2.2 \times 10^2$ l mol^{-1} s^{-1} and $k_{aq} = 5.5 \times 10^{-4}\ s^{-1}$. The additional methyl substituents in the macrocyclic ligand have little or no effect on the hydrolysis rates.

RECENTLY there has been considerable interest in substitution reactions of cobalt(III) complexes of macrocylic ligands and the subject has been recently reviewed.[1] The ligand 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (dtcd) was first described by Kolinski and Korybut-Daszkiewicz.[2] A recent crystal-structure

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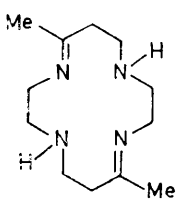
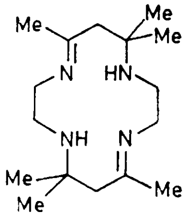
[1] C. K. Poon, *Co-ordination Chem. Rev.*, 1973, **10**, 1; see also C. K. Poon and M. L. Tobe, *ibid.*, 1966, **1**, 38.

[2] A. Kolinski and B. Korybut-Daszkiewicz, *Bull. Acad. polon. Sci.*, 1969, **17**, 13.

determination[3] on *trans*-[Co(dtcd)$(SCN)_2$][SCN]·OH_2 confirmed that the ligand has the *trans*-diene structure (I) analogous to the Curtis macrocycle (II).[4] The present



(I)



(II)

paper describes kinetic studies on the [Co(dtcd)(NO_2)-Cl]$^+$ complex.

EXPERIMENTAL

trans-Dichloro(5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) perchlorate, *trans*-[Co(dtcd)-Cl_2][ClO_4] was prepared as previously described[5] (Found: C, 32.0; H, 5.4; N, 12.3. Calc. for $C_{12}H_{24}Cl_3N_4O_4$: C, 31.8; H, 5.3; N, 12.3%).

trans-*Chloro*(5,12-*dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*nitrocobalt*(III) *Perchlorate*, trans-[Co(dtcd)(NO_2)-Cl][ClO_4].—The complex was prepared by stirring *trans*-[Co(dtcd)Cl_2][ClO_4] (0.4 g) in hot 95% methanol (100 cm^3) with 1 mol equiv. (0.062 g) of sodium nitrite. After heating for *ca.* 20 min, the red-brown solution was filtered hot and cooled in an ice-bath. The resulting fine red-brown precipitate was filtered off, washed with ice-cold ethanol then diethyl ether, and dried *in vacuo*. A second fraction was obtained on addition of ether to the filtrate and further cooling in an ice-bath. The *complex* has absorption maxima at 502 (ε 105) and 355 nm (ε 1 780 l mol^{-1} cm^{-1}), measured in dry acetonitrile (Found: C, 31.2; H, 5.2; N, 14.9. $C_{12}H_{24}ClN_5O_6$ requires C, 31.1; H, 5.2; N, 15.1%).

trans-*Chloro*(5,7,7,12,14,14-*hexamethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*nitrocobalt*(III) *Perchlorate*, trans-[Co(htcd)(NO_2)Cl][ClO_4].—The complex was prepared from *trans*-[Co(htcd)Cl_2][ClO_4][6] essentially as described above for the corresponding dtcd complex (Found: C, 36.7; H, 6.3; N, 13.6. $C_{16}H_{32}ClN_5O_6$ requires C, 36.9; H, 6.2; N, 13.5%).

Kinetic Measurements.—Hydrolysis kinetics were monitored using a Gilford 2400-S spectrophotometer thermostatted to ±0.1 °C. In general, reactions were initiated by injecting a small aliquot portion (Hamilton microsyringe) of the requisite complex (dissolved in acetonitrile) to the reaction medium previously equilibrated at the appropriate temperature. The solution was then rapidly stirred and the absorbance change monitored at 270 nm. In every case the final concentration of the complex was in the range 2×10^{-4}—5×10^{-4}M.*

Base hydrolysis was studied using tris(hydroxymethylamino)methane–HCl buffers adjusted to $I = 0.1$M with Na[ClO_4]. For the dtcd complex the reaction was studied over the pH range 7.7—8.9 at five different temperatures. The observed first-order rate constants at constant pH ($k_{obs.}$) were evaluated using the LETAGROP program[7] adapted for use on a PDP-11 computer. Values of the hydroxide-ion concentrations were obtained using the appropriate pK_w values and activity coefficients estimated from the Davies equation.[8]

The activation energies ($E^‡$) were evaluated from the gradients ($= -E^‡/2.303R$) of plots of log (k/s^{-1}) against $1/T$. Values of $\Delta H^‡$ were obtained from the expression $\Delta H^‡ = E^‡ - RT$. The entropies of activation were evaluated using the equation $\Delta S^‡/4.576 = \log k - 10.753 - \log T + (E^‡/4.576T)$.

RESULTS AND DISCUSSION

Aquation.—The aquation reaction *trans*-[Co(dtcd)-(NO_2)Cl]$^+$ $\longrightarrow$ *trans*-[Co(dtcd)$(NO_2)(OH_2)$]$^+$ + Cl^- was studied using 0.1M-HNO_3 as solvent at five different temperatures (Table 1). At 25 °C, $k_{aq} = 4.36 \times 10^{-4}$ s^{-1}.

TABLE 1

Rate constants for aquation of *trans*-[Co(dtcd)(NO_2)Cl]-[ClO_4] in 0.1M-HNO_3

θ_c/°C	10^4k_{aq}*/s^{-1}
15.6	1.59
20.1	2.47
25.0	4.36
30.0	7.89
35.2	12.60

* Average of at least three runs, the concentration of the complex being 2×10^{-4}—5×10^{-4}M. From the above data, $\Delta H^‡ = 77.4$ kJ mol^{-1} and $\Delta S^‡ = -49.8$ J K^{-1} mol^{-1} at 298 K.

The corresponding thermodynamic parameters are $\Delta H^‡ = 77.4$ kJ mol^{-1} and $\Delta S^‡ = -49.8$ J K^{-1} mol^{-1} at 298 K. For the complex *trans*-[Co(cyclam)(NO_2)Cl]$^+$ the reported aquation rate at 25 °C in 0.01M-HNO_3 is 4.3×10^{-5} s^{-1} [9] (cyclam = 1,4,8,11-tetra-azacyclotetradecane) with $\Delta H^‡ = 86.2$ kJ mol^{-1} and $\Delta S^‡ = -37$ J K^{-1} mol^{-1}. The ten-fold rate acceleration observed with *trans*-[Co-(dtcd)(NO_2)Cl]$^+$ is due to a more favourable enthalpy of activation, although this is offset to a degree by a less favourable entropy of activation.

The aquation rate of *trans*-[Co(dtcd)(NO_2)Cl]$^+$ is intermediate between that of *trans*-[Co(cyclam)(NO_2)-Cl]$^+$ and *trans*-[Co$(en)_2(NO_2)$Cl]$^+$ (en = ethylenediamine). For the latter reaction $k_{aq} = 1 \times 10^{-3}$ s^{-1} at 25 °C and $\Delta H^‡ = 87.4$ kJ mol^{-1} and $\Delta S^‡ = -8.4$ J K^{-1} mol^{-1}.[9,10] The slower aquation rates of *trans*-[Co(cyclam)(A)Cl]$^+$ complexes than those of corresponding *trans*-[Co$(en)_2$-(A)Cl]$^+$ has been rationalised in terms of the greater ability of cyclam to expand the 3*d* shell of the central metal ion.[9]

Base Hydrolysis.—Base hydrolysis was studied in tris(hydroxymethylamino)methane–HCl buffers at $I = 0.1$M (Na[ClO_4]) over the pH range 7.7—8.9 at five different temperatures in the range 16.2—35.2 °C. The rate data obtained are summarised in Table 2. Plots of the observed first-order rate constants against the hydroxide-ion concentration are shown in the Figure. These do not pass through the origin, but have positive intercepts. It is clear that both base hydrolysis and aquation are occurring within the pH range investigated,

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* 1M = 1 mol dm^{-3}, 1 cal = 4.184 J.

[3] R. J. Restivo, J. Horney, and G. Ferguson, *J.C.S. Dalton*, submitted for publication.

[4] N. F. Curtis, *Co-ordination Chem. Rev.*, 1968, **3**, 3.

[5] R. W. Hay and G. A. Lawrance, *J.C.S. Dalton*, 1466.

[6] J. A. Kernohan and J. F. Endicott, *Inorg. Chem.*, 1970, **9**, 1504.

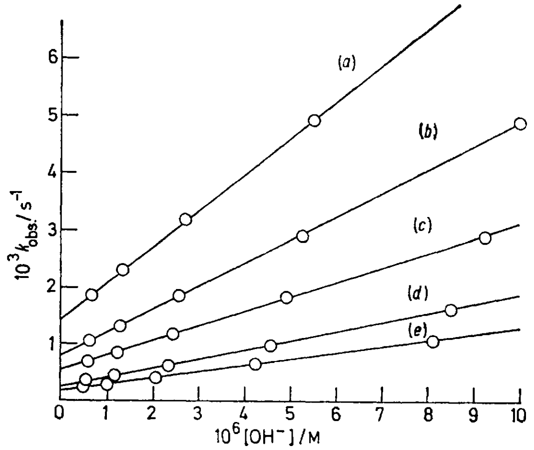
[7] N. Ingri and L. G. Sillen, *Arkiv. Kemi*, 1964, **23**, 97.

[8] C. W. Davies, *J. Chem. Soc.*, 1938, 2093.

[9] K. S. Mok and C. K. Poon, *Inorg. Chem.*, 1971, **10**, 225.

[10] S. Asperger and C. K. Ingold, *J. Chem. Soc.*, 1956, 2862.

so that $k_{obs.} = k_{aq} + k_{OH}[OH^-]$. Values of k_{aq} and k_{OH} were obtained from the intercept and gradient of such plots. At 25 °C and $I = 0.1$M, $k_{aq} = 5.5 \times 10^{-4}$ s^{-1} and $k_{OH} = 2.5 \times 10^2$ l mol^{-1} s^{-1}. There is reasonable agreement between the former rate constant and that of 4.36 × 10^{-4} s^{-1} obtained in the direct aquation studies. The reaction was also subject to slight general base catalysis; thus at $I = 0.1$M, 25 °C, and pH 8.27, $k_{obs.} = 1.18 \times 10^{-3}$ s^{-1} in 0.01M ($I = 0.1$M) buffer and 1.30×10^{-3} s^{-1} in 0.10M ($I = 0.1$M) buffer.



Plots of $k_{obs.}$ against the hydroxide-ion concentration for the hydrolysis of *trans*-[Co(dtcd)(NO$_2$)Cl]$^+$ at $I = 0.1$M at (*a*) 35.2, (*b*) 30.0, (*c*) 25.0, (*d*) 20.1, and (*e*) 16.2 °C

The activation parameters for the base-hydrolysis reaction are $\Delta H^\ddagger = 69$ kJ mol^{-1} and $\Delta S^\ddagger = +24.5$ J K^{-1} mol^{-1} at 298 K. The base hydrolysis of the analogous complex *trans*-[Co(htcd)(NO$_2$)Cl]$^+$ was also studied at 25 °C in the pH range 7.6—8.9 (Table 2). The value of k_{OH} was 2.17×10^{-4} l mol^{-1} s^{-1}, very similar to that obtained with the dtcd complex. It is clear that the additional methyl substitution has little effect on the base-hydrolysis rates.

At higher pH, base hydrolysis of the nitro-group also occurred. These reactions were studied at 25 °C using 0.1M-KOH as reaction medium. The reaction was first order in hydroxide ion and complex concentrations. For *trans*-[Co(dtcd)(NO$_2$)(OH)]$^+$ $k_{obs.} = 2.1 \times 10^{-1}$ s^{-1} giving a value of $k_{OH}^{NO_2} = 2.1$ l mol^{-1} s^{-1} at 25 °C. A much slower decomposition of the complex also occurred in basic solution ($k_{obs.} = 2.2 \times 10^{-3}$ s^{-1} in 0.1M-base) presumably due to hydrolysis of the imine linkages of the ligand. Base hydrolysis of *trans*-[Co(htcd)(NO$_2$)(OH)]$^+$ had $k_{obs.} = 2.2 \times 10^{-1}$ s^{-1} in 0.1M-base with $k_{OH}^{NO_2} = 2.2$ l mol^{-1} s^{-1} at 25 °C. Thus, there is little or no effect of methyl substitution on nitro-hydrolysis, as with chloride base hydrolysis, in these macrocycles. The rate constants for aquation and base hydrolysis are summarised in Table 3, and compared with those obtained for other *trans*-[CoL(NO$_2$)Cl]$^+$ complexes. Overall the rate constants fit well with the general pattern that a rapid acid-aquation rate is connected with a slow base-hydrolysis rate and *vice versa*. The available evidence

TABLE 2

Kinetics of base hydrolysis of *trans*-[Co(dtcd)(NO$_2$)Cl][ClO$_4$] and *trans*-[Co(htcd)(NO$_2$)Cl][ClO$_4$] at $I = 0.1$M *

θ_c/°C	pH	$10^6[OH^-]$/M	$10^3k_{obs.}$/s^{-1}	$10^{-2}k_{OH}$/l mol^{-1} s^{-1}	10^4k_{aq}/s^{-1}
(*a*) *trans*-[Co(dtcd)(NO$_2$)Cl][ClO$_4$]					
16.2	9.10	8.11	1.07	1.09	1.8
	8.82	4.25	0.64		
	8.51	2.08	0.41		
	8.21	1.04	0.30		
	7.89	0.50	0.24		
20.1	8.98	8.50	1.61	1.6	2.5
	8.71	4.56	0.97		
	8.40	2.34	0.61		
	8.11	1.15	0.41		
	7.78	0.54	0.35		
25.0	8.85	9.24	2.88	2.54	5.5
	8.57	4.91	1.83		
	8.27	2.43	1.18		
	7.97	1.22	0.84		
	7.67	0.58	0.68		
30.0	8.72	10.01	4.89	4.08	8
	8.44	5.25	2.91		
	8.13	2.57	1.85		
	7.83	1.29	1.32		
	7.51	0.62	1.06		
35.2	8.58	10.49	8.10	6.34	0.14
	8.30	5.50	4.92		
	7.99	2.70	3.20		
	7.69	1.35	2.29		
	7.38	0.66	1.85		
(*b*) *trans*-[Co(hctd)(NO$_2$)Cl][ClO$_4$]					
25.0	8.85	9.24	2.68	2.17	6.8
	8.57	4.91	1.74		
	8.27	2.43	1.21		
	7.97	1.22	0.94		
	7.65	0.58	0.79		

* Aquation rates determined from these data must be regarded as approximate. Aquation studies of *trans*-[Co(htcd)(NO$_2$)Cl][ClO$_4$] in 0.1M-HNO$_3$ gave a value of $k_{aq} = 5.5 \times 10^{-4}$ s^{-1}.

suggests that in both aquation and base hydrolysis retention of configuration occurs in the macrocyclic complexes.

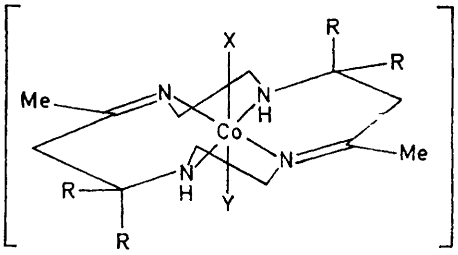
TABLE 3

Aquation and base-hydrolysis rate constants for complexes of *trans*-$[CoL(NO_2)Cl]^+$ at 25 °C

L	k_{aq}/s^{-1}	$k_{OH}/l\ mol^{-1}\ s^{-1}$	Ref.
dtcd	4.4×10^{-4}	2.5×10^2	*a*
htcd	5.5×10^{-4}	2.2×10^2	*a*
cyclam	4.3×10^{-5}	6.0×10^2	9, *b*
$(en)_2$	9.8×10^{-4}	2.75 [c]	10
$(NH_3)_4$	2.7×10^{-2}	0.13	*d*
mhtcd	4.1×10^{-2}		11

[a] This work. [b] C. K. Lui and C. K. Poon, *J.C.S. Dalton*, 1972, 216. [c] Calculated from $E^‡ = 24.4$ kcal mol^{-1} and log $A = 18.4$ quoted by Poon (ref. 1). [d] C. K. Poon and H. W. Wong, *J. Chem. Soc.* (*A*), 1971, 2151.

At 25 °C the relative rates of acid aquation are cyclam (1) < dtcd (10.2) < htcd (12.8) < $(en)_2$ (22.8) < $(NH_3)_4$ (630) < mhtcd (950).* The macrocyclic complexes can be divided into two categories: (*a*) those derived from the saturated ligands cyclam and mhtcd; and (*b*) those derived from the unsaturated macrocycles dtcd and htcd. Acid hydrolysis of the mhtcd complex is *ca.* 10^3 times faster than for the cyclam derivative.[11] The chloro-substituent in the former complex is subject to steric congestion by the axial methyl substituents. The experimental observations are consistent with steric acceleration of the expected dissociative path for aquation.



(III) R = H or Me

In the diene complexes the situation is somewhat different. These complexes can be represented as in (III). [In addition to the N-*racemic*-diastereoisomer illustrated the N-*meso*-diastereoisomer can occur in these systems, but the former is favoured in both planar and folded complexes of cobalt(III) and nickel(II).] [12] The C(Me):N groups are pseudo-equatorial and the most favoured conformation of the molecule is probably one in which the axial methyl substituents are ' pitched ' away from the axial groups on cobalt. Molecular models indicate that neither the groups X or Y are subject to steric compression. For this reason the aquation rates for the dtcd and htcd complexes are very similar. It has also been argued that unsaturation in the amine macrocycles increases the softness of Co^{III} due to the possibility of increased electronic delocalisation between the metal ion and the ligand. Such an effect may result in increased lability in complexes of this type due to the possibility of stabilising five-co-ordinate intermediates. For the macrocycles, where steric effects appear to be minimal, a ten-fold rate acceleration with respect to cyclam is observed in acid aquation.

Base hydrolysis of the macrocyclic complexes is considerably faster than for L = $(NH_3)_4$ or $(en)_2$. For base hydrolysis of $[Co(en)_2(NO_2)Cl]^+$, $\Delta H^‡ = 99.6$ kJ mol^{-1} and $\Delta S^‡ = +99$ J K^{-1} mol^{-1} at 298 K, while for $[Co(cyclam)_2(NO_2)Cl]^+$ $\Delta H^‡ = 81.2$ kJ mol^{-1} and $\Delta S^‡ = +82$ J K^{-1} mol^{-1} (values calculated from Poon[1]). Edwards *et al.*[13] recently reviewed ligand-replacement reactions in M^{III} complexes. For an $S_N1(CB)$ mechanism the estimated value of $\Delta S^‡$ is *ca.* +142 J K^{-1} mol^{-1} while for an S_N2 process $\Delta S^‡$ is *ca.* −63 J K^{-1} mol^{-1}. The bulk of the experimental data[13] obtained for base hydrolysis of aminechloro-complexes of Co^{III} have $\Delta S^‡$ values in the range +84 to +167 J K^{-1} mol^{-1} consistent with an $S_N1(CB)$ mechanism. The $\Delta S^‡$ value for cyclam falls in the expected range, although that for dtcd is somewhat below the norm (+24.5 J K^{-1} mol^{-1}) but still in an area consistent with an $S_N1(CB)$ process.

For reasons previously discussed, steric effects appear to be minimal for the macrocyclic complexes and the base-hydrolysis rates are quite similar to those of cyclam. It would be expected that base hydrolysis of the mhtcd complex would be faster than cyclam due to steric acceleration. The more rapid base hydrolysis of the macrocyclic compared with the non-macrocyclic complexes is due to a lower enthalpy of activation. The entropy of activation for the macrocyclic complexes is less positive when compared with the values observed for the non-macrocyclic complexes and is thus less favourable to the reaction.

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* mhtcd = *meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradecane (tet *a*).

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

[12] N. F. Curtis, *Austral. J. Chem.*, 1974, **27**, 71.

[13] J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta*, 1974, **11**, 47.