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Kinetics of *mer* to *fac* Isomerisation of Diethylenetriamine in Some Octahedral Cobalt(III) Complexes

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The trans-*$Co(dien)(A)(OH_2)_2^{3+}$ cations (A = OH_2, NH_3 pyridine, benzylamine, cyclohexylmethylamine and cyclohexylamine) have been generated in aqueous acidic solution (0.95* M *HNO_3) by the Hg^{2+} (0.02* M *$Hg(NO_3)_2$) assisted chloride release from the* trans-*$[CoCl_2(dien)(A)]ClO_4$ salts. Rates of* mer *to* fac *isomerisation have been measured spectrophotometrically in this medium (μ = 1.0* M*) over a 15 K temperature range. At 298.2 K, the kinetic parameters for the isomerisation, in the order 10^4 k_{isom} (298.2) (s^{-1}), E_a (kJ mol^{-1}), and $\Delta S_{298}{}^{\#}$ (J K^{-1} mol^{-1}) for the above A groups, respectively, are: 2.47, 108.7, +42.3; 16.2, 100.0, +29; 4.65, 116.3, +73; 13.7, 95.8, +13.5; 25.3, 92.7, +8; and 46.0, 96.3, +25. The rate of* mer → fac *isomerisation of $Co(dien)(OH_2)_3^{3+}$ in $HClO_4$ is accelerated by NO_3^- ions and at 313.2 K (μ = 1.0* M*) $k_{obs} = k_1 + k_2[NO_3^-]$ where $k_1 = 3.1 \times 10^{-4}$ s^{-1} and $k_2 = 17.1 \times 10^{-4}$* M^{-1} *s^{-1}. Rates of* mer *to* fac *dien isomerisation have also been measured (μ = 1.0* M*, 0.95* M *$HClO_4$, 0.02* M *$Hg(NO_3)_2$) for the* mer-*$Co(AA)(dien)(OH_2)^{3+}$ (AA = $(NH_3)_2$, tmd, pn) cations. Kinetic parameters, in the order 10^7 k_{isom} (298.2), E_a, $\Delta S^{\ddagger}_{298}$ (units as above) are: 9.7, 115, +17; 71.7, 105, –1; and 1.7, 126, +39 respectively. The increase in the rate of isomerisation of* trans-*$Co(dien)(NH_3)(OH_2)_2^{3+}$ relative to* mer-*$Co(dien)(NH_3)_2(OH_2)^{3+}$ is reflected mainly in a decrease in activation energy.*

Introduction

Diethylenetriamine is a tridentate polyamine ligand that can form two fused five-membered chelate rings on coordination with a transition metal ion. In an octahedral complex, *e.g.* with Co(III), the ligand can adopt either the meridional or facial configuration [1]. The reasons for the adoption of a particular configuration are not yet established – aniono ligands, *e.g.* NO_2^-, N_3^- or Cl^- in the other three octahedral sites appear to favour the *mer-* configuration [2–4] while neutral ligands such as dien [5] or H_2O [4] can adopt either arrangement. As a consequence, *mer* to *fac* aqua isomerisation is often observed when the aniono ligands are rapidly removed [6–9].

We have prepared a series of *trans*-$CoCl_2(dien)(A)^+$ complexes (A = NH_3 [9], py, $BzNH_2$, cyclohexNH_2, cyclohexCH_2NH_2) [10] which rapidly produce the *trans*-$Co(dien)(A)(OH_2)_2^{3+}$ ions by removal of the coordinated Cl^- in acidic solution with Hg^{2+}. The rate of *mer* → *fac* isomerisation can then be measured spectrophotometrically.

An additional, but related series of *mer*-$CoCl(dien)(AA)^{2+}$ complexes (AA = $(NH_3)_2$ [11], en [12], pn [13], tmd [14, 15]) have also been prepared and a similar generation of the *mer*-$Co(dien)(AA)(OH_2)^{3+}$ ions allows the *mer* → *fac* isomerisation rate to be measured.

Perhaps the most significant observation is that *mer*-$Co(dien)(NH_3)_2(OH_2)^{3+}$ isomerises about 1000 times more slowly than the *trans*-$Co(dien)(NH_3)(OH_2)_2^{3+}$ ion.

Experimental

The commercially available amines were used without further purification. All other chemicals were the best reagent grade. Acid concentrations of solutions used for kinetic runs were determined by titration with standard alkali. The $Hg(NO_3)_2$ concentration was calculated from weighed amounts of the monohydrate. $CoCl_3(dien)$ and *trans*-$[CoCl_2(dien)(NH_3)]ClO_4$ were prepared by the literature methods [4, 9, 16, 17].

CAUTION: Although we have experienced no difficulties with the perchlorate salts of the complexes mentioned herein, these compounds should be treated as potentially explosive and handled with care.

trans-*(Amine) (diethylenetriamine) (dichloro) cobalt(III) Perchlorate:* trans-*$[CoCl_2(dien)(A)]ClO_4$*

These complexes, together with *fac*-$[CoCl(dien)(A)_2]ZnCl_4$, are isolated from the work-up of the reaction between *mer*-$CoCl_3(dien)$ and 2.5 mol of the amine in water or aqueous methanol. Thus, 10 g of $CoCl_3(dien)$ was slurried with 10 ml of water and 7.5 ml of pyridine added. The mixture was heated at 80 °C (bunsen) for 5–10 min until all the solid dissolved and a reddish purple solution formed. Addi-

TABLE I. Analytical Data for *trans* [$CoCl_2$(dien)(A)]ClO_4 and *mer*-[CoCl(dien)(AA)]$ZnCl_4$ Salts and Isosbestic Points Observed in the Isomerisation of the Corresponding Aqua Ions.[a]

A (or AA)	F.W. (calc.)	%Cl (calc.)	%Cl (found)[b]	Isosbestic Points (± 2 nm)		
Cl	268.5	39.7	39.5		498[c]	585[c]
					498	587
NH_3	350	20.3	20.0	376[d]	468[d]	564[d]
				376	466	562
py	383.5[e]	27.7	27.8		465	564
3,5-lut[f]	440[g]	16.1	15.9			
$BzNH_2$	476[g]	14.9	15.1	384	455	552
cyclohexNH_2[h]	468[g]	15.2	15.3			
cyclohexCH_2NH_2	482[g]	14.7	14.5	373	464	555
$(NH_3)_2$[i]	439	40.4	40.2		502	565
pn[h]	477	37.2	37.0			
tmd[h]	477	37.2	37.1			

[a] This research unless noted otherwise. [b] Non-perchlorate chloride determined gravimetrically as AgCl. [c] Reference 6. [d] M. C. Couldwell, *Ph.D. Thesis*, University of Canterbury, Christchurch, New Zealand (1973). [e] As the chloride dihydrate salt. [f] Not used for rate studies. [g] As the dihydrate. [h] Isosbestic points not determined. [i] Visible absorption spectral parameters (0.1 *M* HCl): λ(nm), ε (M^{-1} cm^{-1}): 530sh, 58.5; 476 max, 75.1; 418 min, 32.5; 370 max, 71.8; 333 min, 39.6.

TABLE II. Visible Absorption Spectra of some *trans*-$CoCl_2$(dien)$(A)^+$ Complexes in 3*M* HCl at 22–24 °C.

A	λ (max)	λ (min)	λ (max)	λ (min)	λ (max)	λ (min)
NH_3	620 (40.9)	550 (22.4)	460 (80.3)		430sh (76.4)	395 (56.3)
NH_3[a]	617 (40.5)	545 (15.7)	460sh		435 (77.5)	376 (44.3)
$BzNH_2$	625 (43.9)	552 (20.2)	465sh (97.4)		430 (101)	378 (51.0)
cyclohexNH_2	627 (40.7)	565 (21.0)	470 (102)		435sh (99)	400 (75.7)
cyclohexCH_2NH_2	625 (33.5)	568 (22.6)	470 (111)			410 (73.6)
py	622 (41.7)	550 (15.2)	462 (92.0)	450 (91.4)	430 (93.1)	378 (50.0)
3,5-lut	622 (41.5)	552 (15.8)	465 (96.0)	448 (95.2)	435 (95.4)	395 (70.7)

[a] In 0.3 *M* HNO_3 (reference 9).

tion of HCl (25 ml, 12 *M*) to the hot solution and cooling, caused the precipitation of *trans*-[$CoCl_2$-(dien)(py)]Cl·$2H_2O$ (1.5 g). This was filtered from the red solution and washed with 2-propanol and ether. The mother liquor was warmed to 60 °C and the addition of $ZnCl_2$ (15 g) resulted in red crystals (10 g) of *fac*-[CoCl(dien)$(py)_2$]$ZnCl_4$, slightly contaminated with further amounts of the green *trans*-dichloro. The red salt was purified by recrystallisation from dilute HCl, followed by conc. HCl containing $ZnCl_2$. 3,5-lutidine behaved similarly, but the perchlorate salt of the *trans*-dichloro was isolated by the addition of $HClO_4$ to the mother liquor after recrystallisation of the initially formed red-green mixture and removal of *fac*-[CoCl(dien)$(3,5\text{-lut})_2$]$ZnCl_4$. The other amines did not form crystalline chlorides after the initial addition of HCl to the reaction mixture, but red *fac*-[CoCl(dien)$(A)_2$]$ZnCl_4$ salts were obtained by the addition of $ZnCl_2$. Addition of $HClO_4$ to the mother liquor resulted in the precipitation of the *trans*-dichloro perchlorate salts. These green products were recrystallised by gentle warming with 0.1 *M* NaOH until all the solid dissolves (too much heating results in amine loss), followed by the addition of conc. HCl and $HClO_4$. Analytical data are presented in Table I. Visible absorption spectral parameters were determined in 3 *M* HCl (Table II) to prevent the formation of chloroaqua ions.

TABLE III. Visible Absorption Spectral Parameters for some *mer* and *fac*[a] Co(dien)(A)$(OH_2)_2^{3+}$ Complexes.[b]

A	Configuration	λ (max)	λ (max)	λ (min)	λ (max)	λ (min)
NH_3	*mer*[c]	536sh	453	406	380	
		(33.5)	(83.1)	(58.7)	(61.6)	
	fac[a,c]		496	418	357	
			(92.1)	(25.1)	(71.6)	
$BzNH_2$	*mer*	520sh	485	444	390sh	
		(70.8)	(78.9)	(59.3)	(97.1)	
	fac[a]		502	424	370sh	
			(121)	(32.2)	(97.3)	
cyclohexNH_2	*mer*		490	428		
			(91.0)	(58.4)		
	fac[a]		500	422	350	335
			(118)	(36.2)	(190)	(184)
cyclohexCH_2NH_2	*mer*		472	420		
			(98)	(65.7)		
	fac[a]		490	418		
			(120)	(38.5)		
py	*mer*	570sh	465	425	395sh	
		(36.2)	(88.1)	(70.8)	(80.6)	
	fac[a]		498	415	360	335
			(122)	(23.9)	(85.8)	(67.6)
3,5-lut	*mer*		477	420		
			(83.5)	(54.4)		
	fac[a]		500	415	355sh	
			(119)	(19.9)	(105)	

[a] Spectral parameters cited for the *fac* isomer are in fact those for the *mer* ⇌ *fac* equilibrium mixture (see text). [b] In 0.57 *M* $HClO_4$, 0.012 *M* $Hg(NO_3)_2$, the dichloro perchlorate salts were dissolved in 10 ml of water before diluting to 25.0 ml with 1.0 *M* $HClO_4$, 0.02 *M* $Hg(NO_3)_2$. [c] In 1.0 *M* HNO_3 (reference 9).

Kinetics

Small quantities of the *trans*-dichloro salts (or *mer*-$CoCl_3$(dien)) were dissolved in 0.95 *M* HNO_3 containing 0.02 *M* $Hg(NO_3)_2$ to produce the *trans*-diaqua ions. The orange solutions (visible absorption spectral parameters in Table III) were transferred to a jacketed 5.0 cm spectrophotometer cell and after 1–2 min (for thermal equilibrium) the fixed wavelength or repeat scan modes were initiated. Similar techniques were used for the *mer*-Co(dien)-(AA)$(OH_2)^{3+}$ ions except that 0.95 *M* $HClO_4$ containing 0.02 *M* $Hg(NO_3)_2$ was used as the reaction medium. The effect of nitrate ion on the *mer* → *fac* Co(dien)$(OH_2)_3^{3+}$ isomerisation was investigated in a series of $HNO_3/HClO_4$, $[H^+] = 1.0$ *M*, $\mu \sim 1.0$ *M* solutions containing ~ 0.02 *M* $Hg(NO_3)_2$. The total $[NO_3^-]$ was determined spectrophotometrically at 300 mn using a value of 5.5 M^{-1} cm^{-1} for the molar absorptivity of NO_3^- [18]. In 0.2 cm cells, the maximum absorbance was 1.10.

First order rate constants were calculated from the absorbance *vs.* time data using the previously described methods [7] and from the variation of k_{isom} with temperature, the activation parameters were calculated [19].

Results

Preliminary investigations on the *mer* → *fac* isomerisation of the *trans*-Co(dien)$(NH_3)(OH_2)_2^{3+}$ ion showed that the value of the observed rate constant was dependent upon hydrogen ion concentration and ionic strength. Similar observations had also been made for the *mer* → *fac* isomerisation of *mer*-Co(dien)$(OH_2)_3^{3+}$ [6]. To avoid these complications, the aqua ions were generated from the chloro precursors by Hg^{2+} assisted (0.02 *M* as $Hg(NO_3)_2$) chloride ion release in 0.95 *M* H^+ at $\mu = 1.0$ *M*, rather than by ion exchange, base hydrolysis and acidification [9]. HNO_3 was used as the medium for the diaqua ions, as the parent dichloro perchlorate salts were only slowly soluble in $HClO_4$ containing Hg^{2+}. The latter medium was quite satisfactory for the mono-aqua ions as chloro tetrachlorozincate(II) salts were used as starting materials. In the appropriate medium, the chloride release reaction was complete within the time of dissolution, mixing, transference to the spectrophotometer cell and temperature equilibrium (2–5 min).

The visible absorption spectra of the *trans*-Co(dien)$(NH_3)(OH_2)_2^{3+}$ ion generated in this manner (Table III) was identical with that produced from the

TABLE IV. 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 °C [K]/A	OH_2	py	$BzNH_2$	NH_3	$cyclohexCH_2NH_2$	$cyclohexNH_2$
14.9 [288.1]		0.902 ± 0.05		3.93 ± 0.07	6.82 ± 0.05	11.8 ± 0.1
calc.[b]		0.899		3.94	6.81	11.8
20.0 [293.2]			7.15 ± 0.2	8.18 ± 0.04	13.5 ± 0.2	23.9 ± 0.4
calc.[b]			7.13	8.14	13.4	23.7
25.0 [298.2]	2.49 ± 0.05	4.69 ± 0.03	13.8 ± 0.7	16.2 ± 0.6	24.9 ± 1.0[c]	45.6 ± 0.2[c]
calc.[b]	2.47	4.65	13.7	16.2	25.3	46.0
27.0 [300.2]	3.31 ± 0.02[c]	6.30 ± 0.16[c]	17.7 ± 1.1	20.9 ± 0.5	33.3 ± 0.8	60.6 ± 1.3
calc.[b]	3.32	6.36	17.8	21.2	32.5	59.7
30.0 [303.2]			26.0 ± 0.3	32.1 ± 0.6		
calc.[b]			26.0	31.5		
33.0 [306.2]			38.1 ± 0.9	46.2 ± 0.8		
calc.[b]			37.8	46.5		
35.0 [308.2]	10.3 ± 0.4	21.5 ± 0.6				
calc.[b]	10.3	21.3				
40.0 [313.2]	20.2 ± 0.2[d]					
calc.[b]	20.2					

[a] In 0.95 *M* HNO_3, 0.02 *M* $Hg(NO_3)_2$ Values quoted are the mean ± the standard deviation of 10–12 point-by-point calculations, for each run, spanning at least two half lives. [b] Calculated from the kinetic parameters cited in Table VI. [c] Means from duplicate determinations. [d] In 0.95 *M* $HClO_4$, 0.02 *M* $Hg(NO_3)_2$, 10^4 k_{isom} = (3.9 ± 0.09) s^{-1}, see Table VII.

TABLE V. Pseudo-first-order Rate Constants (10^5 k_{isom}, s^{-1}) for the *mer* → *fac* Isomerisation of Some $Co(OH_2)(dien)(AA)^{3+}$ Complexes at $\mu = 1.0$ *M*.[a]

AA	Configuration	T °C [K]	10^5 k_{obs} (s^{-1}) ± 5%	10^5 k_{calc}[b] (s^{-1})
$(NH_3)_2$	a,bf,cde	65.4 [338.6]	27.0	24.4
		72.3 [345.5]	49.7	55.1
			51.0	
		76.2 [349.4]	82.1	86.1
		79.5 [352.7]	128	125
			138	
pn	a,fb,cde	69.6 [342.8]	12.1	12.4
		74.9 [348.1]	25.1	24.4
		79.8 [353.0]	45.7	44.6
		85.0 [358.2]	81.0	83.2
tmd	a,bf,cde	46.2 [319.4]	11.9	11.8
		54.1 [327.3]	30.1	30.6
		58.6 [331.8]	51.6	51.6
			52.0	51.6
		60.5 [333.7]	64.2	64.0

[a] In 0.95 *M* $HClO_4$, 0.02 *M* $Hg(NO_3)_2$. [b] Calculated from the kinetic parameters cited in Table VI.

dichloro by base hydrolysis and acidification [9]. Spectrophotometric scans showed sharp isosbestic points (Table I) and the final spectrum (Table III) corresponded to that found previously [9] for a *mer–fac* equilibrium mixture of 83 ± 4% *fac*-diaqua. The other diaqua ions behaved similarly but no attempt was made to establish the final position of equilibrium.

The mono-aqua *mer*-$Co(dien)(AA)(OH_2)^{3+}$ ions isomerised much more slowly, but good isosbestic points (Table I) were also observed in the spectral scans, and the final absorption spectra corresponded well to those produced by Hg^{2+} assisted aquation from the predicted *fac*-$CoCl(dien)(AA)^{2+}$ isomers.*

Tables IV and V present the pseudo-first-order rate constants observed under the cited conditions. The variation in rate constant with temperature has allowed us to calculate [19] activation parameters (Table VI) associated with these reactions.

While changes in the medium (ionic strength and counter ion) do not significantly change the activation energy calculated for the isomerisation of *mer*-$Co(dien)(OH_2)_3^{3+}$ (Table VI), the value of k_{isom} (obs) is certainly dependent on these conditions. Wilairat and Garner [6] have shown that a change in ionic strength (μ) from 3.5 *M* to 0.7 *M* ($NaClO_4$) results in a rate increase of 1.3 for this reaction. The

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*There are two possible *fac*-$CoCl(dien)(AA)^{2+}$ isomers. The ones produced from the *mer*-$Co(dien)(AA)(OH_2)^{3+}$ isomerisation are predicted (and found) to have configuration I in Figure 1.

TABLE VI. Kinetic Parameters for the Rate of *mer* to *fac* Isomerisation of Some *mer*-Co(dien)(A)(AA)$^{3+}$ Complexes at 298.2 K (μ = 1.0 *M*).

A	AA (configuration)	k_{isom} (298.2) (s^{-1})	log PZ (s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ (J K^{-1} mol^{-1})	Reference
OH_2	$(OH_2)_2$	3.37×10^{-5}	14.6	108 ± 3	+26 ± 12	a
		2.47×10^{-4}	15.440	109 ± 0.2	+42.3 ± 0.4	b
NH_3	$(OH_2)_2$	1.62×10^{-3}	14.736	100 ± 0.6	+29 ± 2	b
$BzNH_2$	$(OH_2)_2$	1.37×10^{-3}	13.937	95.8 ± 0.5	+13.5 ± 1	b
cyclohexCH_2NH_2	$(OH_2)_2$	2.53×10^{-3}	13.656	92.7 ± 1.5	+8 ± 3	b
cyclohexNH_2	$(OH_2)_2$	4.60×10^{-3}	14.536	96.3 ± 1.0	+25 ± 2	b
py	$(OH_2)_2$	4.65×10^{-4}	17.039	116 ± 0.6	+73 ± 2	b
OH_2	en (K)	1.22×10^{-7}	14.861	124 ± 3	+31 ± 6	c, f
OH_2	pn (B)	1.67×10^{-7}	15.295	126 ± 3	+39 ± 6	d,g
OH_2	$(NH_3)_2$(K)	9.70×10^{-7}	14.109	115 ± 8	+17 ± 16	d, f
OH_2	Metmd (I′)	15.1×10^{-7}	15.178	120 ± 6	+37 ± 12	e, g
OH_2	Metmd (II′)	11.2×10^{-7}	9.96	91 ± 5	−63 ± 10	e, f
OH_2	tmd (a)	71.7×10^{-7}	13.191	105 ± 1	−1 ± 2	d, f, h
trans-$Co(en)_2(OH_2)_2^{3+}$ → *cis*		7.0×10^{-6}		107.3 ± 0.5	+8 ± 1	i
trans-$Co(en)_2(NH_3)$-$(OH_2)^{3+}$ → *cis*		1.66×10^{-8}		145 ± 2	+84 ± 4	j

[a] Reference 6, limiting values for the acid independent path at μ = 3.5 *M* ($NaClO_4$). [b] This research in 0.95 *M* HNO_3, 0.02 *M* $Hg(NO_3)2$. [c] Reference 7, in 0.76 *M* $HClO_4$, 0.24 *M* $NaClO_4$. [d] This research in 0.95 *M* $HClO_4$, 0.02 *M* $Hg(NO_3)_2$. [e] Reference 34, in 0.95 *M* $HClO_4$, 0.02 *M* $Hg(NO_3)_2$. [f] The a,bf,cde-(H↓)- isomer, reference 34. [g] The a,fb,cde-(H↓)- isomer, reference 34. [h] References 14, 15. [i] Reference 23 in 1.0 *M* $HClO_4$. [j] Reference 27, limiting values for the acid independent path at μ = 0.1 *M* ($NaClO_4$).

TABLE VII. Effect of $[NO_3^-]$ on the *mer* to *fac* Isomerisation of *mer*-$Co(dien)(OH_2)_3^{3+}$ at 40 °C.[a]

$[NO_3^-]$[b] (*M*)	10^4 k_{isom} (obs)[c] (s^{-1})	10^4 k_{isom}(calc.)[d] (s^{-1})
1.0	20.2 ± 0.2	20.2
0.81	17.2 ± 0.2	17.0
0.63	13.7 ± 0.3	13.9
0.54	13.0± 0.4	12.3
0.41	10.5 ± 0.1	10.1
0.22	7.1 ± 0.1	6.9
0.06	3.9 ± 0.1	4.1
0.00	3.5 ± 0.1[e]	3.1

[a] $[H^+]$ = 1.0 *M*, $\mu \sim$ 1.0 *M*, $Hg^{2+} \sim 0.02$ *M*. [b] $[NO_3^-]$ determined spectrophotometrically at 300 nm (ϵ_{max} = 5.5 M^{-1} cm^{-1}) ± 5%. [c] Mean of at least two determinations. [d] Calculated from the equation $k_{obs} = k_1 + k_2[NO_3^-]$ where $k_1 = 3.1 \times 10^{-4}$ s^{-1} and $k_2 = 17.1 \times 10^{-4}$ M^{-1} s^{-1}. [e] Reference 6, $[H^+]$ = 1.061 *M* ($HClO_4$), μ = 3.5 *M* ($NaClO_4$).

change in counter ion is also significant and using HNO_3 as a medium results in an increase in k_{isom} (obs) of 5 times that observed in $HClO_4$ (Table IV, footnote d). This effect has been further investigated (Table VII) and the observed rate constant at 313.2 K can be expressed as

$$k_{obs} = k_1 + k_2[NO_3^-]$$

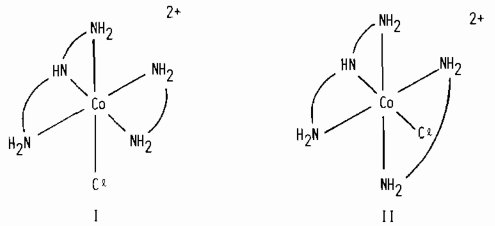

Figure 1. Possible isomers of *fac*-CoCl(dien)(AA)$^{2+}$.

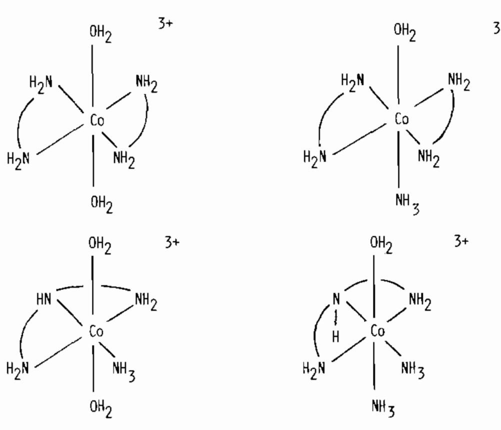

Figure 2. Relationships between *trans*-$Co(en)_2(OH_2)_2^{3+}$, *trans*-$Co(en)_2(NH_3)(OH_2)^{3+}$, *mer*-$Co(dien)(NH_3)(OH_2)_2^{3+}$ and *mer*-(H↓)-$Co(dien)(NH_3)_2(OH_2)^{3+}$. Values of 10^8 $k_{isom}(298)(s^{-1})$ are in parenthesis and values of E_a (kJ mol^{-1}) in square brackets.

where the values of k_1 and k_2 are given in footnote d of Table VII.

This suggests that the NO_3^- ion directly participates in the reaction according to the equations

$$\begin{tikzcd}
mer\text{-}R(OH_2)_3^{3+} + NO_3^- \arrow[r, phantom, "\rightleftharpoons K_m \Longrightarrow"] \arrow[d, "k_1"] & mer\text{-}R(NO_3)(OH_2)_2^{2+} + H_2O \arrow[d, "k_1'"] \\
fac\text{-}R(OH)_2)_3^{3+} + NO_3^- \arrow[r, phantom, "\rightleftharpoons K_f \Longrightarrow"] & fac\text{-}R(NO_3)(OH_2)_2^{2+} + H_2O
\end{tikzcd}$$

where R = Co(dien) and $k_2 = k_1'K_m$. If $K_m \sim 9 \times 10^{-2}$ [21], then $k_1' \sim 200 \times 10^{-4}\ s^{-1}$ at 313.2 K, however, this is about 10 times faster than the aquation of $Co(NO_3)(NH_3)_5^{2+}$ [22] or *cis*-$Co(NO_3)(NH_3)_4(OH_2)^{2+}$ [23].

Discussion

Trans to *cis* isomerisation in $Co(en)_2(A)(B)^{3+}$ systems are reasonably well studied reactions, where A = B = OH_2 [24–26] or A = NH_3, B = OH_2 [27, 28] and while Basolo and Pearson [29] comment on the possible mechanistic differences between the two systems, we feel that the 400 times difference in rate (Table VI and Figure 2) warrants further discussion. Figure 2 shows the relationship between these *trans*-bis(ethylenediamine) complexes and the *mer*-(dien)-(NH_3) systems studied here.

Assuming a water exchange mechanism and constant solvation effects (all have +3 ionic charge and similar activation entropies) the rates of isomerisation probably reflect the ease of dissociation of the leaving group (H_2O). This in turn is related to (i) the group in the *trans* position and (ii) the type of chelate ring system ((dien)(NH_3) or $(en)_2$) present.

For a constant chelate ring system, the *trans* labilising effect on the aqua ligand is $OH_2 \gg NH_3$ as illustrated in Figure 2 and a decrease of 15–30 kJ mol^{-1} in activation energy is observed in changing the *trans* donor atom from N (NH_3) to O (H_2O). It is tempting to attribute this effect to differences in polarisation ("hardness" [30]) of the two donor atoms, but the range of atoms is very limited.

With the constant donor atom systems, those complexes with the meridional (dien)(NH_3) chelate rings isomerise more rapidly than those with the *trans* $(en)_2$ system. (A decrease of 7–30 kJ mol^{-1} in activation energy is observed, Figure 2). We have argued previously [21] that, in terms of reactivity, ease of distortion of the non-replaced polyamine ligands in octahedral cobalt(III) complexes is important in forming a trigonal bipyramid transition state. In this present situation, the meridional dien ligand is in a strained configuration and is nicely poised to move into a facial arrangement in a five-coordinate transition state. The strain is best illustrated in the "square-planar" NH_2–NH–NH_2 angle of 95.7 ± 0.4° compared with the unstrained value of 90.0° [31].

The rates of isomerisation of several *mer*-Co(dien)-(A)$(OH_2)_2^{3+}$ complexes show some variation with A (Table VI), with values of $k_{isom}(298)$ increasing in the order A = OH_2 py, $BzNH_2$, NH_3, cyclohexCH_2-NH_2, cyclohexNH_2 This order in isomerisation rate is about the same as that for the effect of A on the rate of chloride release for *cis*-$CoCl(en)_2(A)^{2+}$ complexes [21] and is probably electronic rather than steric in origin, although the two effects are difficult to separate.

In the pentaamine series, the rates of *mer* → *fac* dien isomerisation are in the order en < pn < $(NH_3)_2$ < Metmd < tmd which is just as would be predicted from the "distortion" theory [15, 32] with due regard for the effects of C-methyl [33] and N-methyl [34] substitution.

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10 Abbreviations used: py = pyridine, 3,5-lut = 3,5-dimethylpyridine, $BzNH_2$ = benzylamine, cyclohexNH_2 = cyclohexylamine, cyclohexCH_2NH_2 = cyclohexanemethylamine, en = $NH_2(CH_2)_2NH_2$, pn = $NH_2CH(CH_3)CH_2NH_2$, tmd = $NH_2(CH_2)_3NH_2$, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, Metmd = $CH_3NH(CH_2)_3NH_2$.

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