Inorganica Chimica Acta, 38 (1980) 167–176
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Anionopentaaminecobalt(III) Complexes with Polyamine Ligands. XIV. The Kinetics of Aquation, Mercury(II) Assisted Aquation and Base Hydrolysis of some Chloro(diethylenetriamine)bis(monoamine)cobalt(III) Complexes

FOO CHUK HA and DONALD A. HOUSE
Department of Chemistry, University of Canterbury, Christchurch, New Zealand

Received May 16, 1979

Second order rate constants for the Hg^{2+} *assisted aquation of some* unsym-fac-cis-$CoCl(dien)(A)_2^{2+}$ *complexes (A =* NH_3, $MeNH_2$, $EtNH_2$, $nPrNH_2$, $nBuNH_2$, *pentylamine, hexylamine, benzylamine, pyridine, 4-propylpyridine, 3-ethyl-4-methylpyridine and 3,5-dimethyl pyridine) have been determined spectrophotometrically over a 20 K temperature range. The benzylamine and pyridine-type complexes react about ten times more slowly than their alkylamine analogues and in the latter sequence, the reactivity generally decreases with increasing chain length. Two* unsym-mer-cis- *(A =* NH_3, $EtNH_2$*) and one* sym-fac-cis- *(A =* NH_3*) isomers react at rates not markedly different from their* unsym-fac-cis- *forms. The thermal aquation of the alkylamine complexes (1.0* M $HClO_4$, *343 K) is complicated by a subsequent reaction, but spectrophotometric rate data were successfully obtained for the A =* NH_3 *isomers. Kinetic parameters for the thermal aquation of the* unsym- *and* sym-fac-cis-$CoCl(dien)(NH_3)_2^{2+}$ *isomers are* $10^7\ k_H(298)$, s^{-1}; *19.2, 3.16:* E_a *(kJ* mol^{-1}*); 95, 107:* $\Delta S^{\#}_{298}$ *(J* K^{-1} mol^{-1}*); −44, −20, respectively. Similar data for the base hydrolysis of* sym-fac-cis-$CoCl(dien)(NH_3)_2^{2+}$ *are* $k_{OH}(298)$, $M^{-1}\ s^{-1}$; *0.70:* E_a; *84:* $\Delta S^{\#}_{298}$; *+26.*

Introduction

Aniono(diethylenetriamine)bis(monoamine)cobalt(III) complexes can potentially form five configurational isomers (Fig. 1). The most easily synthesised configuration is the *unsym-fac-cis-* (I, Fig. 1), but for certain monoamines, one of the *unsym-mer-cis-* isomers (II, Fig. 1) can also be obtained [1]. The ammine compounds exhibit the greatest isomeric complexity and *unsym-fac-cis*, (H↓)-*unsym-mer-cis-** and *sym-fac-cis-* forms have been prepared [2, 3].

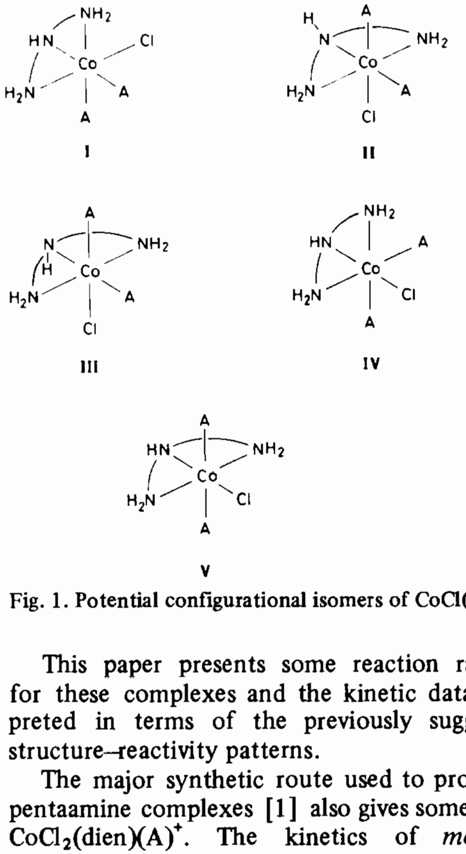

Fig. 1. Potential configurational isomers of $CoCl(dien)(A)_2^{2+}$.

This paper presents some reaction rate studies for these complexes and the kinetic data are interpreted in terms of the previously suggested [4] structure–reactivity patterns.

The major synthetic route used to produce these pentaamine complexes [1] also gives some *trans-mer*-$CoCl_2(dien)(A)^+$. The kinetics of *mer* → *fac* diethylenetriamine isomerisation for A = NH_3, benzylamine, cyclohexylamine, cyclohexylmethylamine and pyridine *trans-mer*-$Co(dien)(A)(OH_2)_2^{3+}$ (generated *in situ* from the *trans*-dichloro) have been measured previously [5]. We also report here additional isomerisation rate data for the complexes with A = $MeNH_2$, $EtNH_2$, $nPrNH_2$ and $nBuNH_2$.

Experimental

The complexes used in this study were prepared and characterised as described previously [1, 2, 5].

---

*See *Inorg. Chim. Acta, 30,* 59 (1978) for the nomenclature used.

TABLE I. Observed Isosbestic Points.

A	Reaction	λ nm	λ nm	λ nm
	unsym-fac-cis-CoCl(dien)(A)$_2^{2+}$ Isomers			
NH_3	Hg^{2+}	345	412	504
NH_3	thermal[a]	345	413	506
		(63)	(18)	(70)
$MeNH_2$	Hg^{2+}	360	418	517
$EtNH_2$	Hg^{2+}	362	423	517
$nPrNH_2$	Hg^{2+}	362	422	517
$nBuNH_2$	Hg^{2+}	363	425	518
$iBuNH_2$	Hg^{2+}	363	430	517
$npentNH_2$	Hg^{2+}	363	422	520
$nhexNH_2$	Hg^{2+}	365	418	522
$BzNH_2$	Hg^{2+}	372	422	525
py	Hg^{2+}	363	422	508
4-pr-py	Hg^{2+}	365	426	512
3,5-Me_2py	Hg^{2+}	362	432	507
3Et,4Mepy	Hg^{2+}	364	427	510
½en[b]	thermal[a]	353	405	508
		(66.0)	(18.2)	(61.0)
	unsym-mer-cis-CoCl(dien)(A)$_2^{2+}$ Isomers			
NH_3	Hg^{2+}	357	420	495
$EtNH_2$	Hg^{2+}	365	425	505
	sym-fac-cis-CoCl(dien)(A)$_2^{2+}$ Isomers			
NH_3	Hg^{2+}	345	412	504
NH_3	thermal[a]	345	410	502
		(61)	(19)	(70)
½en[b]	thermal[a]		411	505
			(19.5)	(70.5)
	mer → *fac* Isom. of Co(dien)(A)$(OH_2)_2^{3+}$ [c]			
$MeNH_2$		378	458	547
$EtNH_2$		378	462	554
$nPrNH_2$		378	464	552
$nBuNH_2$		383	453	555

[a] Numbers in parenthesis are the extinction coefficients at the isosbestic points. [b] Ref. [15]. [c] For additional data see ref. [5].

Kinetics

The rates of thermal aquation of *sym-fac-cis-* and *unsym-fac-cis-* [CoCl(dien)$(NH_3)_2$]X (X = $Cl_2 \cdot 0.5H_2O$, $ZnCl_4$ respectively) were determined spectrophotometrically. Solutions of the complex (*ca.* 10 m*M*, 50 mL) were prepared in 1.0 *M* $HClO_4$ at room temperature. A 'zero time' sample (*ca.* 4 mL) was removed and the reaction vessel was placed in a temperature controlled bath. After 5 min thermal equilibration time, an electronic timer was started. Samples (*ca.* 4 mL) were then withdrawn at known time intervals, cooled in ice, and stored at room temperature for subsequent spectrophotometric analysis.

Rates of Hg^{2+} assisted aquation were determined in Hg^{2+}/$HClO_4$ solution (μ = 1.0 *M*, prepared by dissolving $Hg(NO_3)_2 \cdot H_2O$ in $HClO_4$ and standardising with chloride solution [6]). Small amounts of the $ZnCl_4^{2-}$ salts of the chloropentaamine complexes were dissolved in the solvent at the appropriate temperature and the reaction solution was transferred by syringe to a jacketed 5.00 cm spectrophotometer cell before starting the repeat scan or fixed wavelength mode. About half the complexes used were not readily soluble in the $HClO_4$/Hg^{2+} solutions and in these cases, the salts were dissolved in 0.1–0.15 mL of dimethylformamide (DMF) before adding the solvent. Separate experiments, with and without added DMF, showed that the value of k_{Hg} was not affected by this dissolution procedure. However, even this technique was unsuccessful for the 4-benzylpyridine and cyclohexylmethylamine complexes due to immediate precipitation of the insoluble perchlorates.

Isomerisation rates for the *trans-mer*-Co(dien)(A)$(OH_2)_2^{3+}$ cations were measured as described previously [5] and rates of base hydrolysis of *sym-fac-cis*-[CoCl(dien)(A)$_2$]$Cl_2 \cdot 0.5H_2O$ (A = NH_3, 0.5en[7–10]) were determined using pH-stat techniques [11].

Isosbestic points observed during the spectral scans are listed in Table I.

Calculations

Spectrophotometrically determined pseudo-first-order rate constants were obtained from 8–15 point-by-point calculations (over 2–3 half lives) using the expression:

$$k_{obs}t = \ln[(A_o - A_\infty)/(A_t - A_\infty)]$$

where A_o, A_t and A_∞ are the optical absorbancies (at a suitable wavelength) at reaction time zero, at time t and at 100% reaction (7–10 half lives) respectively. The cited data are the mean ± the standard deviation from these calculations.

The second order rate constants (k_{Hg}) for the Hg^{2+} assisted aquations were calculated using $k_{Hg} = k_{obs}$-[Hg^{2+}]$_i$ where [Hg^{2+}]$_i$ is the total Hg^{2+} concentration.

Second order rate constants for the base hydrolysis reactions (k_{OH}) were calculated from the trace of OH^- uptake *vs.* time using the previously described methods [11].

All activation parameters were computer calculated from the variation of the rate constant with temperature using standard equations [11].

TABLE II. Observed and Calculated Pseudo-First Order Rate Constants for the Aquation of *unsym-fac-cis-* and *sym-fac-cis-*$CoCl(dien)(NH_3)_2^{2+}$ in 1.0 *M* $HClO_4$.

Complex	T °C[K]	10^4 k_{obs} s^{-1}	10^4 k_{calc}[a] s^{-1}
unsym-fac-cis-	87.9[361.1]	15.1 ± 1.9	15.1
	71.2[344.4]	3.35 ± 0.14	3.26
		3.05 ± 0.22	
	64.0[337.2]	1.80 ± 0.09	1.61
	59.0[332.2]	0.91 ± 0.04	0.96
sym-fac-cis-	88.6[361.8]	6.07 ± 0.3	6.11
		5.97 ± 0.6	
		6.32 ± 0.5	
	71.4[344.6]	1.10 ± 0.05	1.04
	71.2[344.2]	0.962 ± 0.05	1.02
	64.0[337.2]	0.459 ± 0.02	0.460
	59.0[332.2]	0.260 ± 0.01	0.259

[a]Calculated from the activation parameters cited in Table III.

TABLE III. Activation Parameters for the Aquation of some $CoCl(dien)(A)_2^{2+}$ Isomers at 298.2 K (μ = 1.0 *M*).

A	Configuration	10^7 k(298) s^{-1}	E_a kJ mol^{-1}	$\Delta S^{\#}_{298}$ J K^{-1} mol^{-1}	Ref.
NH_3	*unsym-fac-cis-*	19.2	94.8 ± 4.0	–44 ± 8	[a]
½en	*unsym-fac-cis-*	2.56	110	–8	[b]
½tmd	*unsym-fac-cis-*	43.0	73	–111	[c]
NH_3	*sym-fac-cis*	3.16	107 ± 1.3	–20 ± 3	[a]
½en	*sym-fac-cis*	0.94	113	–7	[b]
½tmd	*sym-fac-cis*	2.16	110	–10	[c]

[a]This work. [b]Ref. [15]. [c]Ref. [12].

Results and Discussion

Thermal Aquation

Table II lists the pseudo-first-order rate constants observed for the thermal aquation of *unsym-fac-cis-* and *sym-fac-cis-* $CoCl(dien)(NH_3)_2^{2+}$ in 1.0 *M* $HClO_4$ at various temperatures. These data have been used to calculate the activation parameters cited in Table III.

The spectral scans for these two complexes showed sharp isosbestic points (Table I) and the final spectra corresponded to those generated from the original chloro complexes by reaction with Hg^{2+}/$HClO_4$ at room temperature. This was not the case for *unsym-fac-cis*-$CoCl(dien)(MeNH_2)_2^{2+}$ (at 343 K) and the final spectrum did not correspond to that predicted for *unsym-fac-cis*-$Co(dien)(MeNH_2)_2(OH_2)^{3+}$, but was more characteristic of *fac*-$Co(dien)(OH_2)_3^{3+}$. While chloride release rates could be estimated titrimetrically, this aspect of the reaction was not further investigated for any other of the *unsym-fac-cis*-$CoCl(dien)(A)_2^{2+}$ complexes.

For those $CoCl(dien)(A)_2^{2+}$ complexes where thermal aquation data are available, the *unsym-fac-cis* isomers are more labile than their *sym-fac-cis*-analogues (Table III) and the non-replaced ligands increase the lability in the order en < $(NH_3)_2$ ~ tmd for both systems. This latter order is precisely that predicted from the influence of the 'bite'* of the non-replaced ligands [5, 12–14] on the ease of distortion to a trigonal bipyramid transition state. Distortion considerations can also account for the inertness of the *sym-fac-cis-* isomers in so far as edge displacement towards a trigonal bipyramid involves the movement of a diethylenetriamine edge, whereas in the *unsym-fac-cis-* form, the movement only involves a flattening of the diethylenetriamine about the central NH pivot (Fig. 2).

---

*Mean values for the calculated M–N distances across the edge of the Co(III) octahedron for a variety of crystal structures are: en 2.68, $(NH_3)_2$ 2.78 and tmd 2.83 A.

TABLE IV. Spectrophotometrically Determined Rate Constants for the Hg^{2+}-Assisted Aquation of Some $MCl(N_5)^{2+}$ Complexes in Acidic Solution at $\mu = 1.0$ *M* and 298.2 K.[a]

Complex[b]	$[H^+]$ *M*	$[Hg^{2+}]_i$ m*M*	10^3 k_{obs}[c] s^{-1}	10^2 k_{Hg}[d] M^{-1} s^{-1}	Mean 10^2 k_{Hg} M^{-1} s^{-1}
$CoCl(NH_3)_5^{2+}$[e]	0.88(3)[f]	42.4	5.28 ± 0.11	12.4 ± 0.3	12.4 ± 0.3[g]
[h]	0.88(1)	42.4	5.56 ± 0.15	13.1 ± 0.4	
$CoCl(dien)(NH_3)_2^{2+}$	0.80(3)	65.6	1.88 ± 0.12	2.86 ± 0.18	
sym-fac-cis-	0.76(1)	86.8	2.56 ± 0.03	2.95 ± 0.03	2.88 ± 0.05
	0.89(1)[i]	35.5	1.67 ± 0.03	4.69 ± 0.09	
	0.82(1)[i]	57.4	2.55 ± 0.05	4.44 ± 0.09	4.56 ± 0.09
unsym-mer-cis-	0.88(1)	42.4	1.01 ± 0.05	2.38 ± 0.12	
	0.76(2)	86.8	1.76 ± 0.04	2.02 ± 0.05	2.14 ± 0.20
unsym-fac-cis-	0.88(3)	42.4	3.29 ± 0.27	7.76 ± 0.63	
	0.80(1)	65.6	5.06 ± 0.19	7.71 ± 0.29	7.75 ± 0.23
$CoCl(dien)(MeNH_2)^{2+}$	0.88(2)	42.4	3.73 ± 0.08	8.80 ± 0.19	
unsym-fac-cis-	0.80(2)	65.6	6.04 ± 0.12	9.20 ± 0.18	9.00 ± 0.10
$CoCl(dien)(EtNH_2)_2^{2+}$	0.88(2)	42.4	2.48 ± 0.06	5.85 ± 0.14	
unsym-fac-cis-	0.80(2)	65.6	3.55 ± 0.26	5.41 ± 0.40	5.71 ± 0.18
unsym-mer-cis-	0.88(2)	42.4	7.15 ± 0.18	16.9 ± 0.42	16.9 ± 0.42
$CoCl(dien)(nPrNH_2)_2^{2+}$[j]	0.88(2)	42.4	2.34 ± 0.08	5.51 ± 0.19	
unsym-fac-cis-	0.80(2)	65.6	3.42 ± 0.12	5.21 ± 0.18	5.36 ± 0.12
$CoCl(dien)nBuNH_2)_2^{2+}$	0.88(3)	42.4	2.06 ± 0.06	4.86 ± 0.14	
unsym-fac-cis-	0.80(2)	65.6	2.90 ± 0.05	4.42 ± 0.08	
	0.76(1)	86.8	4.05 ± 0.11	4.66 ± 0.14	4.68 ± 0.12
$CoCl(dienO(iBuNH_2)_2^{2+}$	0.88(3)	42.4	1.69 ± 0.09	3.99 ± 0.21	
unsym-fac-cis-	0.80(2)	65.6	2.64 ± 0.26	4.02 ± 0.30	
	0.76(1)	86.8	3.77 ± 0.18	4.34 ± 0.21	4.06 ± 0.16
$CoCl(dien)(nPentNH_2)_2^{2+}$[j]	0.88(2)	42.4	2.00 ± 0.09	4.71 ± 0.18	
unsym-fac-cis-	0.80(1)	65.6	3.28 ± 0.05	4.99 ± 0.08	
	0.76(1)	86.8	4.40 ± 0.08	5.07 ± 0.10	4.88 ± 0.12
$CoCl(dien)(nHexNH_2)_2^{2+}$[j]	0.88(2)	42.4	2.03 ± 0.09	4.78 ± 0.21	
unsym-fac-cis	0.76(1)	86.8	4.49 ± 0.28	5.17 ± 0.33	4.92 ± 0.26
$CoCl(dien)(BzNH_2)_2^{2+}$[j]					
unsym-fac-cis-	0.76(2)	86.8	0.554 ± 0.016	0.638 ± 0.018	0.638 ± 0.018
$CoCl(dien)(tmd)^{2+}$[e]	0.80(2)	65.6	6.57 ± 0.07	10.0 ± 0.11	10.0 ± 0.11
d-isomer(*unsym-fac-cis-*)	0.40(2)	43.4	2.90 ± 0.09	6.68 ± 0.21	6.68 ± 0.21[k]

[a] [Co(III)] ~ 0.2 m*M* and λ = 540, 550 or 560 nm. [b] As $ZnCl_4^{2-}$ salts except where noted. [c] Mean ± the standard deviation. [d] $k_{Hg} = k_{obs}/[Hg^{2+}]_i$. [e] As ClO_4^- salt. [f] Numbers in parenthesis are the number of individual determinations in $HClO_4$. [g] *Cf.* 10^2 $k_{Hg} = 12.2 \pm 0.2$ [17] and 11.6 [18] M^{-1} s^{-1} under similar conditions. [h] As Cl^- salt. [i] In HNO_3. [j] Complex dissolved in *ca.* 0.1 mL of DMF before addition of $HClO_4/Hg^{2+}$ solution. [k] $\mu = 0.5$ *M*.

Hg^{2+} Assisted Aquation

Rate data for the Hg^{2+} assisted aquation of sixteen $CoCl(dien)(A)_2^{2+}$ complexes are presented in Tables IV–VI. The initial $[Hg^{2+}]$ was always greater than ten times the complex concentration and the first order rate plots were linear for at least three half lives. Figure 3 shows a repeat scan kinetic run for the *unsym-fac-cis*-$CoCl(dien)(benzylamine)_2^{2+}$ plus Hg^{2+}/$HClO_4$ reaction and other complexes behaved similarly. The excellent isosbestic points suggest the reaction proceeds with retention of configuration although the possibility of aqua isomers produced in a constant ratio cannot be excluded. Where thermal and Hg^{2+} assisted data can be compared (Table I), the agreement between the observed isosbestic points is quite satisfactory.

The calculated second order rate constants, k_{Hg}, were independent of $[Hg^{2+}]_i$ (Table IV) and no attempt was made to correct for small contributions from the $HgCl^+$ assisted path. This latter ion would

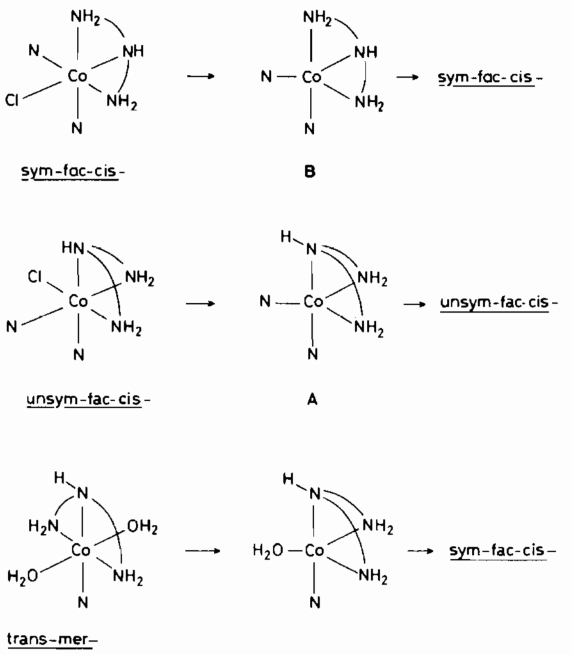

Fig. 2. Distortions required to generate a trigonal bipyramid transition state in the *unsym-fac-cis*-CoCl(dien)(A)$_2^{2+}$, *sym-fac-cis*-CoCl(dien)(A)$_2^{2+}$ and *trans-mer*-Co(dien)(A)(OH$_2$)$_2^{3+}$ systems. Generation of A requires only a slight flattening of the originally facial tridentate, whereas generation of B requires movement of a diethylenetriamine edge.

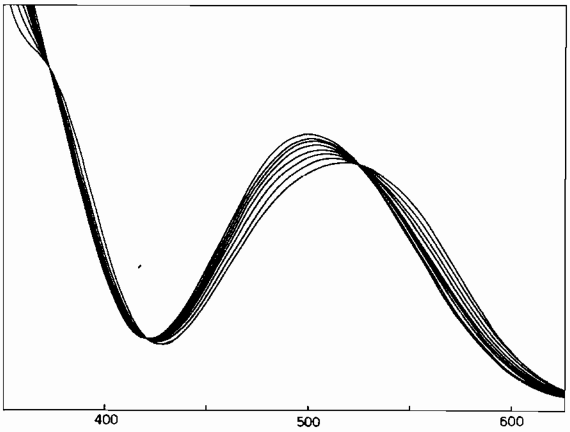

Fig. 3. Spectrophotometric scans of *unsym-fac-cis*-CoCl(dien)(benzylamine)$_2^{2+}$ (*ca.* 2 m*M*) reacting with Hg^{2+} (65.6 m*M*) at 298.2 K (μ = 1.0, HClO$_4$), Each trace (moving upwards at 500 nm) represents a time interval of 300 s.

be present to the extent of four times the initial complex concentration (*ca.* 2 m*M*) assuming complete dissociation of the ZnCl$_4^{2-}$ ion [15].

Although HNO$_3$ was found to be a better solvent than HClO$_4$ for many of the complexes used, the second order rate constants obtained using HNO$_3$/Hg^{2+} were about twice as great as those obtained in

TABLE V. Observed and Calculated Rate Constants for the Hg^{2+} Assisted Aquation of Some *unsym-fac-cis*-CoCl(dien)(A)$_2^{2+}$ Complexes (μ = 1.0 *M*).[a]

T (°C[K])	[H$^+$] *M*	[Hg^{2+}]$_i$ m*M*	10^3 k$_{obs}$ s^{-1}	10^2 k$_{Hg}$[b] *M*$^{-1}$ s^{-1}	10^2 k$_{Hg}$(calc)[c] *M*$^{-1}$ s^{-1}
		CoCl(dien)(NH$_3$)$_2^{2+}$			
25.0[298.2][d]				7.75 ± 0.23	7.76
28.0[301.2]	0.76	86.8	8.67 ± 0.05	9.99 ± 0.06	10.1
32.4[305.6]	0.88	43.4	6.81 ± 0.07	15.7 ± 0.15	14.6
35.2[308.4]	0.88	43.4	7.71 ± 0.08	17.8 ± 0.15	18.5
		CoCl(dien)(MeNH$_2$)$_2^{2+}$			
25.0[298.2][d]				9.00 ± 0.1	8.98
28.0[301.2]	0.80	65.6	7.63 ± 0.1	11.6 ± 0.15	11.5
31.0[304.2]	0.76	86.8	11.9 ± 0.5	13.7 ± 0.6	14.6
32.4[305.6]	0.88	43.4	7.60 ± 0.08	17.5 ± 0.18	16.4
35.2[308.4]	0.88	43.4	8.81 ± 0.08	20.3 ± 0.20	20.5
		CoCl(dien)(EtNH$_2$)$_2^{2+}$			
19.7[292.9]	0.76	86.8	2.89 ± 0.19	3.33 ± 0.22	3.40
25.0[298.2][d]				5.71 ± 0.18	5.67
27.7[300.9]	0.88	42.4	3.17 ± 0.04	7.47 ± 0.10	7.30
30.7[303.9]	0.88	42.4	3.96 ± 0.06	9.34 ± 0.14	9.63
		CoCl(dien)(nPrNH$_2$)$_2^{2+}$			
25.0[298.2][d]				5.36 ± 0.12	5.27

(continued overleaf)

TABLE V. *(Continued)*

T (°C[K])	[H⁺] *M*	$[Hg^{2+}]_i$ m*M*	10^3 k_{obs} s^{-1}	10^2 k_{Hg}[b] M^{-1} s^{-1}	10^2 k_{Hg}(calc)[c] M^{-1} s^{-1}
28.0[301.2]	0.76	86.8	5.67 ± 0.26	6.54 ± 0.30	7.12
31.0[304.2]	0.80	65.6	6.39 ± 0.15	9.55 ± 0.17	9.57
	0.76	86.8	8.26 ± 0.10	9.52 ± 0.12	
32.4[305.6]	0.88	43.4	4.65 ± 0.03	10.7 ± 0.07	10.9
35.2[308.4]	0.88	43.4	6.46 ± 0.13	14.9 ± 0.30	14.3
38.1[311.3]	0.88	43.4	7.97 ± 0.12	18.4 ± 0.28	18.8
		$CoCl(dien)(nBuNH_2)_2^{2+}$			
25.0[298.2][d]				4.68 ± 0.12	4.66
28.0[301.2]	0.76	86.8	5.43 ± 0.08	6.26 ± 0.09	6.40
31.0[304.2]	0.80	65.6	5.76 ± 0.18	8.78 ± 0.28	8.74
	0.76	86.8	7.66 ± 0.06	8.82 ± 0.07	
32.4[305.6]	0.88	43.4	4.23 ± 0.03	9.75 ± 0.07	10.0
35.2[308.4]	0.88	43.4	6.21 ± 0.13	14.3 ± 0.30	13.3
38.1[311.3]	0.88	43.4	7.50 ± 0.24	17.3 ± 0.55	17.8
		$CoCl(dien)(nPentNH_2)_2^{2+}$			
19.7(292.9]	0.76	86.8	2.70 ± 0.2	3.11 ± 0.23	3.00
22.3[295.5]	0.76	86.8	3.07 ± 0.10	3.54 ± 0.11	3.80
25.0[298.2][d]				4.88 ± 0.12	4.83
30.7[303.9]	0.88	42.4	3.35 ± 0.10	7.90 ± 0.23	7.90
		$CoCl(dien)(BzNH_2)_2^{2+}$			
25.0[298.2][d]				0.638 ± 0.18	0.640
37.6[310.8]	0.76	86.8	1.99 ± 0.03	2.29 ± 0.04	2.21
40.4[313.6]	0.76	86.8	2.46 ± 0.05	2.83 ± 0.06	2.87
42.9[316.1]	0.76	86.8	3.06 ± 0.08	3.53 ± 0.09	3.61
45.7[318.9]	0.76	86.8	4.09 ± 0.03	4.71 ± 0.03	4.65
		$CoCl(dien)(py)_2^{2+}$			
25.0[298.2]					0.166
39.8[313.0]	0.76	86.8	0.810 ± 0.01	0.933 ± 0.02	0.982
42.6[315.8]	0.76	86.8	1.20 ± 0.04	1.39 ± 0.05	1.35
45.3[318.5]	0.76	86.8	1.61 ± 0.06	1.85 ± 0.07	1.82
47.7[320.9]	0.80	65.6	1.54 ± 0.04	2.34 ± 0.06	2.36
49.5[322.7]	0.88	42.4	1.32 ± 0.02	3.12 ± 0.04	2.87
52.4[325.6]	0.88	42.4	1.60 ± 0.19	3.77 ± 0.45	3.91
54.8[328.0]	0.88	42.4	2.08 ± 0.06	4.91 ± 0.14	5.04
		$CoCl(dien)(3,5\text{-}Me_2\text{-}py)_2^{2+}$			
25.0[298.2]					0.802
34.9[308.1]	0.76	86.8	2.25 ± 0.03	2.59 ± 0.03	2.51
37.5[310.7]	0.76	86.8	2.92 ± 0.07	3.37 ± 0.08	3.35
39.8[313.0]	0.80	65.6	2.69 ± 0.09	4.11 ± 0.14	4.31
42.6[315.8]	0.88	42.4	2.48 ± 0.04	5.84 ± 0.10	5.82
45.3[318.5]	0.88	42.4	3.27 ± 0.08	7.71 ± 0.19	7.74
47.7[320.9]	0.88	42.4	4.20 ± 0.11	9.90 ± 0.26	9.93
49.5[322.7]	0.88	42.4	5.19 ± 0.09	12.2 ± 0.21	11.9
		$CoCl(dien)(4\text{-}Pr\text{-}py)_2^{2+}$			
25.0[298.2]					0.471
39.8[313.0]	0.80	65.6	1.63 ± 0.02	2.49 ± 0.03	2.54
42.6[315.8]	0.80	65.6	2.18 ± 0.05	3.32 ± 0.07	3.41
45.3[318.5]	0.88	42.4	2.09 ± 0.13	4.94 ± 0.31	4.54
47.7[320.9]	0.88	42.4	2.41 ± 0.05	5.69 ± 0.12	5.82

(continued on facing page)

TABLE V. *(Continued)*

T (°C[K])	[H^+] *M*	[Hg^{2+}]$_i$ m*M*	10^3 k_{obs} s^{-1}	10^2 k_{Hg}[b] M^{-1} s^{-1}	10^2 k_{Hg}(calc)[c] M^{-1} s^{-1}
49.5[322.7]	0.88	42.4	2.96 ± 0.05	6.98 ± 0.12	7.00
52.4[325.6]	0.88	42.4	3.92 ± 0.04	9.25 ± 0.10	9.38
		$CoCl(dien)(3\text{-}Et, 4\text{-}Me\text{-}py)_2^{2+}$			
25.0[298.2]					0.957
34.9[308.1]	0.76	86.8	2.42 ± 0.04	2.79 ± 0.05	2.85
37.5[310.7]	0.76	86.8	3.36 ± 0.11	3.87 ± 0.13	3.76
39.8[313.0]	0.80	65.6	3.17 ± 0.25	4.83 ± 0.34	4.78
42.6[315.8]	0.88	42.4	2.76 ± 0.06	6.50 ± 0.14	6.38
45.3[318.5]	0.88	42.4	3.37 ± 0.10	7.96 ± 0.26	8.37
47.7[320.9]	0.88	42.4	4.50 ± 0.07	10.6 ± 0.17	10.6
49.5[322.7]	0.88	42.4	5.50 ± 0.20	12.9 ± 0.50	12.7
	0.80	65.6	8.35 ± 0.02	12.7 ± 0.03	

---

[a] As $ZnCl_4^{2-}$ salts, using $Hg(NO_3)_2$ dissolved in $HClO_4$. [b] $k_{Hg} = k_{obs}[Hg^{2+}]_i^{-1}$. [c] Calculated using the activation parameters cited in Table VI. [d] See Table III.

TABLE VI. Kinetic Parameters for the Hg^{2+} Assisted Aquation of Some $CoCl(dien)(A)_2^{2+}$ Complexes at 298.2 K (μ = 1.0 *M*).

A	10^3 k_{Hg} (298.2) M^{-1} s^{-1}	E_a kJ mol^{-1}	log *PZ* (s^{-1})	$\Delta S^{\#}_{298.2}$ J K^{-1} mol^{-1}	Ref.
	unsym-fac-cis-Isomers				
NH_3	77.6	65.3 ± 4.5	10.333	−55 ± 9	a
$MeNH_2$	89.8	61.7 ± 3.0	9.760	−66 ± 6	a
$EtNH_2$	56.7	70.0 ± 5.0	11.023	−42 ± 10	a
$nPrNH_2$	52.7	74.9 ± 2.4	11.839	−27 ± 5	a
$nBuNH_3$	46.6	79.0 ± 2.6	12.516	−13 ± 5	a
$iBuNH_2$	40.6				a
$nPentNH_2$	48.3	65.1 ± 5.0	10.089	−60 ± 10	a
$nHexNH_2$	49.2				a
$BzNH_2$	6.40	75.8 ± 1.0	11.086	−41 ± 2	a
py	1.66	93.1 ± 3.3	13.525	+5.7 ± 6	a
4-Pr-py	4.71	88.1 ± 3.9	13.110	−2.2 ± 7	a
3,5-Me_2py	8.02	88.2 ± 1.7	13.351	+2.3 ± 3	a
3Et, 4Mepy	9.57	84.4 ± 1.6	12.758	−9.0 ± 3	a
½en	14.9	58		−93	b
½tmd	100				a
	(H↓)-*unsym-mer-cis*-Isomers				
NH_3	21.4				a
$EtNH_2$	169				a
½en	5.11	81.5		−23	b
	sym-fac-cis-Isomers				
NH_3	28.8				a
½en	4.95	75.2		−4.5	b
½pn	5.58				c
½tmd	47.4				c

---

[a] This work, the cited activation parameters are probably composite and could include contributions from $HgCl^+$, $HgCl_2$ and possibly $Hg(NO_3)^+$ (see text). [b] Ref. [15]. [c] Ref. [17].

TABLE VII. Pseudo-first Order Rate Constants (10^4 k_{isom}, s^{-1}) for the *mer* → *fac* Isomerisation of Some *trans*-Co(dien)(A)-$(OH_2)_2^{3+}$ Complexes at $\mu = 1.0$ *M*.[a]

T	A = $MeNH_2$	$EtNH_2$	$nPrNH_2$	$nBuNH_2$	3,5-Me_2py[d]
25.0 [298.2]	18.7 ± 2.0[c]	21.7 ± 1.6[c]	22.0 ± 1.0[c]	23.1 ± 0.4[c]	8.30 ± 0.15
calc.[b]	18.4	21.8	22.3	23.3	8.17
27.7 [300.9]	25.2 ± 1.4				
calc.[b]	24.7				
30.7 [303.9]	31.6 ± 3.1	42.4 ± 1.0	43.5 ± 2.4	46.7 ± 4.3	17.4 ± 1.0
calc.[b]	34.1	41.1	41.7	43.7	17.9
37.4 [310.6]	69.1 ± 1.0[c]				
calc.[b]	68.2				
37.6 [310.8]		84.8 ± 4.6	85.4 ± 2.2	88.1 ± 2.7	
calc.[b]		85.8	86.1	90.8	
37.7 [310.9]					45.4 ± 0.5[c]
calc.[b]					45.1

[a] In 0.95 *M* HNO_3, 0.02 *M* $Hg(NO_3)_2$. Values quoted are the mean ± the standard deviation. [b] Calculated from the kinetic parameters cited in Table VIII. [c] Means from duplicate determinations. [d] *trans-mer*-$[CoCl_2(dien)(3,5\text{-}Me_2py)]ClO_4 \cdot 2H_2O$ [5] dissolved in 0.1–0.15 mL of DMF before the addition of the HNO_3/Hg^{2+} solution.

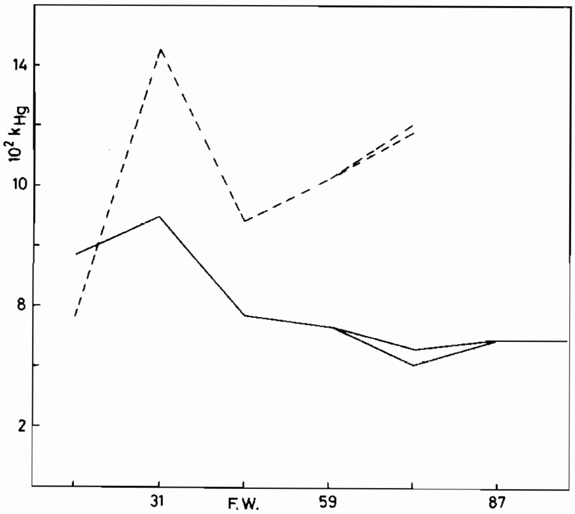

Fig. 4. Plot of 10^2 $k_{Hg}(298)$ ($\mu = 1.0$ *M*), M^{-1} s^{-1} for CoCl-$(en)_2(A)^{2+}$ (------) and *unsym-fac-cis*-CoCl(dien)$(A)_2^{2+}$ (———) *vs.* formula weight of the alkylamine, A.

$HClO_4$ (Table IV, footnote *i*). This is presumably due to $HgNO_3^+$ as the predominant Hg^{2+} species in 0.9 *M* HNO_3 [16] with the lower charge facilitating the approach of the reactants.

In $HClO_4$ medium, variation in $[H^+]$ from 0.88–0.76 *M* had no effect on the reaction rate. Variation in ionic strength, however, does have a considerable effect and a change in μ from 1.0 to 0.5 *M* results in a decrease in k_{Hg} by a factor of 1.5 (Table IV, footnote *k*).

The activation parameters cited in Table VI are probably composite quantities, with contributions from Hg^{2+}, $HgCl^+$, $HgCl_2$ and possibly $HgNO_3^+$. Nevertheless, they accurately reflect the variation of reaction rate with temperature in the medium used and have been used to calculate $k_{Hg}(298)$ where this was not measured directly.

For the *unsym-fac-cis*-CoCl(dien)$(A)_2^{2+}$ (A = alkylamine) cations, the rate of Hg^{2+} assisted aquation is almost independent of alkylamine chain length from A = $nPrNH_2$ to A = $nHexylNH_2$. Figure 4 shows a plot of k_{Hg} *vs.* alkylamine formula weight for the *unsym-fac-cis*-CoCl(dien)$(A)_2^{2+}$ and *cis*-CoCl$(en)_2(A)^{2+}$ [4] complexes. The systems show obvious similarity and a common mechanism presumably operates.

As with thermal aquation, the order of reactivity with respect to the non-replaced ligands is en < $(NH_3)_2$ < tmd for both *unsym-* and *sym-fac-cis-* geometries (Table VI) and the arguments presented to account for this order in the thermal aquation are presumably applicable to the Hg^{2+} assisted aquation.

Isomerisation Reactions

Kinetic parameters for the rates of *mer* → *fac* diethylenetriamine isomerisation for five additional [5] *trans-mer*-Co(dien)(A)$(OH_2)_2^{3+}$ complexes are presented in Tables VII and VIII. An increase in the alkylamine chain length from A = $MeNH_2$ to $nBuNH_2$ has almost no effect on the kinetic parameters, but activation energies are higher and activation entropies more positive for complexes with A = NH_3, benzylamine and pyX.

Inspection of Fig. 2 shows that the trigonal bipyramid transition states proposed in the Hg^{2+} assisted or thermal aquation of *unsym-fac-cis*-CoCl-(dien)$(A)_2^{2+}$ and the *mer* → fac-Co(dien)(A)$(OH_2)_2^{3+}$ isomerisation are rather similar, although different distortions are required for their generation. While there is little correlation in the values for the rate

TABLE VIII. Kinetic Parameters for the Rate of *mer* to *fac* Isomerisation of Some *mer*-Co(dien)(A)$(OH_2)_2^{3+}$ Complexes at 298.2 K.

No.	A	$k_{isom}(298)$ (s^{-1})	log *PZ* (s^{-1})	E_a (kJ mol^{-1})	$\Delta S^{\#}_{298}$ (J K^{-1} mol^{-1})	Ref.
1	NH_3	1.62×10^{-3}	14.763	100 ± 1.0	+29 ± 2	a
2	$MeNH_2$	1.84×10^{-3}	11.509	81.3 ± 2.6	−33 ± 5	b
3	$EtNH_2$	2.18×10^{-3}	11.991	83.6 ± 1.5	−24 ± 3	b
4	$nPrNH_2$	2.23×10^{-3}	11.804	82.5 ± 3	−27 ± 6	b
5	$nBuNH_2$	2.33×10^{-3}	11.912	83.0 ± 4	−25 ± 8	b
6	$BzNH_2$	1.37×10^{-3}	13.937	96.0 ± 0.5	+13 ± 1	c
7	py	4.65×10^{-4}	17.039	116 ± 0.6	+73 ± 2	a
8	3,5-Me_2py	8.17×10^{-4}	15.069	104 ± 2	+35 ± 4	b

[a] Ref. [5]. [b] This work.

TABLE IX. Second Order Rate Constants for the Base Hydrolysis of Some $CoX(N)_5^{2+}$ Complexes (μ = 0.1 *M* KCl).

Complex	T °C [K]	k_{OH}[a,b] M^{-1} s^{-1}	k_{OH}(calc)[c] M^{-1} s^{-1}
$CoCl(NH_3)_5^{2+}$	25.0 [298.2]	0.47(1)[d]	
cis-$CoCl(en)_2(NH_3)^{2+}$	25.0 [298.2]	8.1[e]	
sym-fac-cis-$CoCl(dien)(NH_3)_2^{2+}$[f]	25.0 [298.2]	0.704 ± 0.01(8)	0.695
	30.3 [303.5]	1.20 ± 0.06(6)	1.26
	35.1 [308.3]	2.27 ± 0.03(4)	2.12
	40.3 [313.5]	3.59 ± 0.06(4)	3.66
sym-fac-cis-$CoBr(dien)(NH_3)_2^{2+}$	25.0 [298.2]	1.87 ± 0.11(6)	
	40.3 [313.5]	12.3 ± 0.2(2)	
sym-fac-cis-$CoCl(dien)(en)^{2+}$[g]	25.0 [298.2]	4.81 ± 0.18(6)	4.71[h]
	30.3 [303.5]	8.69 ± 0.2(4)	9.07
	35.1 [308.3]	15.9 ± 0.8(4)	16.1
	40.3 [313.5]	30.0 ± 0.9(6)	29.5

[a] $k_{OH} = k_{obs}[OH^-]^{-1}$. [b] Numbers in parenthesis are the number of kinetic runs used to estimate the mean k_{OH} ± the standard deviation. [c] Calculated k_{OH} based on the activation parameters cited in footnotes f and g. [d] D. A. Buckingham, I. I. Olsen and A. M. Sargeson [19] report $k_{OH} = 0.6$ M^{-1} s^{-1} for this reaction at 25.4 °C [298.6 K]. [e] Ref. [20]. [f] E_a = (84.3 ± 1.5) kJ mol^{-1}, $\Delta S^{\#}_{298}$ = (+26.5 ± 3.0) J K^{-1} mol^{-1}. [g] E_a = 93.2 ± 1.2 kJ mol^{-1}, $\Delta S^{\#}_{298}$ = (+72 ± 2.4) J K^{-1} mol^{-1}. [h] R. W. Hay and K. B. Nolan [10] report k_{OH} = 7.26 M^{-1} s^{-1} for this reaction.

constants (k_{Hg}, k_{isom}) for these two reactions, Fig. 5 shows a plot of E_a(Hg) *vs.* E_a(isom), together with a line of unit slope. Although there is some scatter, these data give encouragement to the concept of a similar transition state for both reactions.

Base Hydrolysis Reactions

The activation parameters (Table IX) for the base hydrolysis of *sym-fac-cis*-CoCl(dien)$(A)_2^{2+}$ (A = NH_3, 0.5en [10]) are normal for this type of reaction [4] and the value of $k_{OH}(298)$ increases in the order NH_3 < 0.5en < 0.5tmd [12] (0.70, 4.7, 10.6 M^{-1} s^{-1}, respectively). The apparent similarity of the k_{OH} values may only be a consequence of the larger differences manifested in the activation parameters, E_a (kJ mol^{-1}) = 84.3, 93.2, 123 and $\Delta S^{\#}_{298}$ (J K^{-1} mol^{-1}) = +26, +72, +179 respectively. Nevertheless, these are small 'ring size' effects on K_{OH} and proton acidity (involving a conjugate base mechanism [4]) is probably more important than distortion to a favourable transition state.

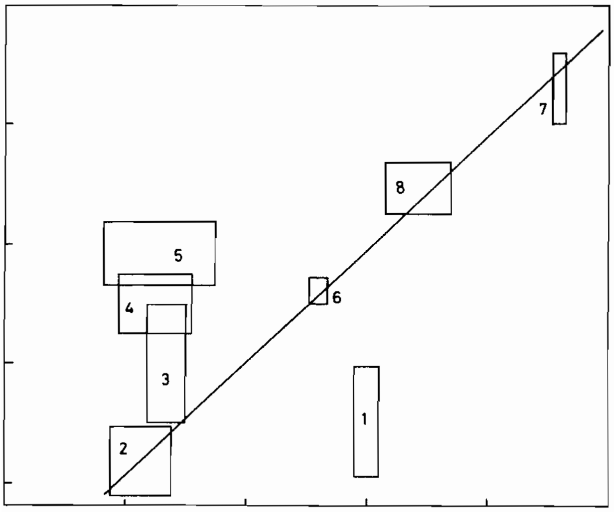

Fig. 5. Plot of E_a(Hg) (abscissa) *vs.* E_a(isom) (ordinate) together with a line of unit slope. The numbers correspond to the complexes listed in Table VIII and each axis division corresponds to 10 kJ mol^{-1}.

Acknowledgements

We thank the Universities Grants Committee for providing funds to purchase instruments used in this research and the University of Canterbury for research grant 78/3/11.

References

1 Foo Chuk Ha, D. A. House and J. W. Blunt, *Inorg. Chim. Acta, 33,* 269 (1979).
2 J. W. Blunt, Foo Chuk Ha and D. A. House, *Inorg. Chim. Acta, 32,* L5 (1979).
3 R. G. Holloway, D. A. House and B. R. Penfold, *Cryst. Struct. Commun., 7,* 139 (1978).
4 D. A. House, *Coord. Chem. Rev., 23,* 223 (1977).
5 D. A. House, *Inorg. Chim. Acta, 30,* 281 (1978).
6 A. I. Vogel, 'Quantitative Inorganic Analysis', 3rd Edn., Longmans, Green, London, 274 (1962).
7 B. Bosnich and F. P. Dwyer, *Australian J. Chem., 19,* 2045 (1966).
8 A. R. Gainsford and D. A. House, *Inorg. Chim. Acta, 3,* 367 (1969); *5,* 544 (1971).
9 J. H. Johnston and A. G. Freeman, *J. Chem. Soc. Dalton,* 2153 (1975); A. V. Ablov, M. D. Mazus, E.V. Popa, T. I. Malinovskii and V. N. Biyushkin, *Dokl. Akad. Nauk SSSR, 194,* 701 (1970).
10 R. W. Hay and K. B. Nolan, *J. Inorg. Nucl. Chem., 38,* 2118 (1976).
11 J. McKenzie and D. A. House, *J. Inorg. Nucl. Chem., 39,* 1843 (1977); A. J. Cunningham, D. A. House and H. K. J. Powell, *J. Inorg. Nucl. Chem., 33,* 572 (1971).
12 Lim Say Dong and D. A. House, *Inorg. Chim. Acta, 19,* 23 (1976).
13 B. M. Oulaghan and D. A. House, *Inorg. Chem., 17,* 2197 (1978).
14 D. Keppert, *Prog. Inorg. Chem., 23,* 1 (1978).
15 Tee Kim Huan, J. N. Mulvihill, A. R. Gainsford and D. A. House, *Inorg. Chem., 12,* 1517 (1973).
16 A. R.Davis and D. E. Irish, *Inorg. Chem., 7,* 1699 (1968).
17 B. S. Dawson and D. A. House, *Inorg. Chem., 16,* 1354 (1977).
18 C. Bifano and R. G. Linck, *Inorg. Chem., 7,* 908 (1968).
19 D. A. Buckingham, I. I. Olsen and A. M. Sargeson, *Inorg. Chem., 7,* 174 (1968).
20 R. W. Hay and P.L. Crop, *J. Chem. Soc. A,* 42 (1969).