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Anionopentaaminecobalt(III) Complexes with Polyamine Ligands. XII. Geometric and Chiral Interconversions Associated with the Coordination of N-Methyl-1,3-Diaminopropane in Isomers of Chloro and Aqua(N-methyl-1,3-diaminopropane)(diethylenetriamine)cobalt(III) Complexes

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Six (I, I', II, II', IV and V) of the seven possible geometric isomers of CoCl(Metmd)(dien)$^{2+}$ have been isolated and the aqua ions generated in solution. These isomers correspond to the a,fb,cde-*(H↑)-*, a,fb,cde-*(H↓)-*, a,bf,cde-*(H↑)*, a,bf,cde-*(H↓)-*, a,bc,def- *and* a,cb,def-*aniono(4-azapentane-1-amine)(diethylenetriamine)cobalt(III) configurations respectively and can be stepwise interconverted in the sequential order II, I', V, I, II', IV. Isomer V has been resolved to give two (*a,cb,edf-*(Λ)-(R)-* *and* a,cb,def-*(Δ)-(S)-) of the eight possible chiral forms and this has allowed the sequential interconversions Λ-(R)-V, (R)-I, (R)-II', ΔΛ-(R)-IV to be studied. A knowledge of the aquation and base hydrolysis rates for chloride release, as well as rates of aqua ion isomerisation has allowed a more controlled synthesis for several of these isomers.*

Introduction

Chirality due to the formation of an asymmetric nitrogen center coordinated to cobalt(III)[†#] is now well established in *trans*-$CoCl_2(Meen)_2^+$, $Co(NH_3)_4$(sarcosine)$^{2+}$, *trans*-$CoCl_2(trien)^+$ and *trans*-$CoCl_2$(2,3,2-tet)$^+$ [1–4].

To extend these studies, and to complement our recent investigations with six-membered ring cobalt (III) complexes, we have investigated the CoX(Metmd)(dien)$^{n+}$ system (X = Cl, OH_2). N-Methyl-1,3-diaminopropane (Metmd) is capable of forming an unsymmetric six-membered chelate ring and in the present CoX(AB)(ABA)$^{n+}$ situation, such a ligand will increase the number of potential geometric isomers from four for a symmetric bidentate (AA) to seven [5] (Figure 1). Each of these seven forms is potentially chiral by virtue of the asymmetric N(H)(CH_3)($CH_2CH_2CH_2$-NH_2)(Co) center introduced on coordination. In addition, there is the possibility of chirality due to dissymmetric arrangements of the chelate rings in one form of the facially coordinated tridentate. Most of the above situations have been realised for the CoX(Metmd)(dien)$^{n+}$ complexes described in this work.

At the start of this investigation, different isomers were isolated from reaction mixtures using often tedious fractional crystallisation techniques [6]. For some isomers, the yields were low because most of the parent isomer had been removed from solution in a previous crystallisation step. Subsequent rate studies, coupled with a knowledge of the isomerisation sequences and some luck, has allowed us to develop synthetic routes which produce mainly one form and these are the procedures described here. We would emphasise, however, that such routes were not the

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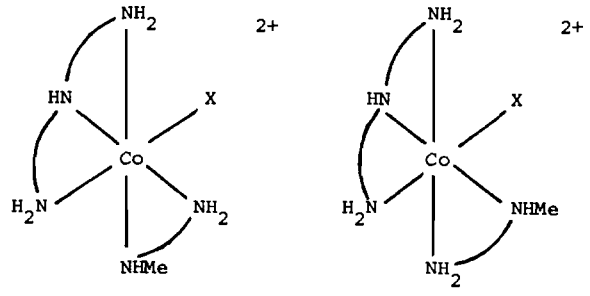
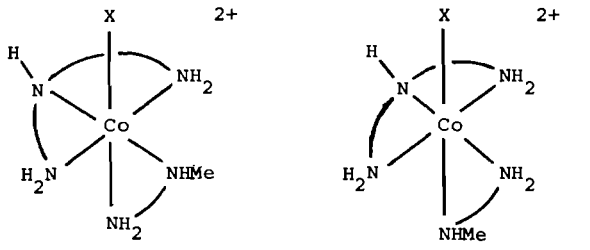
†The nomenclature used is that recommended by the Commission on the Nomenclature of Inorganic Chemistry, *Pure Appl. Chem.*, *28*, 1 (1971). The prefixed lower case letters refer to the position of the donor atoms in the octahedron (*a* and *f* in the axial positions) in the order in which they are written 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(Metmd)(dien)$^{2+}$ and *ab,cdf,e*-Co(Metmd)(dien)$(OH_2)^{3+}$ both have configuration (IV), 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 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 aquo ligand.

#Abbreviations used: en = $NH_2(CH_2)_2NH_2$, Meen = CH_3-$NH(CH_2)_2NH_2$, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, trien = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$, 2,3,2-tet = NH_2-$(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$, tmd = $NH_2(CH_2)_3NH_2$, Metmd = $CH_3NH(CH_2)_3NH_2$, bamp = 2,6-bis(aminomethyl)-pyridine, dan = $NH_2CH_2C(CH_3)_2CH_2NH_2$, dpt = NH_2-$(CH_2)_3NH(CH_2)_3NH_2$, NH_4-(+)-BCS = ammonium(+)-α-bromocamphor-π-sulphonate.



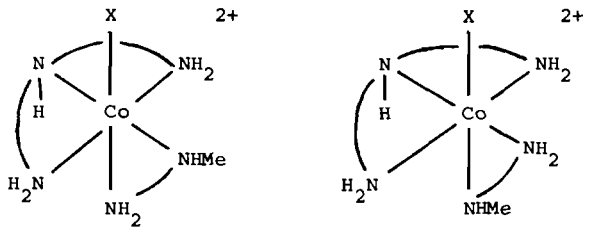
a,bc,edf-(Λ)-IV a,cb,edf-(Λ)-V

Both can be Λ-(R), Λ-(S), Δ-(R), Δ-(S), ΔΛ-(R), ΔΛ-(S), Λ-(RS) or Δ-(RS).



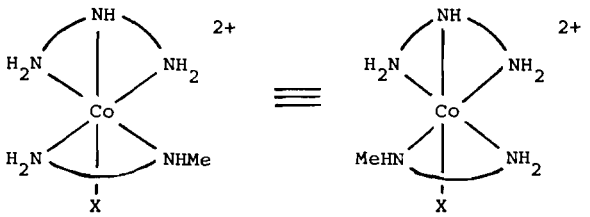
a,fb,cde-(H↑)-I a,bf,cde-(H↑)-II

Both can be (R) or (S) or (RS).



a,fb,cde-(H↓)-I' a,bf,cde-(H↓)-II'

Both can be (R) or (S) or (RS).



a,bc,dfe-A a,cb,dfe-B

Either can be (R) or (S) but if A is (R) then B must be (S) and vice-versa.

Figure 1. Isomers of chloro(4-azapentane-1-amine)(diethylenetriamine)cobalt(III).

first ones used and were only developed after considerable insight into the isomeric interrelationships had been established.

Experimental

The commercially available amines (Fluka) were used without further purification. All other chemicals were reagent grade quality. *Mer*-$CoCl_3$(dien) was prepared by the literature methods [7–9]. Unless otherwise stated, the products were washed with 2-propanol and then ether and air dried. Aqua ions were generated in solution from the corresponding chloro tetrachlorozincate(II) salts by the Hg^{2+} (0.02 *M* in $HClO_4$) assisted aquation and constant spectral parameters were obtained after one hour at room temperature. I.r. spectra of the pure [CoCl(Metmd)(dien)]$ZnCl_4$ isomers are shown in Figure 2 and analytical data are given in Table I.

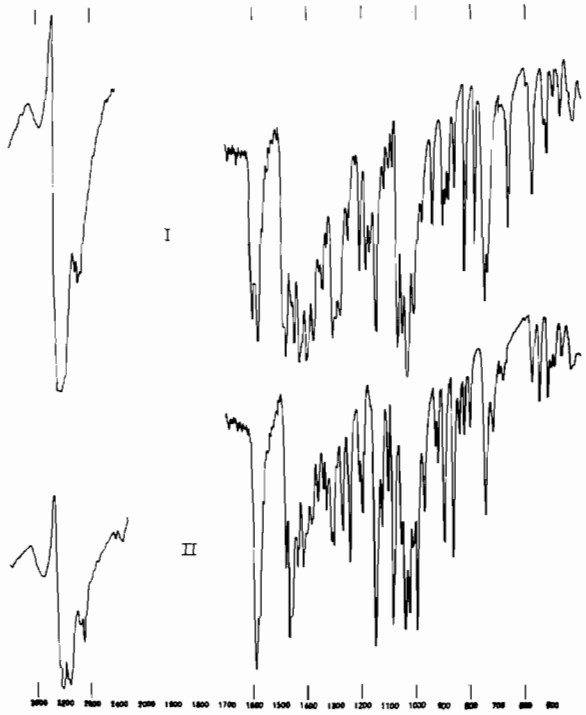
Isomers of [CoCl(Metmd)(dien)]$ZnCl_4$.

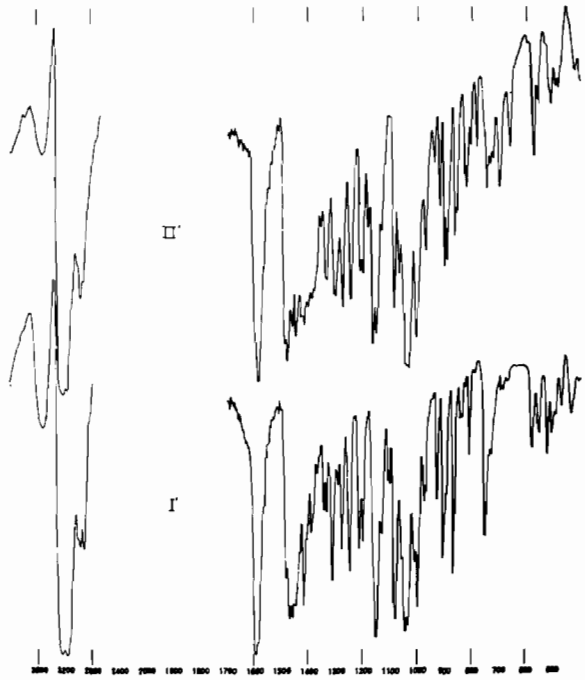
[A]. *Mer*-$CoCl_3$(dien) (16 g) was suspended in methanol and N-methyl-1,3-diaminopropane (5 g) added. The mixture was refluxed for 30 min, during which time the trichloride dissolved and a red-brown crystalline product (crude isomer II as the chloride salt, 19 g) deposited. This was filtered hot to give a brown mother liquor which was poured into 12 *M* HCl (15 ml) containing $ZnCl_2$ (10 g). Brown crystals (crude isomer I, 0.8 g) formed from the ice cooled solution.

The crude isomer II was dissolved in 100 ml of 0.1 *M* HCl at 40 °C, filtered hot (1.2 g of $CoCl_3$(dien) was removed) and added to 100 ml of 12 *M* HCl containing $ZnCl_2$ (30 g) at 60 °C. Pure isomer II (11 g) was obtained from the ice cooled solution. As the mother liquor was concentrated on the steam bath, a red to violet colour change took place and five crops (1–2 g each, total yield, 6 g) of crude isomer V (violet) were successively collected. The second of these crops contained considerable amounts of isomer I'.

Pure isomer I was obtained from the crude material after one recrystallisation from HCl containing $ZnCl_2$.

[B]. Preparation [A] was repeated but using water (25 ml) and methanol (75 ml) in place of the pure methanol. Thirty minutes refluxing produced a clear purple red solution which was poured into 100 ml of 12 *M* HCl containing 25 g of $ZnCl_2$. Crude violet isomer V (7 g) deposited from the hot solution which was filtered at 30 °C. On standing overnight, the mother liquor deposited 3 g of crude isomer I' and subsequent evaporation to 150 ml and cooling gave a further 5.5 g of crude isomer V. The first crop (7 g) was recrystallised as described for isomers I and II, to give 5 g of pure isomer V. These preparations illustrate the isomerisation sequence II → I' → V. Absorption spectral parameters in 0.1 *M* $HClO_4$: *a,fb,cde*-(H↓)-CoCl(Metmd)(dien)$^{2+}$, isomer I', λ(nm), ε (M^{-1} cm^{-1}): 550sh, 58.7; 490max, 100; 425min, 34.9; 360sh, 136. *a,bf,cde*-(H↑)-CoCl(Metmd)(dien)$^{2+}$,





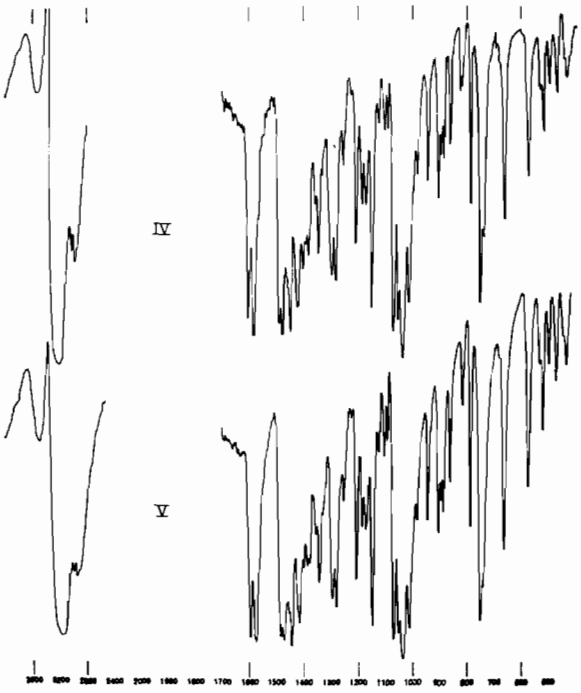


Figure 2. Infrared spectra (KBr disc) of isomeric chloro-4-azapentane-1-amine)(diethylenetriamine)cobalt(III) tetrachlorozincate(II) salts.

isomer II, λ, ϵ: 550sh, 53.7; 495max, 95.6; 427min, 31.6. *a,fb,cde*-(H↓)-Co(Metmd)(dien)$(OH_2)^{3+}$, isomer I′, λ, ϵ: 482max, 112; 412min, 30.5; 350sh, 170. *a,bf,cde*-(H↓)-Co(Metmd)(dien)$(OH_2)^{3+}$, isomer II, λ, ϵ: 485max, 106; 412min, 27.0.

Resolution of Isomer V

The violet isomer (5 g) was dissolved in 80 ml of 0.05 *M* HCl at 70 °C and 5 g of solid NH_4-(+)-BCS was stirred in. Violet crystals commenced to deposit as the temperature dropped and the product (2.2 g $(\Delta\epsilon)_{573}$ = +0.7 M^{-1} cm^{-1}) was collected after six hours at room temperature. A further 0.1 g of $\{+\}_{570}$* product was collected after 48 hours and 25 ml of 2-propanol was added to the filtrate to give 1.2 g of crystalline material ($(\Delta\epsilon)_{573}$ = −0.7 M^{-1} cm^{-1}) after two hours. HCl (30 ml, 12 *M*) containing $ZnCl_2$ (10 g) precipitated 1.2 g of inactive material and a further 0.5 g of inactive product deposited over two days. An X-ray crystal structure of the $ZnCl_4^{2-}$ salt [11] derived from the less soluble diastereoisomeride shows this $\{+\}_{570}$* fraction to be the Λ-(R)-*a,cb,edf*-chloro (4-azapentane-1-amine)(diethylenetriamine)cobalt(III) isomer (Figure 1). The more soluble $\{-\}_{570}$ diastereoisomeride is the strict enantiomer and thus the Δ-(S)- form. Spectral parameters in 0.1 *M* $HClO_4$: λ, ϵ: 542max, 82.1; 500sh, 69.9; 432min, 22.6; 375max, 112. λ(nm), Δϵ (M^{-1} cm^{-1}): 573, ±0.705; 530, 0; 480, ±0.785; ~405sh, ~±0.12; 385, 0; 355, ±0.336; 320, 0. Treatment of Δ-(S)-*a,cb,def* CoCl(Metmd)(dien)$^{2+}$ with Hg^{2+} in $HClO_4$ solution generates Δ-(S)-*a,cb,def*-Co(OH_2)(Metmd)-(dien)$^{3+}$ [λ, ϵ: 500max, 91.5; 415min, 21.1; 355max,

*Symbol in the braces gives the sign of the CD at the cited wavelength.

TABLE I. Analytical Data and Rate Studies for Some CoX(Metmd)(dien)$^{n+}$ Isomers.

Isomer		X	Anion	Found[a]				Reaction	Method[b]
				C	H	Co	Cl		
a,fb,cde (H↑)	I	Cl	$ZnCl_4$	19.40	5.06	11.90	35.83 →	I-OH_2	Cl^-, CD
a,fb,cde (H↑)	I	OH_2					→	II′-OH_2	CD
a,bf,cde (H↓)	II′	Cl	$ZnCl_4$	19.45	5.10	11.92	35.93 →	Cl^-	spectro
a,bf,cde (H↓)	II′	OH_2					→	IV-OH_2	CD
a,bc,def	IV	Cl	$ZnCl_4$	19.59	5.05	11.90	35.92 →	IV-OH_2	Cl^-
a,bf,cde (H↑)	II	Cl	$ZnCl_4$	19.57	5.03	11.92	35.99 →	Cl^-	Cl^-, pH-stat[c]
a,bf,cde (H↑)	II	OH_2					→	I′-OH_2	spectro
a,fb,cde (H↓)	I′	Cl	$ZnCl_4$	19.79	5.14	11.98	35.90 →	Cl^-	Cl^-, pH-stat[c]
a,fb,cde (H↓)	I′	OH_2					→	V-OH_2	spectro
a,cb,def	V	Cl	$ZnCl_4$	19.71	5.06	11.88	35.93 →	V-OH_2	Cl^-, spectro, CD, pH-stat[d]

[a]Calculated: C, 19.50; H, 5.11; N, 11.96; Cl, 35.96%. [b]Method used to monitor the reaction. Cl^- = chloride release titrations; CD = circular dichroism spectral scans; spectro = visible absorption spectral scans, pH-stat = base hydrolysis rate constants determined using a pH-stat to maintain constant $[OH^-]$. [c]As the perchlorate salt. [d]As the iodide salt.

122. λ, Δε: 500, −0.792; 458, 0; 435, +0.16; 405, +0.11; 380, +0.155; 345, 0] which mutarotates to the ΔΛ-(S)-*a,cb,def*- form [λ, Δε: 555, +0.045; 535, 0; 498, −0.126; 458, 0; 435, +0.023; 350, +0.032]. The isolation of ΔΛ-(S)-*a,cb,def*-[CoCl(Metmd)-(dien)]$ZnCl_4$ from a heated solution (0.1 *M* HCl) of the Δ-(S)- isomer, followed by HCl/$ZnCl_2$, was frustrated by the spontaneous resolution into the Δ-(S)- and Λ-(S)- [λ, Δε: 550, +0.820; 505, 0; 460, −0.758; ~400sh, ~−0.27; 348, +0.369] salts.

(R)-a,fb,cde-*(H↑)-CoCl(Metmd)(dien)ZnCl$_4$, Isomer I*

A 1.3 g sample of Λ-(R)-*a,cb,def*-[CoCl(Metmd)-(dien)] (+)BCS (isomer V, less soluble diastereoisomeride) was dissolved in 20 ml of 0.2 *M* HCl and $NaNO_2$ (3 g) was stirred in. The solution was heated at 80 °C for 30 min until the violet to yellow colour change was complete. The hot solution was poured into 100 ml of 50/50 acetone/2-propanol containing 5 g of $ZnCl_2$ and 1 ml of 12 *M* HCl. Yellow-orange crystals of (R)-*a,fb,cde*-(H↑)-[Co(NO_2)(Metmd)(dien)]$ZnCl_4$ deposited after 30 min cooling in ice (1.0 g). Calcd. for $CoC_8H_{25}N_6O_2ZnCl_4$: Co, 11.75; Cl, 28.27. Found: Co, 11.68; Cl, 28.15. Spectral data: λ, ε: 465max, 125; 404min, 31. λ, Δε: 480, +0.494; 447, 0; 425, −0.268; 338, 0. The yellow solid was heated to almost boiling with 15 ml of 12 *M* HCl and 2 g of $ZnCl_2$ were added to the hot solution. Brown crystals of (R)-isomer I (0.48 g) were collected from the ice cooled solution. Spectral data: λ, ε: 520sh, 60; 479max, 85.3; 420min, 37.5. λ, Δε: 575, +0.440; 532, 0; 500, −0.256; 470, −0.213; 390, 0.286; 388, 0. This preparation is rather critical upon heating time and HCl concentration. Too little heating results in incomplete nitro → chloro conversion and too much results in isomerisation to II′ or IV (see below). Racemic isomer V undergoes a similar isomerisation to give racemic-(RS)-I.

a,bf,cde-*(H↓)-[CoCl(Metmd)(dien)]ZnCl$_4$, Isomer II′*

A 4.0 g sample of yellow *a,fb,cde*-(H↑)-[Co(NO_2)-(Metmd)(dien)]$ZnCl_4$ (isomer I nitro, from racemic isomer V) was dissolved in 50 ml of warm 0.2 *M* HCl and 50 ml of 12 *M* HCl added. This solution was boiled for 5 min, and the colour changed to brownish pink. $ZnCl_2$ (15 g) was then added and the brownish pink product (3 g, mixture of isomers II′ and IV) deposited from the hot solution. Two recrystallisations from dilute HCl with 12 *M* HCl/$ZnCl_2$ added gave pure isomer II′ (pink) as the more soluble fraction. Spectral parameters in 0.1 *M* $HClO_4$: λ, ε: 550sh, 53.7; 490max, 95.6; 422min, 31.6. Aqua ion in 0.57 *M* $HClO_4$, 0.012 *M* $Hg(NO_3)_2$: λ, ε: 485max, 106; 412min, 27.0.

a,bc,def-*[CoCl(Metmd)(dien)]ZnCl$_4$, Isomer IV*

The above procedure was repeated with the boiling time increased to 15 min. The initial product (2.5 g) was violet and one recrystallisation (as above) gave pure isomer IV. Spectral parameters in 0.1 *M* $HClO_4$: λ, ε: 542max, 82.0; 500sh, 73; 421min, 25.3; 370max, 120; 342min, 69. Aqua ion in 0.57 *M* $HClO_4$, 0.012 *M* $Hg(NO_3)_2$: λ, ε: 495max, 91.4; 415min, 21.1; 355max, 116; 332min, 94.

Kinetics

Solutions for kinetic runs were prepared, and the rate data analysed as described previously [11]. Tetrachlorozincate(II) salts were not suitable for base hydrolysis studies and the parent isomers were recrystallised as perchlorates or iodides for this purpose.

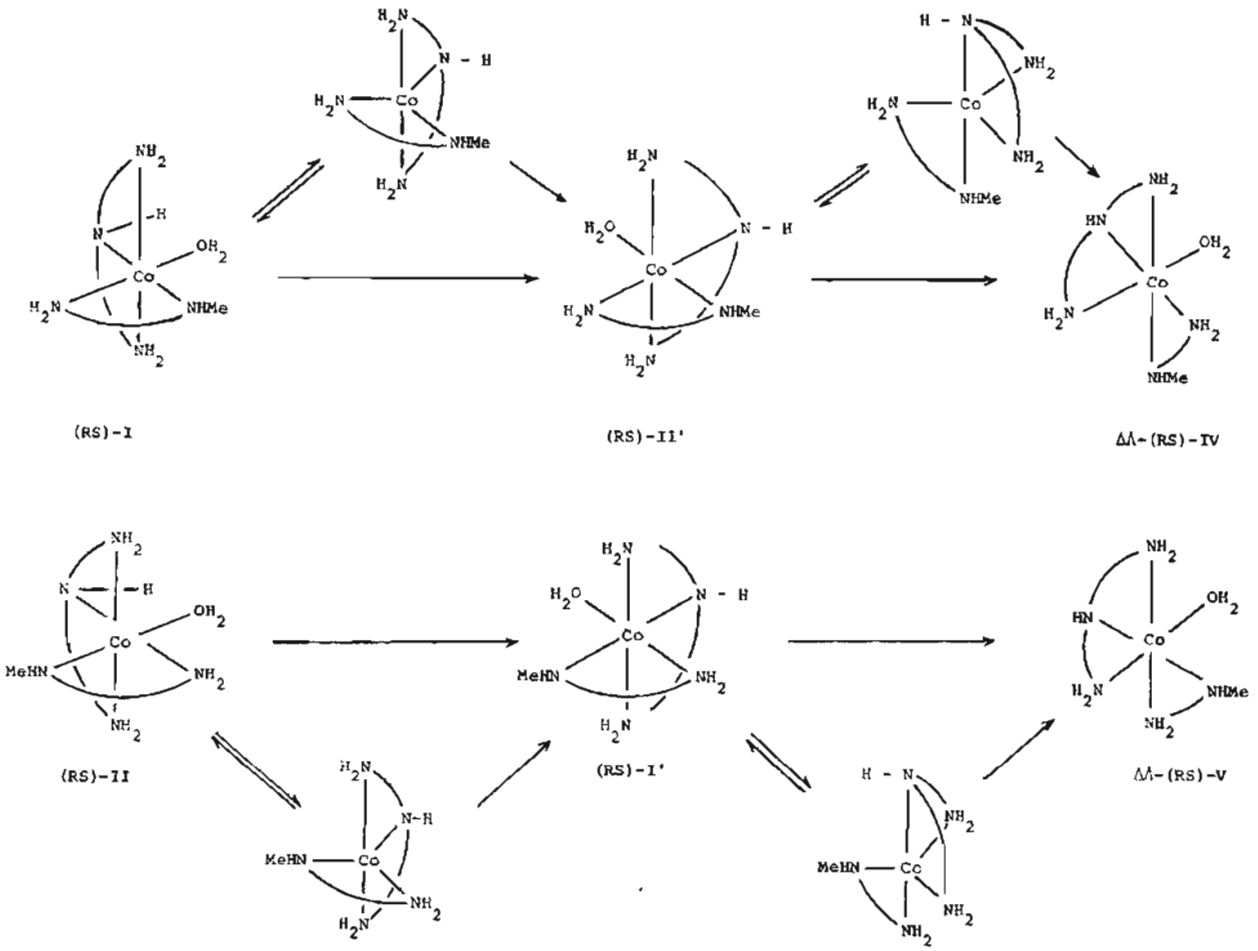


Figure 3. Isomeric interconversions for the $Co(OH_2)(Metmd)(dien)^{3+}$ ions *via* water exchange mechanisms and trigonal bipyramid transition states.

Results

Six isomers with differing infrared and visible absorption spectra have been isolated for the [CoCl(Metmd)(dien)] $ZnCl_4$ system and the structural assignments illustrated in Figure 1 have been made using a combination of X-ray, rate and chemical interconversion data.

An X-ray crystal structure [10] of the $ZnCl_4^{2-}$ salt derived from the less soluble (+)-BCS diastereoisomeride of isomer V shows this to have the (R) configuration at the chiral nitrogen which is coordinated *trans* to the sec NH of the facially coordinated diethylenetriamine with the chelate rings in the Λ configuration. Thus the form of isomer V can be represented as $\{+\}_{570}$-Λ-(R)-*a,cb,edf*-[CoCl(Metmd)(dien)] $ZnCl_4$ with the enantiomeric more soluble diastereoisomeride being the $\{-\}_{570}$-Δ-(S)-*a,cb,def*-form.

The I → II′ → IV and II → I′ → V reaction sequences are experimentally observed and are compatible with dissociative water exchange mechanisms involving trigonal bipyramid transition states (Figure 3). The V → I isomerism via I-NO_2 is exactly paralleled in the π → κ-CoCl(en)(dien)$^{2+}$ system, where the structures of both parent and daughter have been confirmed by X-ray analysis [12]. Thus the reaction of *mer* $CoCl_3$(dien) with Metmd in methanol gives two isomers (I and II) that are related by the alternate modes of coordination of the unsymmetric bidentate ligand. In methanol/water, there is subsequent isomerisation, probably via base hydrolysis to produce further isomers (see later).

Table I shows the types of reaction investigated kinetically for these systems and the pseudo-first-order rate constants obtained for the chloride release in acidic solution for these systems are presented in Table II. Kinetic data for the interconversions of the aqua ions, as shown in Figure 3, are given in Table III.

The rate of change of optical activity of (R)-*a,fb,cde*-(H↑)-$Co(OH_2)(Metmd)(dien)^{3+}$ (isomer I) was found to take place in two successive steps corresponding to the I → II′ → IV sequence in Figure 3. A similar sequence was spectrophotometrically observed in the II → I′ → V series (Figure 3) although

TABLE II. Pseudo-first-order Rate Constants for the Aquation of Some CoCl(Metmd)(dien)$^{2+}$ Isomers in 1.0 *M* $HClO_4$.

Configuration[a]	T (K)	10^5 k_H (obs)[b] s^{-1} (±5%)	10^5 k_H (calc)[c] s^{-1}	Method[d]
ΔΛ-(RS) and	321.2	7.0	6.95	H
Δ-(S)-*a,cb,def*-	323.3	9.6	9.03	H
Isomer V	323.6	8.8	9.37	S
	323.8	9.7	9.61	CD
	325.7	11.8	12.1	H
	326.8	13.4	13.8	H
	327.2	14.1	14.5	H
	328.4	17.3	16.4	CD
		17.2	16.4	S
	328.5	16.8	16.6	H
	330.3	20.7	21.1	H, S
ΔΛ-(RS)-	321.2	5.5	5.5	H
a,bc,def-	325.2	8.6	8.6	H
Isomer IV	328.2	12.0	11.9	H
	330.2	14.7	14.8	H
a,fb,cde-(H↓)-	316.2	8.6	8.6	H
Isomer I′	319.2	12.3	12.3	H
	321.2	15.4	15.4	H
	323.2	19.4	19.4	H
	326.2	27.3	27.3	H
a,bf,cde-(H↓)-	334.3	34.3	34.1	S
Isomer II′	337.4	48.4	48.8	S
	340.7	70.8	70.9	S
	343.2	94.3	93.8	S
	345.6	122	122.1	S
a,bf,cde-(H↑)-	319.2	9.85	9.9	H
Isomer II	320.2	11.2	11.0	H
	322.7	14.3	14.5	H
	323.2	15.3	15.3	H
	324.2	17.0	17.0	H
	325.2	18.3	18.9	H
	325.7	20.2	19.9	H
	326.7	22.6	22.2	H
(RS)- and (S)-	320.2	3.97	4.02	H
a,fb,cde-(H↑)-	321.2	4.40	4.45	CD
Isomer I		4.46	4.45	H
	323.2	5.51	5.46	CD
	324.2	6.33	6.03	H
	325.7	6.90	7.01	H
	326.7	7.55	7.73	CD
		8.02	7.73	H
	327.7	8.36	8.54	H
	329.7	10.1	10.4	H
	329.7	10.6	10.4	CD

[a]Complex ion configurations are illustrated in Figure 1. [b]Observed rate constant (± 5%). [c]Rate constants calculated from the activation parameters cited in Table V. [d]Method used to monitor the reaction: H = halide titration, S = spectrophotometric scans, CD = circular dichroism scans.

the separation of the rate data into its sequential steps was more difficult due to overlapping kinetics. Fortunately, the *a,fb,cde*-(H↓)-Co(OH_2)(Metmd)-(dien)$^{3+}$ (isomer I′) was available to accurately measure the I′ → V interconversion step. Overlapping kinetics were not such a problem in the I → II′ → IV sequence, as a relatively low activation energy is associated with the II′ → IV step. Thus, while at 298 K, the second step is about three times slower than the first (for both series), at 340 K the II′ → IV reaction is much the slower second step (Table III).

TABLE III. Pseudo-first-order Rate Constants for the Racemisation, Mutarotation and Isomerisation of Some Co(OH_2)-(Metmd)(dien)$^{3+}$ Ions in 1.0 *M* $HClO_4$.[a]

Reaction[b]	T (K)	10^5 k (obs)[c] (s^{-1})±5%	10^5 k (calc)[d] (s^{-1})
Δ-(S)-*a,cb,def*-	320.2	16.2	16.6
→	321.2	19.2	19.2
ΛΔ-(S)-*a,cb,def*-	322.2	22.4	22.2
Racemisation of	324.2	30.0	29.5
isomer V[e]	326.2	40.3	39.1
	328.2	49,9	51.6
	330.2	68.0	68.0
(R)-*a,fb,cde*-(H↑)	319.2	11.0	11.5
→	321.2	17.0	15.9
(R)-*a,bf,cde*-(H↓)	322.2	21.8	21.8
Mutarotation of	325.2	30.0	29.7
isomer I → II′[e]	328.2	46.0	46.9
(R)-*a,bf,cde*-(H↓)	334.2	5.81	5.79
→	337.2	7.90	7.75
ΔΛ-(R)-*a,bc,def*-	340.2	9.85	10.3
Mutarotation of	343.2	14.0	13.7
isomer II′ → IV[e]			
(RS)-*a,bf,cde*-(H↑)-	319.4	17.4	17.5
→	323.1	32.5	32.0
(RS)-*a,fb,cde*-(H↓)-	325.0	43.8	43.3
Isomerisation of	326.7	55.8	56.7
isomer II → I′[f]	328.3	72.1	72.8
		73.8	
(RS)-*a,fb,cde*-(H↓)-	324.5	7.80	7.60
→	329.1	13.0	14.1
ΔΛ-(RS)-*a,cb,def*-	333.6	28.2	25.5
Isomerisation of	336.8	37.2	38.5
isomer I′ → V[f]	339.3	52.5	52.8

[a]In 1.0 *M* $HClO_4$, 0.02 *M* $Hg(NO_3)_2$. [b]Complex ion configurations are illustrated in Figure 1. [c]Observed rate constants (±5%). [d]Rate constants calculated using the activation parameters cited in Table V. [e]Rate constants determined spectropolarimetrically. [f]Rate constants determined spectrophotometrically.

Base hydrolysis data (μ = 0.1 *M*) have been obtained for three of the chloro complexes described here. Table IV lists the second order rate constants calculated from the pH-stat data [11, 13]. Activation parameters, computer calculated from plots of log k *vs.* 1000/T K are presented in Tables V and VI along with similar data for related systems.

TABLE IV. Second Order Rate Constants for the Base Hydrolysis of Some $CoCl(Metmd)(dien)^{2+}$ Isomers at Constant pH (μ = 0.1 *M* $NaClO_4$).

Configuration[a]	Isomer	T (K)	pH[b]	k_{OH} (obs)[c] M^{-1} s^{-1}	k_{OH}(calc)[d] M^{-1} s^{-1}
a,bf,cde-(H↑)	II[e]	273.7	7.5–7.6	$(9.36 \pm 0.12) \times 10^4$	9.24×10^4
		278.6	7.2	$(1.37 \pm 0.01) \times 10^5$	1.39×10^5
		283.3	6.7	$(2.06 \pm 0.02) \times 10^5$	2.03×10^5
a,fb,cde-(H↓)	I′[e]	273.7	7.6	$(4.1 \pm 0.07) \times 10^4$	4.12×10^4
		278.2	7.1	$(8.02 \pm 0.01) \times 10^4$	7.99×10^4
		283.1	6.8	$(1.60 \pm 0.05) \times 10^5$	1.60×10^5
a,cb,def	V[f]	273.7	10.4	$(4.27 \pm 0.3) \times 10$	4.03×10
		288.2	9.3–9.4	$(2.33 \pm 0.21) \times 10^2$	2.25×10^2
		293.2	8.6	$(5.10 \pm 0.15) \times 10^2$	4.62×10^2
		278.2	8.4	$(7.57 \pm 0.18) \times 10^2$	8.21×10^2
		303.2	7.9	$(1.60 \pm 0.08) \times 10^3$	1.43×10^3

[a]Complex ion configurations are illustrated in Figure 1. [b]pH or pH range used. The set pH was converted to $[OH^-]$ using the expressions in reference 13. [c]Average value of the observed second order rate constant ± the standard deviation of three determinations. [d]The second-order rate constant calculated from the kinetic parameters listed in Table VI. [e]Perchlorate salt. [f]Iodide salt, using 0.09 *M* $NaClO_4$ plus 0.005 *M* $Na_2S_2O_3$.

TABLE V. Kinetic Parameters for the Aquation and Isomerisation of Some Chloro- and Aquapentaaminecobalt(III) Complexes at 298.2 K in 1.0 *M* $HClO_4$.

Complex	Isomer[a] (configuration)	10^7 k (298) (s^{-1})	E_a (kJ mol^{-1})	$\Delta S^{\ddagger}_{298}$ (J K^{-1} mol^{-1})	Reference
Aquation Reactions					
$CoCl(NH_3)_5^{2+}$		17.6	96.7 ± 1	−39 ± 2	b
$CoCl(en)(dien)^{2+}$	π(IV/V)	2.56	110 ± 5	−8 ± 10	c
$CoCl(Metmd)(dien)^{2+}$	IV	33.4	97 ± 1	−33 ± 2	e
$CoCl(Metmd)(dien)^{2+}$	V	30.7	107 ± 4	+3 ± 10	e
$CoCl(tmd)(dien)^{2+}$	d(IV/V)	43.0	73 ± 4	−111 ± 8	d
$CoCl(en)(dien)^{2+}$	κ(I′/II′)	1.78	105 ± 5	−31 ± 10	c
$CoCl(Metmd)(dien)^{2+}$	I′	88.6	99 ± 5	−18 ± 10	e
$CoCl(Metmd)(dien)^{2+}$	II′	30.3	108 ± 1	+4 ± 2	e
$CoCl(tmd)(dien)^{2+}$	a(I′/II′)	56.5	95 ± 3	−36 ± 6	d
$CoCl(en)(bamp)^{2+}$	(I′/II′/I/II)	16			g
$CoCl(tmd)(bamp)^{2+}$	(I′/II′/I/II)	170			g
$CoCl(dan)(bamp)^{2+}$	(I′/II′/I/II)	4.6			g
$CoCl(en)(dpt)^{2+}$	β(I′/II′)	213	94.5 ± 2	−25 ± 4	c
$CoCl(Metmd)(dien)^{2+}$	I	35.7	87 ± 2	−64 ± 4	e
$CoCl(Metmd)(dien)^{2+}$	II	82.8	93 ± 2	−37 ± 4	e
$CoCl(en)(dpt)^{2+}$	α(I/II)	116	105 ± 3	−10 ± 6	c
$CoCl(tmd)(dpt)^{2+}$	i(I/II)	174	87 ± 6	−52 ± 12	c
Isomerisation Reactions					
$Co(OH_2)(en)(dien)^{3+}$	κ(I′/II′) → π(IV/V)	1.2	124 ± 2	+31 ± 3	c
$Co(OH_2)(Metmd)(dien)^{3+}$	I → II′	31.9	135 ± 6	+95 ± 12	e
	II′ → IV	11.2	91 ± 5	−63 ± 10	e
	II → I′	41.9	139 ± 2	+111 ± 4	e
	I′ → V	15.1	120 ± 6	+37 ± 12	e
$Co(OH_2)(tmd)(dien)^{3+}$	a(I′/II′) → d(IV/V)	71.7	105 ± 1	−1 ± 2	d, f

(Continued overleaf)

TABLE V. *(Continued.)*

Complex	Isomer[a] (configuration)	10^7 k (298) (s^{-1})	E_a (kJ mol^{-1})	$\Delta S^{\ddagger}_{298}$ (J K^{-1} mol^{-1})	Reference
Racemisation Reactions					
$\Lambda \rightarrow \Lambda\Delta$-$Co(OH_2)(en)_2(NH_3)^{3+}$		0.018	150 ± 6	+82 ± 12	h
Δ-(S) → $\Delta\Lambda$-(S)-V-$Co(OH_2)(Metmd)(dien)^{3+}$		53.4	124 ± 2	+61 ± 4	e
$\Lambda \rightarrow \Lambda\Delta$-d-$Co(OH_2)$-(tmd)$(dien)^{3+}$		9.1	130 ± 2	+68 ± 4	d

[a]Complex ion configurations are illustrated in Figure 1. [b]Reference 5. [c]Reference 18. [d]Reference 10. [e]This research. [f]D. A. House, unpublished research. [g]Reference 25. [h]D. Fenemor and D. A. House, *Int. J. Chem. Kinetics, 8,* 573 (1976), in 0.1 *M* $HClO_4$.

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

Complex	Isomer[a] (Configuration)	k_{OH} (298) M^{-1} s^{-1}	E_a kJ mol^{-1}	$\Delta S^{\ddagger}_{298}$ J K^{-1} mol^{-1}	Reference
$CoCl(NH_3)_5^{2+}$		0.86	121	+155	b
$CoCl(en)(dien)^{2+}$	π(IV/V)	26.6			c
$CoCl(tmd)(dien)^{2+}$	d(IV/V)	138	91.4 ± 2	+94 ± 3	d
$CoCl(Metmd)(dien)^{2+}$	V	821[f]	83.4 ± 2	+82 ± 4	e
$CoCl(en)(dien)^{2+}$	κ(I′/II′)	3.0×10^4			c
$CoCl(tmd)(dien)^{2+}$	a(I′/II′)	5.0×10^5	83.3 ± 2	+135 ± 4	d
$CoCl(Metmd)(dien)^{2+}$	I′	1.19×10^5[f]	93 ± 1	+175 ± 2	e
$CoCl(en)(dpt)^{2+}$	β(I′/II′)	2.2×10^3			g
$CoCl(Metmd)(dien)^{2+}$	II	6.24×10^5[f]	52.9 ± 1	+35 ± 2	e
$CoCl(en)(dpt)^{2+}$	α(I/II)	8.6×10^3			g
$CoCl(en)(bamp)^{2+}$	(I′/II′/I/II)	480			h

[a]Complex ion configurations are illustrated in Figure 1. [b]Reference 5. [c]R. W. Hay and K. B. Nolan, *J. Inorg. Nucl. Chem., 38,* 2118 (1976). [d]Reference 10. [e]This research. [f]This number is incorrectly cited in reference 5, Table 26. [g]R. W. Hay, personal communication.

Discussion

Stereochemistry

The reaction of *mer*-$CoCl_3$(dien) with Metmd in methanol gives two isomers, I and II, that are related by the alternate modes of coordination of the unsymmetric bidentate ligand. The dien configuration remains unchanged and the two isomers are produced in a ratio of about 1:20 respectively. Previous work on the *mer*-$CoX_3(dien)^{n+}$ system [14] suggests that the leaving group *trans* to the sec NH of the dien is the most labile. If this is the case, and the diamine coordinates in a stepwise manner, then the isomer ratio can be accounted for by the relative ease of coordination of the primary *vs.* secondary ends. The configurations assigned to isomers I and II are in agreement with the accepted theory that primary amines are better donors than secondary amines.

The initial coordination of one end of the diamine to the position *trans* to the sec NH of the dien can also account for the lack of formation of the seventh *a,bc,dfe*-CoCl(Metmd)$(dien)^{2+}$ isomer corresponding to the ω form in the $CoCl(en)(dien)^{2+}$ system [15–17]. In this configuration, the ends of the diamine are *trans* to the -NH_2 ends of the diethylenetriamine. The synthetic strategy used to produce isomers of this configuration requires a kinetically inert leaving group (*e.g.* NO_2 [11] or NH_3 [14]) in the position *trans* to the dien secondary amine. Thus, our experience here, and in the reaction of *mer*-$CoCl_3$(dien) with other bidentate amines [6], suggests that the initial coordination is at the position *trans* to the sec NH of the dien, to give the *a,bf,cde*-CoX(AA)$(dien)^{n+}$ configuration and that subsequent isomers are formed by proton inversion and *mer* → *fac* dien isomerism to form *a,bc,def*-CoX(AA)$(dien)^{n+}$ as the final kinetically favoured configuration (Figure 3).

Coordination of the N-methyl end of the diamine results in a potentially chiral coordinated nitrogen center. There is no stereospecificity associated with

the formation of this chiral center and the *mer*-dien isomers contain equal amounts of the (R) and (S) forms. For the *fac*-dien isomers IV and V, the chelate rings introduce further asymmetry and the racemic mixture apparently contains equal amounts of the Δ-(S)-, Δ-(R)-, Λ-(S)- and Λ-(R)- forms. The resolution procedure described here for isomer V allows the isolation of the Δ-(S)-, Λ-(R)- and racemic (Δ-(R)-)-(Λ-(S)-) forms. The Λ-(S)- and Δ-(S)- forms were also isolated from an attempt to produce the ΔΛ-(S)-isomer. We believe that this is one of the few systems where both geometric and chiral isomers have been isolated for an asymmetric nitrogen center.

Kinetics

Aquation

The introduction of six-membered chelate rings into an octahedral cobalt(III) complex generally causes an increase in lability of aniono ligands when compared with the five-membered ring analogues [11]. The present situation is no exception although the exact five membered ring analogues (those with N-methyl-1,2-diaminoethane) have not been studied. Nevertheless, rate comparisons can be made between the en [18], tmd [11] and Metmd systems. Inspection of Table V, and comparing isomers of similar geometry, shows that the rates of aquation at 289 K are in the order en < tmd ~ Metmd for $CoCl(AA)(dien)^{2+}$. Increasing substitution on the carbon atoms of five-membered chelate ring systems is known to cause an increase in the rate of aquation [19, 20] but the effect of N-substitution is not so well established. *Trans*-$CoCl_2(Meen)_2^+$ aquates about 2 times slower [21] than its ethylenediamine analogue, but in the present systems, rate comparisons between the tmd and Metmd analogues cannot easily be made because of considerable differences in the activation parameters (Table V), especially for the *a,bc* (or *cb*), *def* configuration. However, the increased rates of aquation due to the introduction of a six-membered chelate are clearly evident and can be explained in terms of the previously proposed 'distortion' theory [11].

Isomerisation and racemisation

The kinetic parameters for the rates of isomerisation of the $Co(OH_2)(Metmd)(dien)^{3+}$ ions are, in general, characterised by relatively high activation energies and positive activation entropies, the only exception being the II′ → IV (and perhaps the *a* → *d*-$Co(OH_2)(tmd)(dien)^{3+}$) isomerisation (Table V). In these two systems, the lower activation energy is compensated by a more negative activation entropy and in the three systems with six-membered rings, all *mer* → *fac* dien isomerise by a factor of 10 or more times faster than the ethylenediamine analog. The order of $k_{isom}(298)$ for the *mer* → *fac* isomerisation is (Table V) en < Metmd < tmd, perhaps reflecting an N-methyl retardation as observed in the aquation of the *trans*-$CoCl_2(Meen)_2^+$ system [21]. The positive entropies of activation observed are in accord with Tobe's theory [22] that positive entropy is a characteristic of reactions which involve considerable geometric rearrangement.

The racemisation series in Table V shows a trend towards lower activation energies with increasing ring size (activation entropy is approximately constant). Water exchange mechanisms, via a trigonal bipyramid transition state are generally accepted as the mode of these isomerisation and racemisation reactions [23] and the six-membered ring chelates clearly allow a more facile distortion to this configuration than do the "tight" five-membered ring systems.

It is significant that the proton inversion of the *mer*-dien can be achieved in acid solution without deprotonation, via a water exchange mechanism and a trigonal bipyramid intermediate (Figure 2) and that *mer* → *fac*-dien isomerisation does not occur until this takes place.

Base hydrolysis

The expected trends [5, 24] in reaction rates are observed in the base hydrolysis reactions studied here. Complexes with the meridional triamine configuration react about 100 times faster than those with the facial diethylenetriamine [10, 18]. N-methyl substitution on 1,3-diaminopropane may also be causing an acceleration in reaction rate (Table VI), perhaps due to the introduction of a new sec-NH site which is more susceptible to deprotonation.

Further evidence that the sec-NH proton of the dien in a *mer* configuration is unusually acidic comes from a base hydrolysis study of $CoCl(bamp)(AA)^{2+}$ [25]. Here the tridentate ligand is meridionally coordinated but has no proton on the central nitrogen atom and the rate of base hydrolysis is not significantly greater than for dien ligands in the *fac* configuration (Table VI).

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