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Kinetic Behaviour and Crystal Structure of $(-)_{589}$-Δ(*S*)-*cis*-(1-aminopropane-2-ol-*N*)-chlorobis(1,2-diaminoethane)cobalt(III) Tetrachlorozincate(II)

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The tetrachlorozincate(II) salt of $\Delta\Lambda$(RS)-cis-*(1-aminopropane-2-ol-*N*)chlorobis(1,2-diaminoethane)cobalt(III) has been resolved by asymmetric association with sodium arsenyl tartrate. The chiroptical properties suggest the* Δ*-configuration for the arrangement of the chelate rings and this has been confirmed by a single crystal X-ray structure analysis of the resolved complex. The structure also confirms that the 1-aminopropane-2-ol (pnol) is* N*-bonded and reveals that the potentially asymmetric carbon atom in pnol has the* S*-configuration and the 1,2-diaminoethane (en) rings adopt the* $\delta\lambda$ *conformation. Crystals of* $\delta\lambda$-$(-)_{589}$-Δ(S)-cis-$[CoCl(en)_2(pnol\text{-}N)]ZnCl_4$ *are orthorhombic* $P2_12_12_1$ *with* a = *12.330(1),* b = *13.905(2),* c = *10.916(1) Å and Z = 4. The structure has been refined to an R value of 0.047 on the basis of 767 observed reflections collected by diffractometry. Mercury(II) assisted chloride release in acidic solution (*μ = *1.0* M*) is relatively rapid (*$10^2\ k_{Hg}(298.2) = 2.92\ M^{-1}\ s^{-1}$*) to give* Δ(S)-$Co(en)_2(pnol\text{-}N)(OH_2)^{3+}$ *and this is followed by a slower cyclisation reaction (possibly complicated by racemisation) to give* $\Delta\Lambda$(S)(?)- *plus* Δ(S)-$Co(en)_2(pnol\text{-}NO)^{3+}$ (*$10^5\ k_{pol}(298.2) = 2.0\ s^{-1}$, $E_a = 107 \pm 3$ kJ mol^{-1}, $\Delta S^{\#}_{298} = +14 \pm 6$ J K^{-1} mol^{-1}*). In the absence of* Hg^{2+}*, the final product is again the cyclised complex, but the intermediate aqua ion is not detected as chloride release is about 20 times slower than cyclisation. (*$10^6\ k_H(298.2) = 1.0\ s^{-1}$, $E_a = 103 \pm 3$ kJ mol^{-1}, $\Delta S^{\#}_{298} = -24 \pm 6$ J K^{-1} mol^{-1}*).*

Introduction

Cobalt(III) pentaamine complexes containing *N*-bonded 1,2-aminoalcohols *e.g.* $CoCl(en)_2(NH_2CH_2CH(R)OH)_2^{2+}$ are of interest from a number of points of view [1]. Acid hydrolysis of the coordinated halide may be synchronous with, or followed by, cyclisation [2, 3] (1).

The cyclised products have been extensively investigated as the potentially asymmetric carbon atom can induce large vicinal effects which change considerably on deprotonation of the coordinated OH group [4, 5].

In this paper we report the use of kinetic, spectropolarimetric and crystallographic techniques to investigate the $(-)_{589}$-Δ(S)-*cis*-$CoCl(en)_2(pnol\text{-}N)^{2+}$ system (R = CH_3 in equation (1)).

Experimental

The commercially available (*RS*)-1-aminopropan-2-ol (Fluka) was used without further purification and *trans*-$[CoCl_2(en)_2]Cl$ was prepared as described by Schlessinger [6].

Perchloric acid solutions were prepared by dilution of 70% $HClO_4$ and $[Hg^{2+}]$ concentrations were determined with standard Cl^- solution using diphenylcarbazone indicator [7].

$\Delta\Lambda$-cis-*(*RS-*1-aminopropan-2-ol-*N*)chlorobis(1,2-diaminoethane)cobalt(III) Tetrachlorozincate(II),* $\Delta\Lambda$-(RS)-cis-$[CoCl(en)_2(pnol\text{-}N)]ZnCl_4$

(*RS*)-1-aminopropan-2-ol (4.2 ml, one mol equivalent) was stirred into a slurry of *trans*-$[CoCl_2(en)_2]Cl$ (10 g) in water (10 mL). The colour changed

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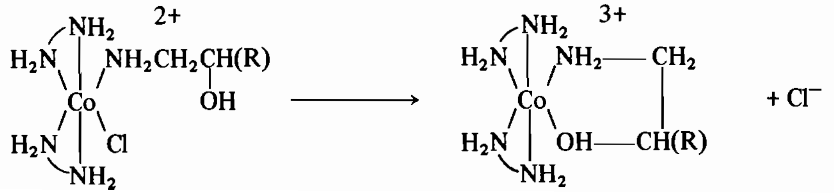

(1)

from green to red and, after 5 min at room temperature, 50 mL of methanol was added to precipitate the product as the chloride salt (70% yield). This crude material was recrystallised as the less water-soluble tetrachlorozincate(II) salt by dissolving the solid in the minimum volume of warm (50°) 0.1 *M* HCl, and adding an equal volume of 12 *M* HCl followed by 15 g of $ZnCl_2$. The bromo bromide has previously been reported [4, 8].

*(–)$_{589}$-Δ(S)-*cis-*[CoCl(en)$_2$(pnol-*N*)] ZnCl$_4$*

The racemic product (2 g) and (+)-tartaric acid (0.2 g) were dissolved in 15 mL of 40 °C H_2O and sodium arsenyl-(+)-tartrate [9] (2 g) was stirred in. The solution was left at room temperature for 3 days and the mother liquor decanted from the red crystals that deposited. These had identical i.r. spectra and elemental analysis to the racemic starting material but were optically active. Found: C, 17.5; H, 5.15; Cl, 35.8%, calculated for $CoC_7H_{25}N_5OZnCl_5$: C, 16.9; *H*, 5.03; Cl, 35.7%. Visible absorption spectra (1.0 *M* $HClO_4$), λ(nm), (ε)(M^{-1} cm^{-1}): 527 max, (76.3); 422 min, (19.8); 367 max, (85.5); 330 min, (33.2). ORD spectra (1.0 *M* $HClO_4$), λ(nm), [M](deg M^{-1} m^{-1}): 593, –85; 556, 0; 530, +84; 488, +55; 442, +17; 404, +14; 362sh, +237. CD spectra (1.0 *M* $HClO_4$), λ(nm), Δε (M^{-1} cm^{-1}): 560, –0.0517; 506, –0.0286; 488, –0.0357; 416, 0; 385, –0.0117; 367, 0. C-13 NMR spectra $[CoCl(en)_2(NH_2CH_2CH(OH)CH_3)]ZnCl_4$ in H_2O relative to dioxane at 67.3_9: en; 46.0_9, 45.5_9, 45.3_8; pnol αCH_2, 51.1_0; βCH, 67.5_7; CH_3, 20.9.

*(–)$_{589}$-Δ(S)-*cis-*Co(en)$_2$(pnol-*N*)(OH$_2$)$^{3+}$*

Weighed amounts of the corresponding chloro tetrachlorozincate(II) salt were dissolved in 1.0 *M* $HClO_4$ containing 0.02 *M* $Hg(NO_3)_2 \cdot H_2O$ and the solution left at room temperature for two hours to complete the Hg^{2+} assisted chloride release. Visible absorption spectra; λ, (ε): 490 max, (80.4); 405 min, (15.0); 350 (82.6); 308 min, (24.1). CD spectra; λ, Δε: 507, –0.199.

*(–)$_{589}$-Δ(S)-Co(en)$_2$(pnol-*NO*)$^{3+}$*

The above solution was heated at 333 K for 2 hr, cooled to room temperature, and the spectral parameters determined. Visible absorption spectra; λ, (ε): 485 max, (78.5); 401 min, (17.4); 345 max, (81.6), 300 min, (14.2). (These parameters were identical to those obtained from ΔΛ(*RS*)-[Co(en)$_2$(pnol-*NO*)] Cl·ZnCl$_4$H$_2$O, see later). ORD spectra; λ, [M]: 556, –688; 521, 0; 478, +1064; 398, +652. CD spectra; λ, Δε: 512, –0.466; 420, 0; 375, –0.03.

ΔΛ(RS)-(1-aminopropan-2-ol-NO)bis(1,2-diaminoethane)cobalt(III) Chloride Tetrachlorozincate(II) Monohydrate, ΔΛ(RS)-[Co(en)$_2$(pnol-NO)] Cl·ZnCl$_4$·H$_2$O

The procedure outlined for ΔΛ(*RS*)-*cis*-[CoCl(en)$_2$(pnol-*N*)] ZnCl$_4$ was repeated except that 6.0 mL of (*RS*)-1-aminopropan-2-ol was used. After 10 min reaction time at room temperature, HCl (15 mL 12 *M*) and $ZnCl_2$ (15 g) were added. A small amount of the red chloro tetrachlorozincate salt was removed from the cooled solution and the mother liquor slowly deposited orange crystals of the cyclised product over several days (3.5 g). This was recrystallised from dilute HCl by the addition of an equal volume of 12 *M* HCl and $ZnCl_2$ (5 g). Found: Cl, 34.4, 34.1%, calcd. for $Co(en)_2(pnol)ZnCl_5 \cdot H_2O$: Cl, 34.43%. The bromide salt (as the 2.5 hydrate) has previously been reported [4].

Kinetics

The rates of thermal (1.0 *M* $HClO_4$) and Hg^{2+}-assisted aquation (μ = 1.0 *M*) of CoCl(en)$_2$(pnol-*N*)$^{2+}$ were determined spectrophotometrically (Varian Superscan) as previously described [10] and rates of change of optical activity (μ = 1.0 *M*, $H^+ \sim 0.8$ *M*) were measured [9] using a JASCO ORD/CD/UV-5 recording spectropolarimeter.

X-ray Structure [11]

(–)$_{589}$-Δ-*cis*-(*S*-1-aminopropane-2-ol-*N*)chlorobis(1,2-diaminoethane)cobalt(III) tetrachlorozincate(II) forms deep red crystals which are stable to X-rays. Precession photographs using Cu-K$_\alpha$ (λ = 1.5418) radiation were used to determine the crystal symmetry. Unit cell dimensions were obtained at room temperature by a least-squares procedure using the setting angles of 12 reflections on a Hilger and Watts computer controlled four-circle diffractometer. The density was determined pycnometrically in bromoform and bromobenzene solution.

Crystal Data

$[CoCl(en)_2(pnol)]ZnCl_4$, $CoC_7H_{25}N_5OZnCl_5$, formula weight 496.8(8) Daltons, orthorhombic with *a* = 12.330(1), *b* = 13.905(2), *c* = 10.9158(8) Å, V = 1871.4(1) Å^3, D_{obs} = 1.8(1) g cm^{-3}, Z = 4 D_{calc} = 1.76 g cm^{-3}, μ(Mo-K$_\alpha$) = 29.55 cm^{-1}. The conditions limiting possible reflections (h00, h = 2n; 0k0, k = 2n; 00l, l = 2n) uniquely indicate space group $P2_12_12_1$.

X-Ray Data Collection and Reduction

Diffraction data were collected from a well formed crystal of irregular habit (14 faces) and average diameter 0.2 mm and the necessary measurements were made to enable accurate absorption corrections to be applied. (Min 1.861, max 1.945). The crystal was mounted with its y-axis coincident with the ϕ

TABLE I. Final Atomic Parameters for [CoCl(en)$_2$(pnol-*N*)] ZnCl$_4$.

Atom	x	y	z	10^2 U (Å^2)
Zn	0.2366(1)	0.6931(2)	0.7269(2)	3.70(7)
Cl(1)	0.0889(4)	0.7382(4)	0.8389(4)	4.4(1)
Cl(2)	0.2837(4)	0.5433(5)	0.7869(5)	5.5(1)
Cl(3)	0.3815(3)	0.7867(4)	0.7934(4)	4.0(1)
Cl(4)	0.2189(5)	0.7168(6)	0.5266(6)	6.9(2)
Co	0.3625(2)	1.0833(2)	0.6747(2)	2.91(7)
Cl(5)	0.2232(3)	1.0390(4)	0.7961(4)	4.3(1)
N(1)	0.3671(10)	1.2127(12)	0.7455(12)	3.0(3)
N(2)	0.3610(10)	0.9590(13)	0.5909(13)	3.8(4)
N(3)	0.2575(10)	1.1398(12)	0.5573(13)	3.7(4)
N(4)	0.4610(10)	1.0294(13)	0.8023(12)	3.1(4)
N(5)	0.4865(11)	1.1103(13)	0.5670(14)	3.6(4)
C(1)	0.3136(15)	1.2877(18)	0.6675(19)	5.4(6)
C(2)	0.2184(15)	1.2342(17)	0.6044(19)	4.9(5)
C(3)	0.5014(15)	1.0307(15)	0.4783(17)	4.1(5)
C(4)	0.4645(15)	0.9378(19)	0.5320(19)	4.7(5)
C(5)	0.4755(13)	1.0822(16)	0.9192(16)	3.6(5)
C(6)	0.5311(14)	1.0259(18)	1.0194(17)	3.8(5)
C(7)	0.5378(15)	1.0839(18)	1.1313(18)	5.1(6)
H(21)	0.6018(156)	0.9846(138)	0.9895(149)	6[a]
O(1)	0.4706(11)	0.9381(13)	1.0313(13)	5.9(4)

[a]Positional parameters for all other hydrogen atoms were fixed at calculated positions (see text) and thermal parameters for all hydrogen atoms were fixed at $\mu = 0.06$.

axis on the four-circle diffractometer and the orientation was precisely specified in the same least squares procedure used for determining the unit cell parameters [12].

The mosaicity of the crystal was examined by means of open-counter ω-scans at a take off angle of 3°. The width at half height for a typical strong low-angle reflection was 0.3°. The intensity data were collected with Zr filtered Mo-K$_\alpha$ radiation. The circular receiving aperature, positioned 23 cm from the crystal was of 5 mm diameter. Data were collected by the θ–2θ scan technique to a θ limit of 24°. A symmetric scan range of 1.2° centered on the calculated peak position, was composed of 60 steps. Stationary-crystal stational-counter background counts of 15 s were measured at each end of the scan range. The intensities of the standard reflections, which were monitored at regular intervals, showed only the deviations from the mean predicted by counting statistics. Crystal transmission factors were calculated and applied [13] using the method of De Meulenar and Tompa [14].

Solution and Refinement of the Crystal Structure

The structure has been successfully solved and refined in the space group $P2_12_12_1$. All Zn, Co and Cl positions were located by direct methods [15]. Lighter atoms were located in Fourier syntheses following structure factor calculations based on these heavy atoms. In the ensuing least-squares refinement, all data for which $F_o^2 \geqslant 2.5\sigma(F_o^2)$ were used. Refinement was based on F and the function $\Sigma w(F_o - F_c)^2$ was minimised. The weights, w, were taken as $w = K/(\sigma^2 F + |g|F^2)$ ($K = 4.3617$, $g = 0$) and $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. Neutral atom scattering factors [16] and anomalous dispersion corrections (Zn, Co, Cl) [17] were applied. The refinement, using 767 data points (81 parameters) which had $F^2 \geqslant 2.5\sigma(F^2)$ converged to R_1 [18] = 0.058 and R_2 [18] = 0.064.

A difference Fourier synthesis revealed peaks corresponding to reasonable locations for several H atoms but all H atoms except for those on O(1) (not located) and C(6) (allowed to refine) were included in their calculated positions (d(N–H) = d(C–H) = 1.00 Å). A further least squares cycle, in which the parameters of the 23 H atoms were not varied, converged with $R_1 = 0.047$ and $R_2 = 0.052$. Analysis of the final difference Fourier synthesis showed no further peaks of significance and no anisotropic refinement was attempted as such expensive calculations were not expected to reveal any further points of chemical interest [19]. Least squares refinement for both enantiomers gave $R_1 = 0.047$ for $\Delta(S)$ and $R_1 = 0.052$ for $\Lambda(R)$, confirming that the enantiomer is $\Delta(S)$, as expected.

The final refined atom parameters are listed in Table I, and a listing of the final observed and cal-

TABLE II. Bond Distances and Angles in [CoCl(en)$_2$(pnol-*N*)] ZnCl$_4$.

Distance (Å)		*Angles (°)*	
Co–Cl(5)	2.255(13)	N(5)–Co–N(3)	93(2)
Co–N(1)	1.959(46)	N(2)–Co–N(3)	92(2)
Co–N(2)	1.955(46)	N(1)–Co–N(5)	92(2)
Co–N(3)	1.984(38)	N(3)–Co–N(1)	85(2)
Co–N(4)	1.994(36)	N(1)–Co–N(4)	93(2)
Co–N(5)	1.965(38)	N(2)–Co–N(5)	84(2)
N(1)–C(1)	1.50(7)	N(2)–Co–N(4)	90(2)
C(1)–C(2)	1.55(8)	Co–N(3)–C(2)	110(3)
C(2)–N(3)	1.49(7)	Co–N(5)–C(3)	110(3)
N(2)–C(4)	1.46(6)	Co–N(1)–C(1)	114(3)
C(4)–C(3)	1.49(8)	N(1)–C(1)–C(2)	105(5)
C(3)–N(5)	1.48(7)	C(1)–C(2)–N(3)	109(4)
N(4)–C(5)	1.48(6)	Co–N(2)–C(4)	112(4)
C(5)–C(6)	1.51(7)	N(2)–C(4)–C(3)	105(5)
C(6)–C(7)	1.47(8)	C(4)–C(3)–N(5)	111(5)
C(6)–H(21)	1.1(5)	Co–N(4)–C(5)	119(3)
C(6)–O(1)	1.44(7)	N(4)–C(5)–C(6)	115(5)
Zn–Cl(1)	2.282(14)	C(5)–C(6)–C(7)	110(5)
Zn–Cl(2)	2.260(19)	C(5)–C(6)–H(21)	115(25)
Zn–Cl(3)	2.326(14)	C(7)–C(6)–H(21)	120(26)
Zn–Cl(4)	2.221(17)	H(21)–C(6)–O(1)	90(28)
Angles (°)		O(1)–C(6)–C(5)	106(4)
Cl(5)–Co–N(1)	92.4(1.1)	Cl(1)–Zn–Cl(2)	107.7(6)
Cl(5)–Co–N(2)	91.5(1.2)	Cl(2)–Zn–Cl(3)	103.1(3)
Cl(5)–Co–N(3)	89.5(1.2)	Cl(3)–Zn–Cl(4)	107.5(6)
Cl(5)–Co–N(4)	87.2(1.1)	Cl(4)–Zn–Cl(1)	114.1(6)
Cl(5)–Co–N(5)	175.1(1.6)	Cl(2)–Zn–Cl(4)	116.6(7)
N(3)–Co–N(4)	176(2)	Cl(1)–Zn–Cl(3)	107.0(6)
N(1)–Co–N(2)	175(2)		
N(4)–Co–N(3)	93(2)		

Close Contacts		position of second atom		
Cl(1). . . .O(1)	3.186	−½ + x	1½ − y	2 − z
Cl(1). . . .N(5)	3.391	½ − x	2 − y	½ + z
Cl(2). . . .N(4)	3.300	1 − x	−½ + y	1½ − z
Cl(2). . . .N(5)	3.381	1 − x	−½ + y	1½ − z
Cl(3). . . .N(2)	3.270	x	y	z
Cl(3). . . .N(1)	3.294	1 − x	−½ + y	1½ − z
Cl(3). . . .N(5)	3.315	1 − x	−½ + y	1½ − z
Cl(4). . . .N(1)	3.390	½ − x	2 − y	−½ + z
Cl(5). . . .N(2)	3.382	½ − x	2 − y	½ + z
N(3). . . .O(1)	3.028	½ − x	2 − y	−½ + z

culated structure factors is available [18]. Bond lengths and angles are in Table II, together with those intermolecular approaches less than 3.4 Å.

Results and Discussion

Crystal Structure

The structure of the chloropentaaminecobalt(III) salt, resolved by asymmetric association as described in the experimental section, consists of monomeric CoCl(en)$_2$(NH$_2$CH$_2$CH(OH)CH$_3$)$^{2+}$ cations packed with well separated ZnCl$_4^{2-}$ anions, the shortest non-hydrogen interionic distance being the O(1)–Cl(1) separation of 3.19 Å (Fig. 1).

Figure 2 shows a general view of the cation and indicates the atom numbering system. As expected, the bidentate 1,2-diaminoethane ligands are coordinated in a *cis*-configuration with *N*-bonded 1-amino-

TABLE III. Spectropolarimetrically Determined Pseudo-first-order Rate Constants (k_{pol}) for the Formation of $\{-\}_{510}$-Co(en)$_2$(pnol-*ON*)$^{3+}$ from $\{-\}_{510}$-Co(en)$_2$(pnol-*N*)(OH$_2$)$^{3+}$ (μ = 1.0 *M*, HClO$_4$/Hg(NO$_3$)$_2$) and Spectrophotometrically Determined Rate Constants (k_H) for the Formation of Co(en)$_2$(pnol-*ON*)$^{3+}$ from CoCl(en)$_2$(pnol-*N*)$^{2+}$ (μ = 1.0 *M*, HClO$_4$).

T °C[K]	10^4 k_{pol} (s^{-1})	10^4 k_{pol} (calc) (s^{-1})	10^4 k_H (s^{-1})	10^4 k_H (calc)^a (s^{-1})
25.0 [298.2]		0.20		0.010
40.6 [313.8]	1.25 ± 0.04	1.39		
41.6 [314.8]	1.70 ± 0.05	1.69		
44.8 [318.0]	2.81 ± 0.10	2.50		
46.1 [319.3]	2.50 ± 0.20	2.59		
48.2 [321.4]	3.82 ± 0.20	3.73		
49.4 [322.6]	4.00 ± 0.20	4.29		
50.0 [323.2]			0.25^b	
50.2 [323.4]	4.87 ± 0.30	4.71		
52.6 [325.8]	6.12 ± 0.25	6.20		
53.6 [326.8]			0.40 ± 0.03	0.376
59.0 [332.2]			0.69 ± 0.02	0.696
60.0 [333.2]			0.72^b	
64.0 [337.2]			1.19 ± 0.10	1.21
			1.14 ± 0.05	
70.0 [343.2]			2.01^b	
71.2 [344.4]			2.80 ± 0.18	2.60
			2.55 ± 0.28	

^{a}Calculated from the activation parameters cited in Table IV. ^{b}Data from Ref [2, 3] obtained by Cl$^-$ release titration. These data were not included in the activation parameters analysis.

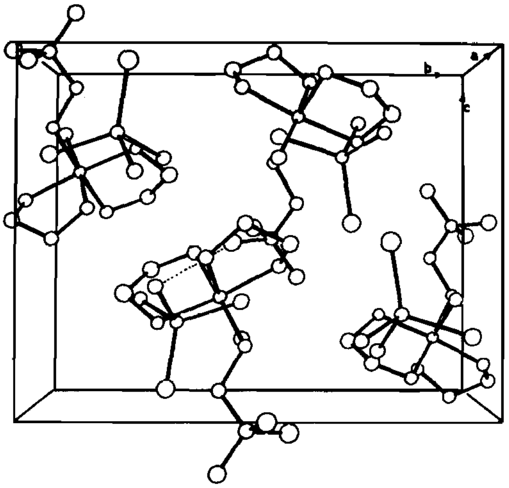

Fig. 1. The packing of the ions in Δ(S)-(–)$_{589}$-[CoCl(en)$_2$(pnol-*N*)] ZnCl$_4$ as viewed down the *a*-axis. The closest non-hydrogen interionic distance of 3.19 A is indicated (. . . . .).

propane-2-ol and chloride ligands occupying the remaining two octahedral sites. The absolute configuration of the complex ion is also shown in Fig. 2 and can be described as Δ(δλ) [21], similar to that found in Δ-(–)$_{589}$-Co(ox)(en)$_2^+$ [22]. The asymmetric carbon atom in the monodentate N-bonded 1-aminopropan-2-ol has the *S* configuration. Thus the stereochemistry of the cation is represented as δλ-Δ(*S*)-*cis*-CoCl(en)$_2$(pnol-*N*)$^{2+}$ with negative rotation at the Na$_D$ line and negative circular dichroism at 506 nm. The determination of the absolute configuration as Δ is in agreement with our previous spectroscopic assignments [23] for *cis*-CoX(en)$_2$(alkylamine)$^{n+}$ and *cis*-CoX(en)$_2$(pyridine type)$^{n+}$ (X = Cl, H$_2$O) complexes where a dominant negative circular dichroism at about 490 nm is apparently characteristic of the Δ configuration.

Bond lengths and bond angles are reported in Table II and torsion angles [24] of –45.3 and 44.7° about the C(1)–C(2) and C(3)–C(4) bonds respectively are normal [25] for this type of complex. Zinc–chlorine bonds within the tetrachlorozincate(II) anion vary between 2.22 and 2.32 Å and again compare very closely with those found in analogous structures [25].

Kinetic Data

The rate of chloride release from *cis*-CoCl(en)$_2$(pnol-*N*)$^{2+}$ has been previously determined in neutral solution by chloride titration [2, 3]. Despite a lowering of pH (1.0 *M* HClO$_4$, to prevent possible base hydrolysis) and an increase in ionic strength, our spectrophotometrically determined rate constants for the rate of disappearance of the cation agree well with the data obtained by chloride release (Tables III and IV). Activation parameters (Table IV) for this reaction are similar to those for other *cis*-CoCl(en)$_2$(alkylamine)$^{2+}$ complexes [26, 27] and although

TABLE IV. Activation Parameters for the Rates of Formation of $Co(en)_2(Aminoalcohol\text{-}ON)^{3+}$ in 1.0 M, $HClO_4$ at 298.2 K.

Reactant	$k(298)$ (s^{-1})	E_a (kJ mol^{-1})	$\Delta S^{\#}_{298}$ (J K^{-1} mol^{-1})	Ref.
$CoCl(en)_2(pnol\text{-}N)^{2+}$	1.0×10^{-6}	103 ± 3	−24 ± 6	a
$CoCl(en)_2(pnol\text{-}N)^{2+}$	1.3×10^{-6}	93	−46	b
$Co(en)_2(pnol\text{-}N)(OH_2)^{3+}$	2.0×10^{-5}	107 ± 3	+14 ± 6	a
$CoCl(en)_2(enol\text{-}N)^{2+}$	1.7×10^{-6}	91	−49	b
$Co(en)_2(enol\text{-}N)(OH_2)^{3+}$	1.7×10^{-5}	100 ± 5	−6 ± 10	c

[a] This work. [b] Ref. [2, 3] by Cl^- titration in H_2O. [c] Ref [29, 30] at $\mu = 0.03$ M by pH-stat.

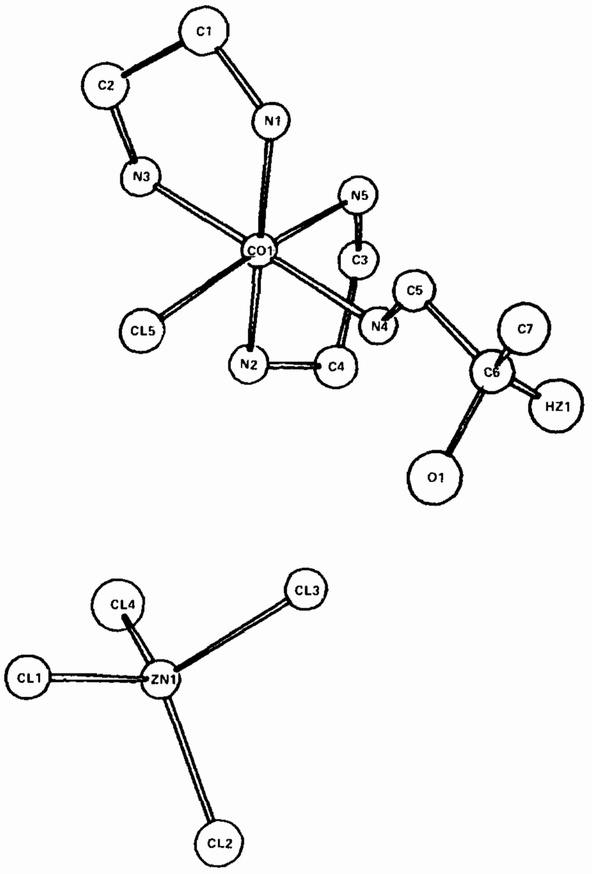

Fig. 2. A general view of the $\Delta(S)$-$(-)_{589}$-$[CoCl(en)_2(pnol\text{-}N)]^{2+}$ cation and $ZnCl_4^{2-}$ anion showing the atom numbering scheme.

$k_H(298)$ is about 3 times larger than for the aquation of *cis*-$CoCl(en)_2(NH_2CH_2(CH_3)_2)^{2+}$ we do not think this difference is mechanistically significant. However, we believe that $Co(en)_2(pnol\text{-}NO)^{3+}$ is the product from the thermal aquation, rather than $Co(en)_2(pnol\text{-}N)(OH_2)^{3+}$ as was suggested previously [2, 3]. The difficulty arises from the fact that the absorption spectra of the two possible products are not easily distinguished. We have overcome this problem by the use of the optically active *cis*-$Co(en)_2(pnol\text{-}N)(OH)_2^{3+}$, where there are significant changes in the circular dichroism spectra between the aqua and cyclised product. $(-)_{589}$-$\Delta(S)$-*cis*-$Co(en)_2(pnol\text{-}N)(OH_2)^{3+}$ can be generated from the active chloro-complex by Hg^{2+} assisted chloride release. The second order rate constant for this reaction (obtained from the racemic chloro), 10^2 k_{Hg} (298) = 2.92 M^{-1} s^{-1} (μ = 1.0 M) (Table V) can be compared with the value of 10^2 $k_{Hg}(298)$ = 1.19 M^{-1} s^{-1} (μ = 0.2 M) [28] for *cis*-$CoCl(en)_2(NH_2CH_2(CH_3)_2)^{2+}$. A slight increase in rate is to be expected at the higher ionic strength [1].

The optically active aqua ion ($[H^+]$ ~ 0.8 M) has a negative circular dichroism at 507 nm ($\Delta\epsilon = -0.199$ M^{-1} cm^{-1}) and this intensifies on heating the solution to give a final product with $\Delta\epsilon = -0.466$ M^{-1} cm^{-1}. We attribute this to the cyclisation of the N-bonded aminoalcohol according to the equation (2),

$$Co(en)_2(pnol\text{-}N)(OH_2)^{3+} \rightarrow Co(en)_2(pnol\text{-}NO)^{3+} + H_2O \qquad (2)$$

and only slight changes occur in the absorption spectrum.

The rate of change of optical activity (k_{pol}, Table III) is about 20 times faster than chloride release at 53 °C and thus in the thermal aquation of the chloropentaamine, no aquapentaamine would be observed. Unfortunately, we cannot rule out aqua racemisation accompanying the cyclisation. Nevertheless we consider such a process would not contribute significantly to the rate of change of optical activity as these are normally [27] characterised by activation energies some 50 kJ mol^{-1} greater than that observed for k_{pol}. Thus we regard k_{pol} as representing the rate of cyclisation and the activation parameters obtained for this reaction are very similar to those found [29, 30] for the spectrophotometrically determined cyclisation of N-bonded 1-aminoethane-2-ol(enol) (Table IV).

TABLE V. Spectrophotometrically Determined Rate Constants for the Formation of $Co(en)_2(pnol\text{-}N)(OH_2)^{3+}$ from ΔΛ-(*RS*)-$[CoCl(en)_2pnol\text{-}N)]\ ZnCl_4$ at 298.2 K in $HClO_4/Hg(NO_3)_2$ (μ = 1.0 *M*).[a]

$[H^+]$ (*M*)	$[Hg^{2+}]_i$ (m*M*)	$10^3\ k_{obs}$[b] (s^{-1})	$10^2\ k_{Hg}$[c] ($M^{-1}\ s^{-1}$)
0.88	42.4	1.38 ± 0.03	3.26 ± 0.07
0.88	42.4	1.21 ± 0.01	2.86 ± 0.03
0.82	65.6	1.86 ± 0.04	2.83 ± 0.06
0.76	86.8	2.35 ± 0.16	2.71 ± 0.19
			(2.92 ± 0.06) Mean

[a] [complex] ~ 2 m*M*. [b] Observed pseudo-first-order rate constants obtained from fixed wavelength scans at 560 nm. [c] $k_{Hg} = k_{obs}[Hg^{2+}]_i^{-1}$.

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