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Acidopentaaminecobalt(III) Complexes with Polyamine Ligands. X. The Kinetics of Aquation, Base Hydrolysis and Racemisation of Some Chloro and Aqua Complexes Containing Six-membered Chelate Rings

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Rates of aquation of three isomers (a, d and h) of $CoCl(tmd)(dien)^{2+}$ *and one isomer (i) of* $CoCl(tmd)(dpt)^{2+}$ *[A. R. Gainsford and D. A. House, Inorg. Chim. Acta, 6, 227 (1972)] have been measured by chloride release titration, spectropolarimetrically and spectrophotometrically at 308–338 K. Calculated kinetic parameters (1.0 M* H^+*) [*$10^7\ k_{298}$ *(*sec^{-1}*), logPZ (*sec^{-1}*),* E_a *(kJ* mol^{-1}*) and* $\Delta S^{\ddagger}{}_{298}$ *(*$JK^{-1}\ mol^{-1}$*)] are: a-isomer, 56.5, 11.36, 94.7, –36; d-isomer, 43.0, 7.40, 72.8, –111; h-isomer, 2.16, 12.69, 110, –10; i-isomer, 174, 10.51, 87.2, –52. Rates of base hydrolysis were determined using pH-stat techniques at 273.7–313 K. Calculated kinetic parameters (*$\mu = 0.1\ M$*) [*k_{298} *(*$M^{-1}\ sec^{-1}$*), other units as above] are: a-isomer,* 5.02×10^5*, 20.29, 83.3, +135; d-isomer, 138, 18.16, 91.4, +94; h-isomer, 10.6, 22.61, 123, +179; i-isomer,* 2.75×10^4*, 22.39, 102, +175.* Δ*-(–)*$_{589}$*-d-*$CoCl(tmd)(dien)^{2+}$ *has been used to generate* Δ*-d-*$Co(tmd)(dien)(OH_2)^{3+}$ *and the kinetic parameters (1.0 M* H^+*) for the rate of racemisation [*$10^8\ k_{298}$ *(*sec^{-1}*), other units as above] are: 91, 16.80, 130, +68. These data have been used to establish structure-reactivity patterns and provide information on the mechanism of aquation of complexes containing six-membered rings.*

Introduction

It is well known that the replacement of a five-membered ring by a six-membered ring in octahedral cobalt(III) complexes causes a considerable increase in the rate of aquation (replacement of a coordinated aniono group by water in acidic solution). Thus the half life for the loss of the first chloro ligand in *trans*-$CoCl_2(en)_2{}^+$[*] at 298 K in aqueous acidic solution is about 330 min[1] whereas the similar reactions with *trans*-$CoCl_2(tmd)_2{}^+$ and *trans*-$CoCl_2(en)(tmd)$, have half-lives of 13 sec[2] and 29 min[3] at 298 K. This rate increase has been attributed to "release of steric strain in forming a dissociated transition state"[2] or to steric acceleration by interaction of the central methylene group of the six-membered ring with the leaving groups.[3,4–6]

Our previous work with mixed bidentate–tridentate chloropentaaminecobalt(III) complexes[7] has provided a series of CoN_5Cl^{2+} compounds containing six-membered rings suitable for kinetic studies. This work describes the results of an investigation of the rates of acid and base hydrolysis of the *a,bf,cde*-(H↓)-, *a,bc,edf*- and *a,bc,dfe*-$CoCl(tmd)(dien)^{2+}$ isomers and *a,bf,cde-(H↑)*-$CoCl(tmd)(dpt)^{2+}$[**] (Figure 1). The results from these and other[6] aquation studies suggest that considerable modifications of the above theories are required to adequately explain the "six-membered ring effect".

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[*] Abbreviations used: en = $NH_2(CH_2)_2NH_2$, dien = $NH_2(CH_2)_2(NH)(CH_2)_2NH_2$, tmd = $NH_2(CH_2)_3NH_2$, dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$, $NH_4[(+)BCS]$ = ammonium (+)-α-bromocamphor-π-sulphonate, CD = circular dichroism, ORD = optical rotatory dispersion.

[**] The nomenclature used is that recommended by the Commission on the Nomenclature of Inorganic Chemistry, *Pure Appl. Chem., 28,* 1 (1971). The prefixed lower case letters refer to the position of the donor atoms in the octahedron (*a* and *f* in the axial positions) in the order which they are written in the cation formula. The convention adopted here is that the polyamine ligands are coordinated stepwise from one end and in the order of the alphabetical letters. According to the above nomenclature system, chloro and aqua cations with the same geometric configuration should have different lettering systems due to the different alphabetical ordering of the donor atoms, *e.g. a,bc,def*-$CoCl(tmd)(dien)^{2+}$ and *ab,cdf,e*-$Co(tmd)(dien)(OH_2)^{3+}$ both have configurations (I), Figure 1. We believe that this can cause undue confusion and the lettering system used for the chloro complex will be retained in the aqua if the geometry is unchanged. The recommended nomenclature systems do not distinguish between the alternative positions for the NH proton of the secondary amine group in the symmetric tridentate ligand. The system adopted here is to use (H↑) or (H↓) for this proton if it is adjacent to, or remote from the coordinated chloro or aqua ligand.

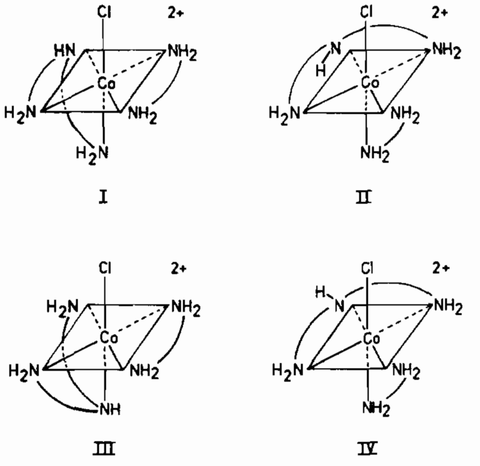

Figure 1. Geometric configurations possible for some CoCl $(AA)(ABA)^{2+}$ isomers. Δ-*a,bc,def*-$CoCl(tmd)(dien)^{2+}$, *d*-isomer, I; *a,bf,cde*-(H$\downarrow$)-$CoCl(tmd)(dien)^{2+}$, *a*-isomer, II; *a,bc,dfe*-$CoCl(tmd)(dien)^{2+}$, *h*-isomer, III; *a,bf,cde*-(H$\uparrow$)-$CoCl(tmd)(dpt)^{2+}$, *i*-isomer, IV.

Experimental

The *a*,$(-)_{589}$-*d*- and *h*-isomers of [CoCl(tmd)(dien)] $ZnCl_4$ and *i*-[CoCl(tmd)(dpt)]$ZnCl_4$ were prepared and purified as described previously.[7,8] These have the *a,bf,cde*-(H$\downarrow$)-, Δ-$(-)_{589}$-*a,bc,def*-, *a,bf,cde*- and *a,bf,cde*-(H$\uparrow$)-configurations (Figure 1) respectively and were characterised by their i.r. and visible absorption spectra.[7]

Aqua ions were generated from acidic solutions of the chloro complexes by the addition of excess Hg $(NO_3)_2$ and warming to 30°C for 15 min.

Kinetic Runs

Solutions for chloride release measurements were prepared by dissolving weighed samples of the $ZnCl_4^{2-}$ salts (*ca.* 100 mg) in 0.01*M* $HClO_4$ (*ca.* 15 ml). These were run through a 10 × 1 cm AMBERLITE IRA 400 Standard Grade anion exchange resin in the nitrate form to remove the ionic chloride. The effluent and washings (0.01*M* $HClO_4$) were collected in a 50 ml flask containing 25 ml of 2.0*M* $HClO_4$. Subsequent titrimetric procedures were the same as those described previously.[4,5] Spectrophotometric data were obtained from spectra scans (600–300 nm) using similarly prepared, but more dilute, solutions and a jacketed 5.00 cm cell was used to maintain constant temperature. A 5.00 cm cell containing 1.0*M* $HClO_4$ was used in the reference beam.

Base hydrolysis rate data were obtained from the perchlorate salts dissolved in 0.1*M* $NaClO_4$ using the pH-stat method described previously.[9]

For the mutarotation and racemisation kinetics, Δ-$(-)_{589}$-*d*-[CoCl(tmd)(dien)]$ZnCl_4$ (ca. 80 mg) was dissolved in 50 ml of 1.0*M* $HClO_4$. Aliquots (5 ml) were diluted with an equal volume of 1.0*M* $HClO_4$ and spectropolarimetric (CD) scans (650–300 nm) were made using a jacketed 5.00 cm cell. The active aqua complex was generated *in situ* by diluting a 5 ml aliquot of the chloro complex with 5 ml of 0.04*M* Hg^{2+} (as the nitrate salt) in 1.0*M* $HClO_4$. CD scans were made using this solution.

Data Analysis

Previously described procedures[4,5,8–10] were followed except that for the *a* and *i*-complexes, the "infinity" titration (eight half-lives) did not correspond to the weight of complex taken and an equilibrium chloro–aqua system was produced. In those cases, pseudo-first-order rate constants (*k*) were calculated from the expression:

$$k\left[\frac{2a-x_e}{x_e}\right] = \frac{2.303}{t}\log\left[\frac{ax_e+x(a-x_e)}{a(x_e-x)}\right]$$

where a = complex concentration at $t = 0$, x = chloride ion concentration at time, *t*, x_e = chloride ion concentration at "infinity".

In all cases, reproducibility was of the order of 5% and plots of log(extent of reaction) *vs.* time were linear for more than two half-lives. Rate constants obtained from different methods to monitor the reaction did not vary by more than 5%. Activation parameters were calculated from the rate constant *vs.* temperature data using a non-linear least squares computer programme using the conventional expressions,[9] and were checked graphically from a plot of log *k* *vs.* 1000/T K.

Results and Discussion

Aquation and Racemisation Reactions

Table I lists the pseudo-first-order rate constants for the aquation of the four chloro complexes studied here. Changes with time in the visible absorption and CD spectra of Δ-$(-)_{589}$-*d*-$CoCl(tmd)(dien)^{2+}$ (I) are illustrated in Figures 2 and 3.

The isosbestic and isocircular dichroic points established as the reaction proceeds are in agreement with those predicted by superposition of the pure chloro and aqua forms, suggesting that the geometric configuration is unchanged during the reaction. Spectrophotometric studies were not made for the other systems, but on the basis of a comparison with the ethylenediamine analogues of similar configuration, we would not expect isomerisation to accompany the chloride release step. It is possible, however, that the *a*-aqua isomer (II) would subsequently isomerise to

TABLE I. Pseudo-First-Order Rate Constants for the Aquation of Some CoCl(tmd)(ABA)$^{2+}$ Complexes in 1.0*M* $HClO_4$.

Complex[a]	T, (°C)	T, (K)	10^5k(obs)[b], (sec^{-1})	10^5k(calc)[c], (sec^{-1})	Method[d]
$\Delta\Lambda$- and Δ-*a,bc,def*-CoCl(tmd)(dien)$^{2+}$	40.8	314.0	1.40 ± 0.07	1.88	H(1)
d-isomer (I)	44.5	317.7	2.40 ± 0.12	2.61	H(1)
	48.8	322.0	3.50 ± 0.17	3.78	H(1)
	52.8	326.0	5.79 ± 0.28	5.28	H(1)
	56.5	329.7	7.20 ± 0.36	7.14	H(2)S(1)
	58.6	331.8	9.20 ± 0.46	8.84	H(1)
	61.2	334.4	10.1 ± 0.50	10.4	H(1)S(1)CD(1)
	64.5	337.7	12.4 ± 0.62	13.4	H(1)
a,bf,cde-(H↓)-CoCl(tmd)(dien)$^{2+}$	37.1	301.3	2.5 ± 0.15	2.51	H(1)
a-isomer (II)	40.8	314.0	3.99 ± 0.20	3.87	H(1)
	44.1	317.3	5.23 ± 0.26	5.65	H(1)
	47.7	320.9	8.72 ± 0.43	8.54	H(1)
	50.8	324.0	12.8 ± 0.64	11.88	H(1)
	53.2	326.4	15.1 ± 0.76	15.39	H(1)
	56.1	329.3	20.3 ± 1.0	20.93	H(1)
a,bc,dfe-CoCl(tmd)(dien)$^{2+}$	53.4	326.6	1.00 ± 0.05	1.04	H(1)
h-isomer (III)	59.0	332.2	2.14 ± 0.15	2.07	H(1)
	64.0	337.2	3.95 ± 0.20	3.75	H(1)
	68.0	341.2	5.99 ± 0.30	5.95	H(1)
	72.0	345.2	8.95 ± 0.45	9.36	H(1)
a,bf,cde-(H↑)-CoCl(tmd)(dpt)$^{2+}$	33.0	306.2	4.1 ± 0.20	4.36	H(1)
i-isomer (IV)	36.0	309.2	6.0 ± 0.30	6.08	H(1)
	40.1	313.3	10.9 ± 0.54	9.84	H(1)
	43.0	316.2	13.4 ± 0.67	12.89	H(1)
	45.0	318.2	15.4 ± 0.77	15.88	H(1)
	47.0	320.2	18.3 ± 0.92	19.51	H(1)
	Racemisation Reaction[e]				
Δ-*a,bc,def*-Co(tmd)(dien)(OH_2)$^{3+}$	50.0	323.2	5.20 ± 0.26	5.34	CD(1)
from *d*-isomer (I)	53.0	326.2	8.52 ± 0.42	8.34	CD(1)
	56.0	329.2	12.9 ± 0.64	12.9	CD(1)
	59.0	332.2	20.5 ± 1.0	19.9	CD(1)
	62.0	335.2	30.1 ± 1.5	30.3	CD(1)
	65.0	338.2	45.2 ± 2.2	45.9	CD(1)

[a] Complex ion configurations are illustrated in Figure 1. [b] Observed rate constant ±5%. [c] Rate constants calculated from the activation parameters in Table II. [d] Method used to monitor the reaction. H = halide titration, S = spectrophotometric scans, CD = circular dichroism scans. The number in parenthesis is the number of determinations at a particular temperature. [e] In 1.0*M* $HClO_4$, 0.02*M* Hg^{2+}.

the *d*-configuration (I) as this is observed in the ethylenediamine analogue.[6,7]

The activation parameters calculated for these reactions are listed in Table II.

In all cases, the six-membered ring complexes aquate more rapidly than their five-membered ring analogues, but for configuration III there is only a 2.4 fold rate increase.

In terms of the previously held theories, complexes with configuration II provide the most difficulty as it seems almost impossible for the bidentate ring to act sterically with the leaving group and yet a 32 fold rate increase is observed in replacing the 1,2-diaminoethane with 1,3-diaminopropane.

It should be noted here that the two chromium(III) complexes isomorphous with *ω*-[CoCl(en)(dien)]Zn $Cl_4 \cdot H_2O$ and *h*-[CoCl(tmd)(dien)]$ZnCl_4 \cdot H_2O$ aquate with identical rates within experimental error and 3 times *faster* than $CrCl(NH_3)_5^{2+}$.[11]

For a dissociative aquation mechanism, both the trigonal bipyramid and tetragonal pyramid transition states are possible.[12]

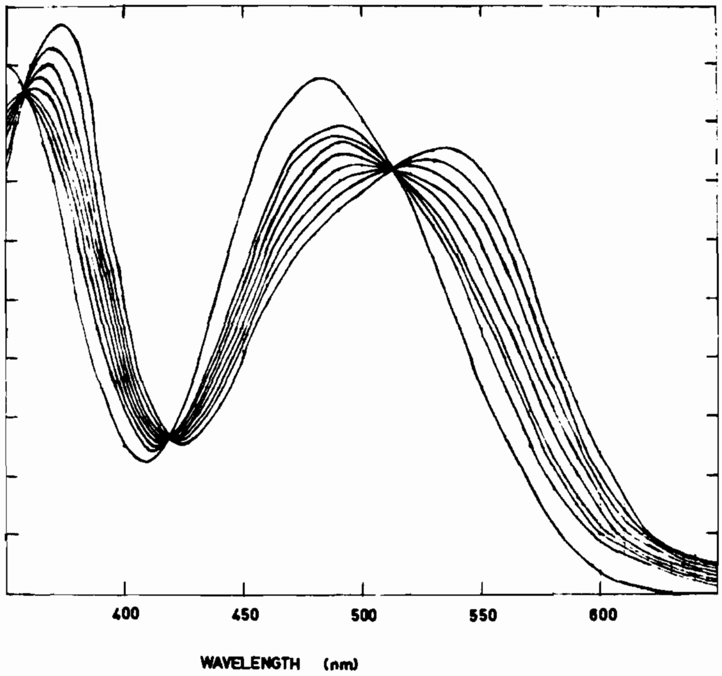

Figure 2. Spectrophotometric changes in the visible absorption spectra of d-CoCl(tmd)(dien)$^{2+}$ at 61.2°C in 1.0M HClO$_4$. Reading downwards at 550 nm, the times are 0, 20, 40, 65, 91, 135, 175 and 225 min. The final spectrum is that calculated for d-Co(tmd)(dien)(OH$_2$)$^{3+}$. The ordinate is in units of ε (M^{-1} cm^{-1}) with each scale division corresponding to $\varepsilon = 10$.

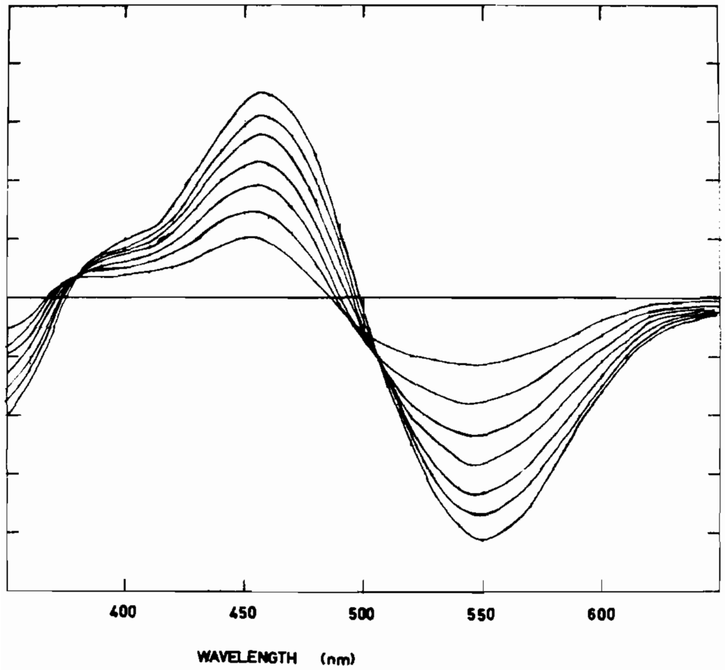

Figure 3. Changes in the CD spectrum of Δ-d-CoCl(tmd)(dien)$^{2+}$ at 61.1°C in 1.0M HClO$_4$. Reading upwards at 550 nm, the times are 0, 20, 40, 70, 100, 145 and 205 min. The ordinate is in units of $\Delta\varepsilon$ (M^{-1} cm^{-1}) with each scale division corresponding to $\Delta\varepsilon = \pm 0.2$.

TABLE II. Kinetic Parameters for the Aquation of some Chloropentaaminecobalt(III) Complexes with Polyamine Ligands at 298.2 K.

Complex	Isomer[a] (Configuration)	$10^7 k_{298}$ (sec^{-1})	log*PZ* (sec^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\ddagger}$ (JK^{-1} mol^{-1})	Ref.
$CoCl(NH_3)_5^{2+}$		17.6	11.19	96.7 ± 1	−39 ± 2	*b*
$CoCl(en)(dien)^{2+}$	π(I)	2.56	12.78	110 ± 5	−8 ± 10	*c*
$CoCl(tmd)(dien)^{2+}$	*d*(I)	43.0	7.40	72.8 ± 4	−111 ± 8	*d*
$CoCl(en)(dien)^{2+}$	κ(II)	1.78	11.57	104 ± 5	−31 ± 10	*c*
$CoCl(tmd)(dien)^{2+}$	*a*(II)	56.5	11.36	94.7 ± 3	−36 ± 6	*d*
$CoCl(en)(dpt)^{2+}$	β(II)	213	11.88	94.5 ± 2	−25 ± 4	*c*
$CoCl(en)(dien)^{2+}$	ω(III)	0.94	12.84	113 ± 4	−7 ± 8	*c*
$CoCl(tmd)(dien)^{2+}$	*h*(III)	2.16	12.69	110 ± 3	−10 ± 6	*d*
$CoCl(en)(dpt)^{2+}$	α(IV)	116	12.68	105 ± 3	−10 ± 6	*c*
$CoCl(tmd)(dpt)^{2+}$	*i*(IV)	174	10.51	87.2 ± 6	−52 ± 12	*d*
	Racemisation Reaction					
$Co(en)_2(NH_3)(OH_2)^{3+}$		0.018	17.49	150	+82	*e*
Δ-$Co(tmd)(dien)(OH_2)^{3+}$	*d*(I)	9.1	16.80	130 ± 2	+68 ± 4	*d*

[a] Complex ion configurations are illustrated in Figure 1. [b] Summary of data from various sources. [c] Reference 6. [d] This work. [e] Reference 17.

We have shown previously[13] that the rate of aquation of *trans*-$CoCl_2(AA)_2^+$ complexes can be correlated with the δ(N–Co–N) in plane infra-red deformation frequencies. We suggest that this correlation reflects the ease in which the octahedral $CoCl_2N_4^+$ complexes can distort to a trigonal bipyramid structure.

While it is by no means established that the Co(III) complexes discussed here aquate totally via a trigonal bipyramid transition state, consideration of such a pathway can adequately explain the reactivity patterns observed. Thus "tight" chelating systems such as (en)(dien) could be expected to restrict distortion to the trigonal bipyramid transition state, whereas the "looser" chelating systems *e.g.* (tmd)(dien), (en)(dpt) and (tmd)(dpt) allow this state to be more readily achieved. While these ideas may appear to be similar to the theory that the "six-membered ring" effect is due to "release of steric strain", it is almost certain that similar strain will be present in the isomorphous Cr(III) complexes[4,5,11] and yet these do not exhibit any six-membered ring rate increase. This implies either a different mechanism is operative in the aquation of Cr(III) complexes[14] or that the reaction involves a different (tetragonal pyramid) transition state.

Other observed structure–reactivity relations may also be explained using the "distortion" theory. Thus, systems with configuration (IV) would not be expected to distort to the trigonal bypyramid transition state as readily as those with configuration (II) due to the unfavourable disposition of the sec-NH proton.[15]

Hence the aquation rates are in the order β-CoCl(en)(dpt)$^{2+}$ (II) > *i*-CoCl(tmd)(dpt)$^{2+}$ (IV) > α-CoCl(en)(dpt)$^{2+}$ (IV) despite the increased chelate ring size of the second complex.

However, there remain some unexplained observations. Is the slow rate of aquation of $CoCl(NH_3)_5^{2+}$ relative to some of the "looser" chelate systems due to a steric effect? Why, for any particular CoCl(AA)(ABA)$^{2+}$ system do the isomers with configuration III aquate the slowest?

The more rapid rate of racemisation of Δ-Co(tmd)(dien)$(OH_2)^{3+}$ (I) relative to the *cis*-$Co(en)_2(A)(OH_2)^{3+}$ systems[10,16,17] is also in agreement with the "distortion" theory as such complexes are thought to racemise by water exchange via a trigonal bipyramid transition state. The activation parameters for this racemisation reaction are listed in Table II and Figure 4 shows a typical set of spectral scans for the change in CD with time. It is interesting that while racemisation is about five times slower than chloride release at 25 °C, and is thus similar to the *cis*-$CoX(en)_2(A)^{n+}$ (X = Cl, OH_2) systems[10,17] it is about three times faster than chloride release at 61 °C. Consequently, the build up of Δ-Co(tmd)(dien)$(OH_2)^{3+}$ in the aquation products from Δ-CoCl(tmd)(dien)$^{2+}$ at 61 °C is not particularly marked (Figure 3). A plot of Δε *vs.* λ for Δ-CoX(tmd)(dien)$^{n+}$ (X = Cl, OH_2) is presented in Figure 5, showing the expected iso-dichroic points if racemisation of the aqua did not occur.

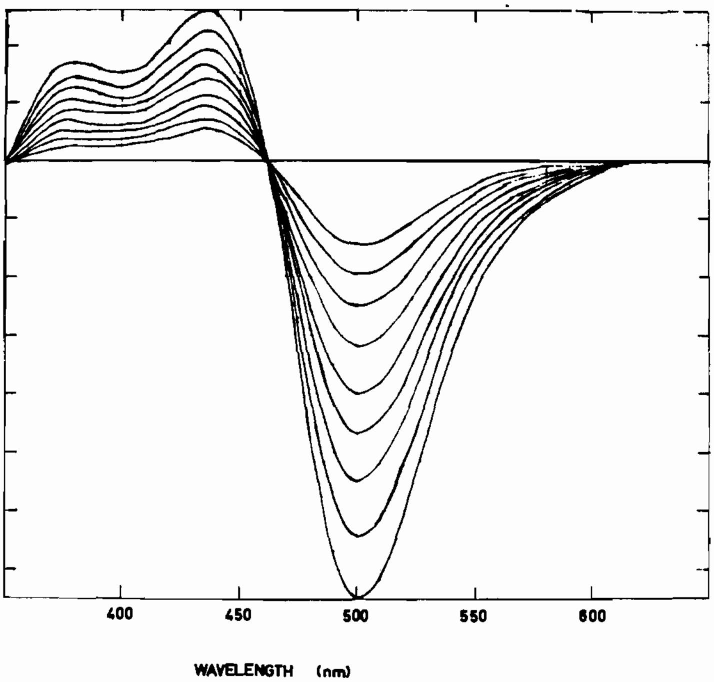

Figure 4. Changes in the CD spectrum of Δ-*d*-Co(tmd)(dien)(OH$_2$)$^{3+}$ at 62.0°C in 1.0*M* HClO$_4$. Reading upwards at 500 nm, the times are 0, 13, 26, 39, 52, 70, 90, 110 and 135 min. The ordinate is in units of $\Delta\varepsilon$ (M^{-1} cm^{-1}) with each scale division corresponding to $\Delta\varepsilon$ = ± 0.1.

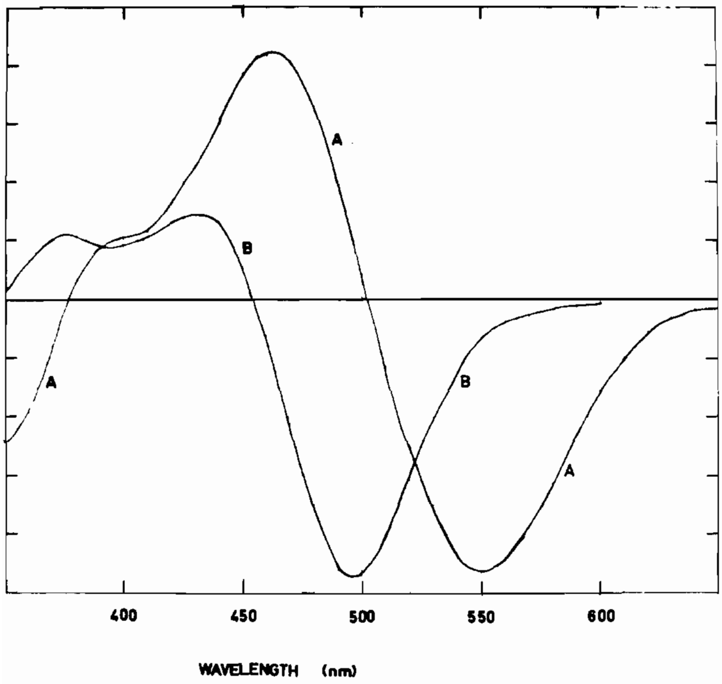

Figure 5. The CD spectrum of Δ-*d*-CoCl(tmd)(dien)$^{2+}$ (A) and Δ-*d*-Co(tmd)(dien)(OH$_2$)$^{3+}$ (B) in 1.0*M* HClO$_4$ at 20–23°C. The ordinate is in units of $\Delta\varepsilon$ (M^{-1} cm^{-1}) with each scale division corresponding to $\Delta\varepsilon$ = ± 0.2.

Base Hydrolysis Reactions

Tables III and IV list the kinetic parameters determined for the rate of hydroxide ion uptake of these complexes in unbuffered aqueous solution at constant pH. The rate of base hydrolysis is dominated by the geometry of the tridentate chelates.[6] Complexes with configuration (II) or (IV) with a meridional triamine, react 10^2–10^3 times faster than those with the triamine in the facial configuration. For the base hydrolysis of cobalt(III) amine complexes, a conjugate base,

TABLE III. Second Order Rate Constants for the Base Hydrolysis of Some $\mathrm{CoCl(tmd)(ABA)}^{2+}$ Complexes at Constant pH (μ = 0.1).

Complex[a]	T,[b] (°C)	T, (K)	pH[c]	k_2(obs),[d] (M^{-1} sec^{-1})	k_2(calc),[e] (M^{-1} sec^{-1})
a,bc,def-$\mathrm{CoCl(tmd)(dien)}^{2+}$	0.5(2)	273.7	11.1	5.71 ± 0.1	5.08
d-isomer (I)	20.1(3)	293.3	9.5	77.3 ± 4.5	74.6
	25.3(9)	298.5	8.5–9.0	130 ± 7	143
	30.1(3)	303.3	8.7	254 ± 4	257
	35.1(3)	308.3	8.1–8.5	479 ± 15	463
	40.0(3)	313.2	7.5	925 ± 26	808
a,bf,cde-$(\mathrm{H}\downarrow)$-$\mathrm{CoCl(tmd)(dien)}^{2+}$	0.5(2)	273.7	7.8–8.0	$(2.53 \pm 0.14) \times 10^4$	2.47×10^4
a-isomer (II)	10.2(3)	283.4	7.1	$(8.69 \pm 0.09) \times 10^4$	8.67×10^4
	15.1(2)	288.3	6.7	$(1.45 \pm 0.02) \times 10^5$	1.58×10^5
	20.1(3)	293.3	6.2–6.4	$(2.98 \pm 0.14) \times 10^5$	2.86×10^5
a,bc,dfe-$\mathrm{CoCl(tmd)(dien)}^{2+}$	25.0(3)	298.2	10.3–10.4	10.6 ± 0.5	10.6
h-isomer (III)[f]	30.0(3)	303.2	9.4–9.5	25.1 ± 3.0	24.2
	35.0(2)	308.2	9.0	50.1 ± 1.5	53.5
	40.0(2)	313.2	8.5	118 ± 4	115
a,bf,cde-$(\mathrm{H}\uparrow)$-$\mathrm{CoCl(tmd)(dpt)}^{2+}$	0.5(3)	273.7	9.5	$(7.15 \pm 0.38) \times 10^2$	6.79×10^2
i-isomer (IV)	10.3(2)	283.5	8.5	$(3.01 \pm 0.04) \times 10^3$	3.22×10^3
	15.1(2)	288.3	8.0	$(5.88 \pm 0.22) \times 10^3$	6.65×10^3
	20.1(3)	293.3	7.3–7.5	$(1.55 \pm 0.09) \times 10^4$	1.38×10^4

[a] Complex ion configurations are illustrated in Figure 1. Perchlorate salts were used except where indicated. [b] Numbers in parentheses are the number of individual determinations used to obtain the mean value of k_2(obs). [c] pH or pH range used. The set pH was converted to [$\mathrm{OH^-}$] using the expressions in Reference 9. No $\mathrm{Na^+}$ ion corrections were required below pH 10.0. [d] Average value of the observed second order rate constant ± the standard deviation. k_2(obs) was calculated from the measured pseudo-first-order rate constant by dividing by the [$\mathrm{OH^-}$]. [e] The second order rate constant calculated from the kinetic parameters listed in Table IV. [f] As the iodide salt. For this complex, the reaction medium was 0.09*M* $\mathrm{NaClO_4}$ plus 0.005*M* $\mathrm{Na_2S_2O_3}$ to prevent possible $\mathrm{I_2}$ formation via air oxidation.

TABLE IV. Kinetic Parameters for the Base Hydrolysis of Some Chloropentaaminecobalt(III) Complexes at 298.2 K (μ = 0.1*M*).

Complex	Isomer[a] (Configuration)	k_{298} (M^{-1} sec^{-1})	log*PZ* (M^{-1} sec^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\ddagger}$ (JK^{-1} mol^{-1})	Ref.
$\mathrm{CoCl(NH_3)_5}^{2+}$		0.86		121	+155	*b*
$\mathrm{CoCl(en)(dien)}^{2+}$	π(I)	26.6				*c*
$\mathrm{CoCl(tmd)(dien)}^{2+}$	*d*(I)	138	18.16	91.4 ± 2	+94 ± 3	*d*
$\mathrm{CoCl(en)(dien)}^{2+}$	ω(III)	7.26				*c*
$\mathrm{CoCl(tmd)(dien)}^{2+}$	*h*(III)	10.6	22.61	123 ± 3	+179 ± 6	*d*
$\mathrm{CoCl(en)(dien)}^{2+}$	$\varkappa$(II)	3.0×10^4				*c*
$\mathrm{CoCl(tmd)(dien)}^{2+}$	*a*(II)	5.02×10^5	20.29	83.3 ± 2	+135 ± 4	*d*
$\mathrm{CoCl(en)(dpt)}^{2+}$	β(II)	2.2×10^3				*c*
$\mathrm{CoCl(tmd)(dpt)}^{2+}$	*i*(IV)	2.75×10^4	22.39	102 ± 3	+175 ± 6	*d*
$\mathrm{CoCl(en)(dpt)}^{2+}$	α(IV)	8.6×10^3				*c*

[a] Complex ion configurations are illustrated in Figure 1. [b] Reference 12, p. 180. [c] R. W. Hay, personal communication, 1975. [d] This work.

S_N1CB, mechanism is now almost universally accepted but problems such as, the site of deprotonation, and whether the rate of deprotonation or the lability of the conjugate base is rate determining, are being investigated.

While Sargeson and his co-workers have presented evidence that deprotonation trans to the leaving group is predominant in certain complexes[18–21], Nordmeyer[22] favours a *cis* deprotonation site. It seems apparent to us, that deprotonation will occur most readily at the site of the most acidic proton, and that this, in turn, will be influenced by the nature of the non-replaced ligands. However, Nordmeyer[22] has pointed out that if the lability of the conjugate base is rate determining, then the conjugate base formed from the most acidic proton site may not necessarily lead to the most stable activated complex. Nevertheless, we feel that in the complexes studied here, the sec-NH proton of the tridentate ligand in the meridonal configuration is the one that is deprotonated, leading to a remarkably labile conjugate base. Tobe and his coworkers[23, 24] have suggested that systems where deprotonation is rate determining (*i.e.* every act of deprotonation leads to chloride release) should have lower energies and entropies of activation than systems where chloride release from the conjugate base is rate determining. No trends of this kind are evident in the activation parameters for the $CoCl(tmd)(dien)^{2+}$ isomers studied here.

We believe that regardless of the controversies with respect to the above points, the observed structure–reactivity relationship for base hydrolysis could be useful in determining the configuration of a tridentate triamine coordinated to cobalt(III) and may even be extended to higher polyamines where –NH– groups should be in either a facial or meridional configuration.[6]

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