Anionopentaaminecobalt(III) Complexes with Polyamine Ligands.
25. The Resolution and Base Hydrolysis Kinetics of *mer*-[CoCl(en)(NH$_2$CH$_2$CH=NCH$_2$CH$_2$NH$_2$)] ZnCl$_4$, a Complex with an Unsymmetrical Triamine Ligand

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Abstract

Racemic *mer*-[CoCl(en)(NH$_2$CH$_2$CH=NCH$_2$CH$_2$-NH$_2$)]ZnCl$_4$, which contains no dissymetric chelate rings, no asymmetric carbon centers and no asymmetric nitrogen centers, has been resolved using sodium arsenic(III)–(+)-tartrate. The chirality arises by virtue of the coordinated unsymmetric tridentate ligand and the less soluble diastereoisomeride is associated with the (+)-cation. The rate of base hydrolysis was measured spectrophotometrically using tris buffers. Kinetic parameters (25 °C, $\mu \sim 0.04$ M) are k_{OH} = 1.28 × 10^3 M^{-1} s^{-1}, E_a = 87.0 ± 0.7 kJ mol^{-1} and $\Delta S^{\#}$ = +98 ± 1.4 J K^{-1} mol^{-1}. Complete racemisation accompanies the base hydrolysis reaction and the rate of loss of optical activity is 0.5 times that of base hydrolysis. These data are interpreted in terms of the formation of a symmetrical trigonal bipyramid intermediate generated from the conjugate base.

Introduction

Optical activity is the ability of chiral molecules to rotate the plane of plane polarised light. A necessary and sufficient condition for chirality is that the molecule lacks an improper axis of rotation. Operationally, there are several sources of chirality in octahedral coordination complexes [1, 16]:

(i) the distribution of unidentate ligands about the central metal;

(ii) the distribution of chelate rings about the central metal;

(iii) the coordination of unsymmetrical multidentate ligands;

(iv) the conformation of chelate rings;

(v) the coordination of a chiral ligand;

(vi) the coordination of an asymmetric donor atom.

Examples of optical activity in octahedral transition metal complexes arising from sources (ii), (v)

and (vi) are quite common. However, very few examples from source (i) are known, apart from some Pt(IV) complexes [2, 3], although the situation is quite commonly discussed in inorganic texts. Optical activity arising from source (iii) is often complicated by a combination of (ii), (iii) and (v) and there appears to be rather little information on complexes where the sole source of optical activity is due to the coordination of an unsymmetrical ligand. The theoretical situation can be illustrated by *sym-fac*-CoCl(dien)(ibn)$^{2+}$* (Fig. 1).
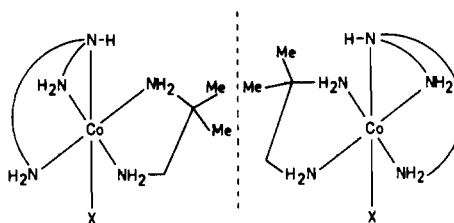

Fig. 1. Optical isomers of *sym-fac*-CoX(dien)(ibn)$^{n+}$.

Here there are no dissymmetric chelate ring configurations, no asymmetric carbon centers and no asymmetric nitrogen centers. The molecule as a whole is asymmetric due to the coordination of the unsymmetric bidentate chelate ligand, ibn.

Recently [7–10] we have isolated some Co(III) complexes of the type *mer*-CoCl(NH$_2$(CH$_2$)$_x$NH$_2$)-(NH$_2$(CH$_2$)$_{x-1}$CH=N(CH$_2$)$_x$NH$_2$)$^{2+}$ (x = 2, 3) which are, like the above example, dissymmetric as a whole by virtue of the coordination of the unsymmetric tridentate ligand (Fig. 2).

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*Abbreviations used: en = NH$_2$(CH$_2$)$_2$NH$_2$; ibn = NH$_2$-C(CH$_3$)$_2$CH$_2$NH$_2$; pn = NH$_2$CH(CH$_3$)CH$_2$NH$_2$; dapo = NH$_2$CH$_2$CH(OH)CH$_2$NH$_2$; dien = NH$_2$(CH$_2$)$_2$NH(CH$_2$)$_2$-NH$_2$. Sodium arsenic(III)–(+)-tartrate is the disodium salt of the binuclear (*RR*)-tartrate(−4) complex of arsenic(III), bis-[μ-(+)-tartrate(−4)-*O,O',O",O"*]-bis[arsenate(III)]$^{2-}$, [As$_2${(+)-C$_4$H$_2$O$_6$}$_2$]$^{2-}$ [4]. It is commonly called sodium arsenyl tartrate [5]. The sign of rotation is for the Na$_D$ lines (589 nm) unless otherwise stated.

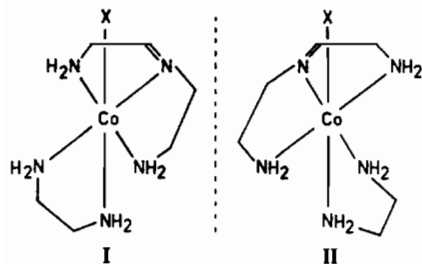*Author to whom correspondence should be addressedd.

Fig. 2. Optical isomers of *mer*-CoX(en)(NH₂CH₂CH=NCH₂CH₂NH₂)^{n+}.

Fig. 2. Optical isomers of mer-CoX(en)(NH$_2$CH$_2$CH=NCH$_2$CH$_2$NH$_2$)$^{n+}$.

We here report the successful resolution of the complex with $x = 2$ (Fig. 2) and the use of this complex as a stereochemical probe in the mechanism of base hydrolysis.

Experimental

Racemic *mer*-chloro(1,4,7-triazahept-3-ene)-(ethane-1,2-diamine)cobalt(III) tetrachlorozincate-(II), $(\pm)$-[CoCl(en)(tri)]ZnCl$_4$, was prepared and purified as previously described [8], as were sodium arsenic(III)–(+)-tartrate [5, 11], *unsym-fac-* and *mer*-[CoCl(en)(dien)]ZnCl$_4$ [12].

Resolution of (±)-[CoCl(en)(tri)]ZnCl$_4$

The brick-red complex (0.5 g) was dissolved in 0.1 M (RR)-(+)-tartaric acid solution (15 ml) by warming to about 40 °C. Twice the weight of solid sodium arsenic(III)–(+)-tartrate was stirred in and the less soluble diastereoisomeride commenced to crystallise on spontaneous cooling to room temperature. Thirty minutes after the addition of the resolving agent, the precipitated apricot solid (0.38 g) was collected, the filtrate removed, and the less soluble salt was washed successively with ice water (5 ml), 2-propanol and ether. The filtrate was allowed to stand overnight at room temperature and a further crop (0.05 g) of solid removed. The mother liquor was then heated to 40 °C and addition of HCl (12 M, 10 ml) and ZnCl$_2$ (2 g), followed by ice cooling, resulted in the isolation of 0.2 g of $(-)$-[CoCl(en)-(tri)]ZnCl$_4$.

The less soluble arsenic(III)–(+)-tartrate salt was dissolved in 3 M HCl (15 ml) at 40 °C and addition of ZnCl$_2$ (2 g), followed by ice cooling, resulted in the isolation of 0.2 g of $(+)$-[CoCl(en)(tri)]ZnCl$_4$. *Anal.* Calc. for [CoCl(en)(tri)] [As(C$_4$H$_2$O$_6$)]$_2$: C, 24.10; H, 3.31; N, 10.04. Found: C, 24.40; H, 3.61; N, 9.89%.

This procedure has been repeated twice as described and once using sodium arsenic(III)–(−)-tartrate and (SS)-(−)-tartaric acid, with essentially the same results, apart from the expected reversal in diastereoisomeride solubility in the 'unnatural' tartrate system.

The ORD and CD spectra of (+) or (−)-[CoCl-(en)(tri)]ZnCl$_4$ were measured in 0.1 M HNO$_3$ using a JASCO ORD-CD-5 recording spectropolarimeter and the complex ion concentration was estimated from the previously determined [8] visible absorption spectral parameters (Table I) using a Varian DMS-100 recording spectrophotometer.

TABLE I. Chiroptical Parameters (300–650 nm) for some (−)-CoX(en)(NH$_2$CH$_2$CH=NCH$_2$CH$_2$NH$_2$)$^{n+}$ (X = Cl, H$_2$O) Complexes in Aqueous Acidic Solution at Room Temperature[a]

CD spectra[b]					
X = Cl⁻ [c]		490	390	335	
		(−0.078)	(0)	(+0.018)	
X = H$_2$O[d]		475	370	335	
		(−0.126)	(0)	(+0.022)	
ORD spectra[e]					
X = Cl⁻ [c]	589	540	508	440	330
	(−62)	(−116)	(0)	(+172)	(0)
X = H$_2$O[d]	589	535	495	420	
	(−72)	(−142)	(0)	(+342)	
Visible absorption spectra[f]					
X = Cl⁻ [b]	520sh	470	402	358	327
	(~79)	(102.7)	(39.1)	(94.5)	(61.6)
X = H$_2$O[g]		458	390	345	
		(122.0)	(33.8)	(90.6)	

[a]Data for the most active ZnCl$_4{}^{2-}$ salt obtained from the mother liquor after removal of the less soluble arsenic (III)–(+)-tartrate salt. [b]λ(nm), $\Delta\epsilon$ (M^{-1} cm^{-1}). [c]In 0.1 M HNO$_3$. [d]In 0.76 M HClO$_4$, 9.34×10^{-2} M Hg(NO$_3$)$_2$. [e]λ (nm), [M] (° M^{-1} m^{-1}). [f]Data from ref. 8. λ(nm), ϵ (M^{-1} cm^{-1}). [g]In 0.9 M HNO$_3$, 3.00×10^{-2} M Hg(Ac)$_2$.

(−)-Co(OH$_2$)(en)(tri)$^{3+}$ was generated from (−)-[CoCl(en)(tri)]ZnCl$_4$ in 0.76 M HClO$_4$, 9.34×10^{-2} M Hg(NO$_3$)$_2$ as previously described [8].

Base Hydrolysis Kinetics

The rates of base hydrolysis of *unsym-fac-* and *mer*-[CoCl(en)(dien)]ZnCl$_4$ were measured in 0.1 M NaCl using a pH-stat to monitor the uptake of OH⁻ [13].

For the *unsym-fac-* isomer, sodium hydroxide solution was added with a syringe to precipitate Zn(OH)$_2$ and to adjust the pH slightly above the set-pH. The set-pH was converted to [OH⁻] using the previously described equations [13]. For *mer*-[CoCl-(en)(tri)]ZnCl$_4$, the rate of base hydrolysis was measured spectrophotometrically (470 nm) in tris buffers (pH = 7.2–7.8, $\mu = 0.045$–0.034 M) [14]. pH was converted to [OH⁻] using the expression $-\log[\text{OH}^-] = (-\log K_\text{w})_T - (\text{pH})_T$ where $d(\text{pH})/dT = -0.028$ K^{-1} [14].

Results and Discussion

Resolution

mer-(±)-[CoCl(en)(NH$_2$CH$_2$CH=NCH$_2$CH$_2$NH$_2$)]·ZnCl$_4$ has been successfully resolved, using the method of racemic modification [15], with disodium bis[arsenic(III)—(+)-tartrate(−4)]. The cation crystallises as the less soluble diastereoisomeride and the (−) cation was isolated from the mother liquor as the ZnCl$_4^{2-}$ salt, by addition of HCl/ZnCl$_2$.

The measured chiroptical parameters are given in Table I and the ORD and CD spectra are shown in Fig. 3. The ORD and CD intensities are quite low
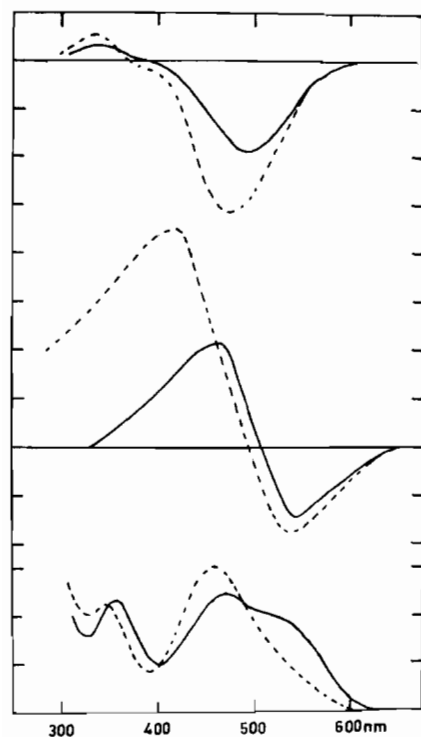

Fig. 3. CD (top), ORD (center) and visible absorption (bottom) spectra for (−)-CoX(en)(tri)$^{n+}$. (X = Cl ———, X = H$_2$O ······) in aqueous acidic solution at room temperature. Each ordinate division corresponds to ±0.04 M^{-1} cm^{-1} (CD), ±80° M^{-1} m^{-1} (ORD) and 60 M^{-1} cm^{-1} (Visible).

(typical values for (+)-Co(en)$_3^{3+}$ are $(\Delta\epsilon)_{490}$ = 1.89 M^{-1} cm^{-1}) [16] indicating that this type of molecular asymmetry contributes only weakly to the complex chromophores.

This is apparently similar to the response to the introduction of an asymmetric center in a coordinated ligand, where the induced CD intensity decreases rapidly as the distance of the asymmetric center from the metal atom increases. Typical values of *mer*-CoCl(dien)(R-pn)$^{2+}$ (average from several *mer* isomers [17]) are $(\Delta\epsilon)_{440}$ = +0.3 M^{-1} cm^{-1} and $[M]_D$ = +150° M^{-1} m^{-1}.
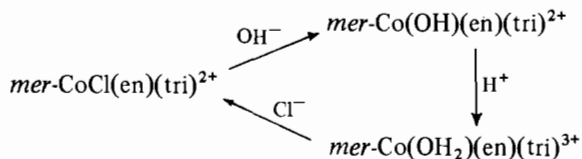
The conventional Δ/Λ nomenclature is not strictly applicable (see following) to the enantiomers of [CoCl(en)(tri)] ZnCl$_4$, but the full locant letter designation [18] does allow the enantiomers to be distinguished. In terms of Fig. 2, I is the *a, bcd, ef*-CoCl(1,4,7-triazahept-3-ene)(ethane-1,2-diamine)$^{2+}$ cation and II is the *a, dcb,ef*-isomer.

The absolute configuration of (−) or (+)-[CoCl-(en)(NH$_2$CH$_2$CH=NCH$_2$CH$_2$NH$_2$)] ZnCl$_4$ remains unknown. However, the five membered chelate rings in the *a, dcb, ef* isomer (II, Fig. 2) can formally be considered as two combinations, Δ(en)(sat) and Λ(en)(unsat), where sat and unsat refer to the saturated and unsaturated (imine) five membered rings resulting from coordination of the tridentate ligand. In terms of these ring configurations, the nett optical activity will depend on which pair dominates. If we assume that this is the saturated combination (these rings are more puckered [7]), and that a negative CD under the first absorption band (470–520 nm) is indicative of the Δ configuration [19], than the more soluble diastereoisomeride (associated with the (−) cation) is assigned to structure II.

Base Hydrolysis Kinetics

The rate of base hydrolysis of *mer*-[CoCl(en)-(NH$_2$CH$_2$CH=NCH$_2$CH$_2$NH$_2$)] ZnCl$_4$ was conveniently measured spectrophotometrically in the pH range 7.3–7.8 (tris buffers, $\mu \sim 0.04$ M). The shoulder at ~520 nm in the chloro complex (Fig. 1) decreased, and the intensity at 470 nm increased with time. Isosbestic points at 315, 355, 385 and 503 nm were maintained throughout the reaction and the observed pseudo-first-order rate constant was calculated from the charge in absorbance at 470 nm. The final absorption spectrum showed maxima at 338 and 471 nm with an intensity ratio A_{471}/A_{338} = 1.192 ± 0.036. Acidification of the final solution produced *mer*-Co(OH$_2$)(en)(tri)$^{3+}$ with maxima at 350 and 460 mn, A_{460}/A_{350} = 1.27 ± 0.018, in satisfactory agreement with the intensity ratio A_{458}/A_{345} = 1.34 obtained for the aqua ion by Hg^{2+} assisted chloride release in acidic solution [8]. Anation of a base hydrolysed solution with HCl/ZnCl$_2$ results in the isolation of [CoCl(en)(tri)] ZnCl$_4$.

All these results show that the base hydrolysis reaction proceeds as in Scheme 1 without extensive

mer-CoCl(en)(tri)$^{2+}$ $\xrightarrow{\text{OH}^-}$ *mer*-Co(OH)(en)(tri)$^{2+}$ $\xrightarrow{\text{H}^+}$ *mer*-Co(OH$_2$)(en)(tri)$^{3+}$, $\xleftarrow{\text{Cl}^-}$

Scheme 1.

decomposition. Kinetic parameters for the base hydrolysis reaction are reported in Tables II and III.

TABLE II. Observed and Calculated Rate Constants for the Base Hydrolysis of some CoCl(en)(tri)$^{2+}$ Cations

T ($^\circ$C)	pH	[OH$^-$]	$10^3 k_{obs}$[c] (s^{-1})	k_{OH} (M^{-1} s^{-1})	k_{OH}[d] (calc.) (M^{-1} s^{-1})
mer-tri = NH$_2$CH$_2$CH$_2$NHCH$_2$CH$_2$NH$_2$[a,b]					
15.0	7.91(6)[e]	4.74×10^{-7}	2.37 ± 0.32	$(5.00 \pm 0.67) \times 10^3$	4.91×10^3
20.0	7.61(3)	3.58×10^{-7}	3.32 ± 0.13	$(9.29 \pm 0.36) \times 10^3$	9.70×10^3
	7.60(3)	3.50×10^{-7}	3.44 ± 0.17	$(9.83 \pm 0.47) \times 10^3$	
25.0	7.19(6)	2.02×10^{-7}	3.77 ± 0.31	$(18.7 \pm 1.54) \times 10^3$	18.7×10^3
30.0	6.81(5)	1.25×10^{-7}	4.47 ± 0.17	$(35.8 \pm 1.35) \times 10^3$	35.4×10^3
mer-tri = NH$_2$CH$_2$CH$_2$N=CHCH$_2$NH$_2$[f]					
24.5	7.80(1)	6.36×10^{-7}	0.757 ± 0.027	$(1.19 \pm 0.04) \times 10^3$	1.21×10^3
25.0	7.80(1)	6.36×10^{-7}	0.833 ± 0.007	$(1.31 \pm 0.01) \times 10^3$	1.29×10^3
30.5	7.66(1)	6.71×10^{-7}	1.65 ± 0.04	$(2.46 \pm 0.06) \times 10^3$	2.43×10^3
	7.46(1)	4.23×10^{-7}	1.02 ± 0.021	$(2.41 \pm 0.05) \times 10^3$	
34.5	7.32(1)	4.36×10^{-7}	1.64 ± 0.036	$(3.76 \pm 0.08) \times 10^3$	3.80×10^3
40.0	6.98(1)	2.78×10^{-7}	2.31 ± 0.05	$(6.92 \pm 0.15) \times 10^3$	6.90×10^3
	6.78(1)	1.76×10^{-7}	1.22 ± 0.03	$(6.91 \pm 0.17) \times 10^3$	
unsym-fac-tri = NH$_2$CH$_2$CH$_2$NHCH$_2$CH$_2$NH$_2$[b]					
20.0	10.55(2)	3.12×10^{-4}	4.54 ± 0.22	$(1.45 \pm 0.07) \times 10^1$	1.32×10^1
	10.50(2)	2.78×10^{-4}	2.93 ± 0.15	$(1.05 \pm 0.05) \times 10^1$	
	10.43(1)	2.37×10^{-4}	3.40 ± 0.17	$(1.44 \pm 0.07) \times 10^1$	
	10.42(4)	2.31×10^{-4}	3.18 ± 0.20	$(1.38 \pm 0.07) \times 10^1$	
25.0	10.06(5)	1.50×10^{-4}	3.59 ± 0.20	$(2.41 \pm 0.13) \times 10^1$	2.39×10^1
30.0	9.7(2)	9.73×10^{-5}	4.25 ± 0.21	$(4.37 \pm 0.22) \times 10^1$	4.24×10^1
	9.6(1)	7.73×10^{-5}	3.41 ± 0.17	$(4.41 \pm 0.22) \times 10^1$	
	9.51(1)	6.28×10^{-5}	2.54 ± 0.13	$(4.05 \pm 0.20) \times 10^1$	
	9.49(1)	6.00×10^{-5}	2.57 ± 0.13	$(4.29 \pm 0.21) \times 10^1$	
35.0	9.38(2)	6.56×10^{-5}	5.72 ± 0.29	$(8.71 \pm 0.44) \times 10^1$	7.38×10^1
	9.20(2)	4.34×10^{-5}	2.82 ± 0.14	$(6.50 \pm 0.33) \times 10^1$	
	9.19(2)	4.24×10^{-5}	3.00 ± 0.15	$(7.07 \pm 0.35) \times 10^1$	

[a]This complex has the sec-NH proton remote from the coordinated chloro ligand [12]. [b]Using a pH-stat to monitor the OH$^-$ uptake with $\mu = 0.1$ M (NaCl). [c]Observed pseudo-first-order rate constant. [d]Calculated from the activation parameters cited in Table III. [e]Number of individual kinetic runs used to determine the mean ± standard deviation of k_{obs}. [f]Spectrophotometrically determined using tris buffers [14], $\mu = 0.045–0.034$ M.

TABLE III. Kinetic Parameters for the Base Hydrolysis of some CoCl(en)(tri)$^{2+}$ Complexes at 25.0 $^\circ$C

| tri		k_{OH} (M^{-1} s^{-1})	E_a (kJ mol^{-1})	$\Delta S^{\#}$ KJ^{-1} mol^{-1}	Reference
mer-dien[a]	(3×10^4)[b]	1.87×10^4	93.2 ± 2.3	$+149 \pm 4.6$	c
unsym-fac-dien	(2.66×10^1)[b]	2.39×10^1	86.3 ± 3	$+62 \pm 6$	c
sym-fac-dien	(7.26)[b]	4.71	87.0 ± 0.7	$+72 \pm 2.4$	e
mer-NH$_2$CH$_2$CH=NCH$_2$CH$_2$NH$_2$		1.28×10^3	87.0 ± 0.7	$+98.0 \pm 1.4$	c
sym-fac-NH$_2$CH$_2$CH$_2$N=C(NH$_2$)CH$_2$NH$_2$		2.43			d

[a]This complex has the sec-NH proton remote from the coordinated chloro ligand [12]. [b]Values in parenthesis are those reported in ref. 27. [c]This research. [d]Ref. 28. [e]Ref. 29.

Anionopentaamine cobalt(III) complexes with a sec-NH system in the *mer*-configuration generally base hydrolyse several orders of magnitude faster than isomeric forms where this structural feature is absent (Table III). This is attributed to enhanced acidity of the sec-NH proton in this configuration. *mer*-CoCl(en)(tri)$^{2+}$ has no sec-NH protons and the rate of base hydrolysis is indeed about 15X slower

than *mer*-CoCl(en)(dien)$^{2+}$ (Table III). Nevertheless, the base hydrolysis rate is still large and it is almost certain that factors in addition to the acidity of a *mer* sec-NH proton contribute to the base hydrolysis rate as it is not necessary that the most acidic amines afford the most reactive conjugate base. Usually, protons at amines *trans* to the leaving group exchange faster than those *cis* to the leaving group, but the general consensus is that it is *cis*-deprotonation that stabilises the five coordinate intermediate derived from the conjugate base.

Base hydrolysis of (−)-*mer*-CoCl(en)(tri)$^{2+}$ results in complete racemisation with the formation of (±)-*mer*-Co(OH)(en)(tri)$^{2+}$. At pH = 7.8 and 25 °C, k_{obs} (base hydrolysis) = 8.33 × 10^{-4} s^{-1} and k_{obs} (loss of optical activity) = ~4 × 10^{-4} s^{-1}.
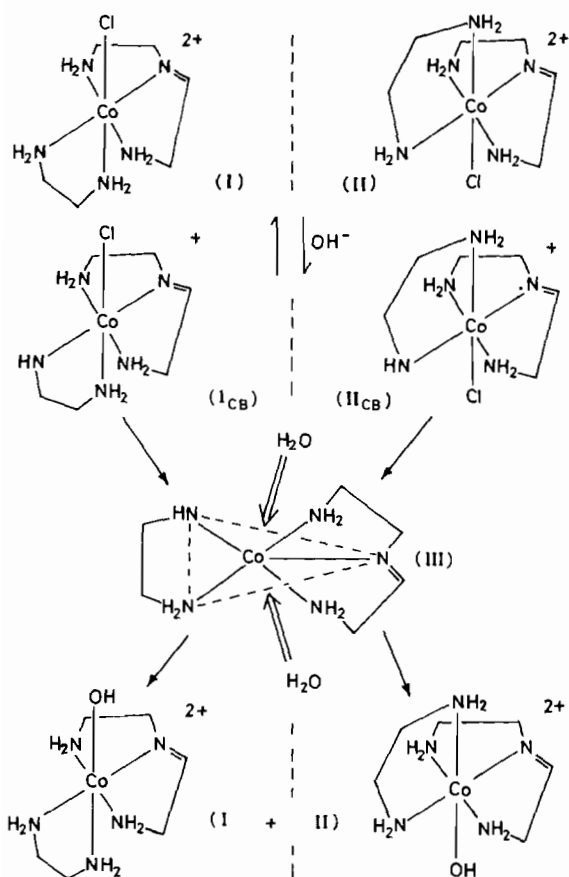
Scheme 2.

These observations suggest a symmetrical and relatively stable five coordinate intermediate that has lost all 'memory' of the recently departed chloro ligand (Scheme 2). This situation is entirely analogous to a similar system, optically active *mer*-CoCl(dien)-(dapo)$^{2+}$ ‡ described by Comba and Marty [20, 21],

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‡This complex has the sec-NH dien proton remote from the coordinated chloro ligand.

where complete racemisation accompanies base hydrolysis.

For chiral *mer*-CoCl(en)(tri)$^{2+}$, the rate of loss of optical activity in base is observed to be one half that of base hydrolysis of the chloro ligand. This is entirely consistent with Scheme 2, where attack of the final water molecule on intermediate **III** on one side will lead to a retained configuration, whereas attack on the other side will lead to the inverted configuration. Thus racemisation should be a factor of two less than base hydrolysis.

The site of deprotonation leading to a stabilised five-coordinate intermediate **III** is probably at the ethylenediamine nitrogen as this leads to the intermediate **III**, Scheme 2. Deprotonation of the −NH$_2$ ends of the tridentate ligand would require one of these to be forced into the trigonal plane, resulting in folding at the −CH$_2$−N=CH− nitrogen. Such a situation would not lead to racemisation and retention of geometric configuration would be unlikely.

The symmetrical intermediate could be generated by deprotonation at either of the two non-equivalent ends of the ethylenediamine. In Scheme 2 we have used the end *cis* to the leaving group but this has no experimental justification. Indeed, there is the possibility of internal intramolecular proton transfer making the deprotonated sites in intermediate **III** equivalent [22–24].

We note, however, that such intramolecular proton transfer has been shown not to occur in the conjugate bases of several *trans*-Co(en)$_2$(XY)$^{n+}$ complexes in liquid ammonia [25, 26].

Despite these uncertainties, the results from the base hydrolysis of *mer*-CoCl(en)(tri)$^{2+}$ indicate the generation of an intermediate by a limiting D mechanism and with sufficient symmetry and lifetime that the incoming water molecule does not discriminate between the two possible sites of attack.

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