Inorganica Chimica Acta, 14 (1975) 185–194

Acidopentaminecobalt(III) Complexes with Polyamine Ligands. IX. Optically Active *cis*-aminechloro- and *cis*-amineaquabis(ethylenediamine)cobalt(III) Complexes. Bonding Effects and Racemisation Rates.

I. J. KINDRED and D. A. HOUSE
Department of Chemistry, University of Canterbury, Christchurch, New Zealand
Received December 11, 1974

The cis-$CoCl(en)_2(amine)^{2+}$ cations (amine = $MeNH_2$, $EtNH_2$, $nBuNH_2$, γ-picoline, isoquinoline, imidazole and benzimidazole) have been resolved using sodium antimony(III)-(+)-tartrate or sodium arsenic(III)-(+)-tartrate, and the active cations separated from the active counter ions by ion exchange. The active aqua cations have been generated from these chloro ions using the mercury(II) catalysed aquation reaction. ORD and CD spectra for these species have been measured and absolute configurations assigned. The rates of racemisation of the active aqua ions where amine = $MeNH_2$, $EtNH_2$ and imidazole, are also reported.

Introduction

Complexes of the type $CoCl(en)_2(A)^{2+}$, where A is an aliphatic or aromatic heterocyclic amine* are well known[1–6] and a considerable amount of data on the rates of both acid and base hydrolysis of the coordinated chloride have been accumulated.[7–15]

The normal preparation procedure is to react an aqueous slurry of *trans*-$CoCl_2(en)_2^+$ with an aqueous or alcoholic solution of the amine. Under these conditions, primary aliphatic and tertiary aromatic amines react readily, but secondary and tertiary aliphatic amines do not usually coordinate and *trans*-$Co(OH)Cl(en)_2^+$ is a major product.[1]

Where pentaamine products have been obtained, they have generally been assigned a *cis* configuration on the basis of i.r. and visible absorption spectral data.[2,3,16] However, although *cis*-$CoCl(en)_2(NH_3)^{2+}$ was one of the first cobalt(III) complexes to be resolved,[17,18] it is only recently[6] that the *cis* configuration has been proved by resolution for complexes other than those with A = NH_3.*

In this paper, we describe the resolution of a considerable series of *cis*-$CoCl(en)_2(A)^{2+}$ complexes, and with these and previously resolved analogues, we have ORD and CD data for A = ammonia,[18] methylamine, ethylamine, *n*butylamine, aniline,[6] benzylamine,[6] pyridine,[6] γ-picoline, *iso*quinoline, imidazole and benzimidazole. These spectra fall into two groups, with the primary and secondary amines in one class and the aromatic tertiary amines in the other. Thus it is apparent that bonding effects are influencing the shapes of the ORD and CD spectra, as in both groups, the $CoClN_5^{2+}$ chromophore has C_{4v} symmetry for the donor atoms. Nevertheless, the absolute configurations of the complexes can be assigned on the basis of the similarity of their ORD and CD spectra to those of complexes with known absolute configuration.

In addition, the active $Co(en)_2(A)(OH_2)^{3+}$ cations from these chloro complexes have been generated in solution, and kinetic parameters for the racemisation rates of A = ammonia,[19] methylamine, ethylamine, benzylamine,[20] pyridine,[20] and imidazole are now available.

Experimental

The commercially available amines were used without further purification. *trans*-$[CoCl_2(en)_2]Cl$[21,22] and $[CoCl(en)_2(A)]Cl_2$, A = $MeNH_2$,[3] $EtNH_2$,[3] $nBuNH_2$,[3] 4-Me-py[15] were prepared by the literature methods, recrystallised once from HCl and ethanol, and characterised by absorption spectra (Table II). The resolving agent Na(+)AsOT was prepared from a modification of Schlessinger's method.[23] Absolute

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* Abbreviations used: en = ethylenediamine, tetren = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$, $MeNH_2$ = methylamine, $EtNH_2$ = ethylamine, $nBuNH_2$ = *n*butylamine, $BzNH_2$ = benzylamine, an = aniline, py = pyridine, 4-Me-py = 4-methylpyridine = γ-picoline, imid = imidazole, bzimid = benzimidazole, *iso*quin = *iso*quinoline, ORD = optical rotatory disperion, CD = circular dichroism, Na(+)AsOT = sodium arsenic(III)-(+)-tartrate, Na(+)SbOT = sodium antimony(III)-(+)-tartrate, NH_4(+)BCS = ammonium (+)-α-bromo-camphor-π-sulphonate.

* For the resolution of *cis*-$CoCl(en)_2(A)^{n+}$, where A = glycine ester see Reference 6.

alcohol was used to precipitate the salt from aqueous solution, rather than evaporation to dryness. Na(+)SbOT was made similarly using Sb_2O_3 rather than As_2O_3.

The new complexes with A = imid, bzimid and isoquin were prepared by adapting the general method of Bailar and Clapp.[2] The stoichiometric amount of the amine, dissolved in methanol (40 ml) was added to a slurry of *trans*-$[CoCl_2(en)_2]Cl$ (10 g) in water (10 ml). The mixture was stirred mechanically at room temperature for various times, the volume being maintained periodically with methanol. Red crystals of the imidazole complex deposited within 0.5 hr, but with the others, the products formed more slowly and the reaction was continued for 1 week. Yields were between 50 and 70%. In each case, the product was recrystallised from the minimum volume of dilute HCl, by the addition of concentrated HCl and ethanol. The red-pink products were washed with 2-propanol and then ether and air dried. *Analyses:* $[CoCl(en)_2(imidazole)]Cl_2 \cdot {}^1/_2H_2O$: calcd. for $CoC_7H_{20}N_6Cl_3 \cdot {}^1/_2H_2O$: C, 23.19; H, 5.82; N, 23.18. Found: C, 23.07; H, 5.51; N, 23.02. $[CoCl(en)_2(benzimidazole)Cl_2 \cdot {}^1/_2H_2O$: calcd. for $CoC_{11}H_{24}N_6Cl_3 \cdot {}^1/_2H_2O$: C, 31.86; H, 6.07; N, 20.27. Found: C, 31.71; H, 5.70; N, 19.69. $[CoCl(en)_2(isoquinoline)]Cl_2 \cdot H_2O$: calcd. for $CoC_{13}H_{25}N_5Cl_3O$: C, 36.09; H, 5.82; N, 16.19. Found: C, 36.28; H, 5.81; N, 16.63.

Resolution Procedure

The recrystallised chloropentaamine salt (2 g) was dissolved in water (10 ml) at room temperature (or with warming if necessary) and the solid resolving agent (5 g) stirred in. Crops of the product were collected periodically (see Table I), washed with 2-propanol, then ether and air dried. In some cases, excess $NaNO_3$ or $NaClO_4 \cdot H_2O$ was added to the mother liquor after the crystallisation of the less soluble diastereoisomeride appeared to be complete.

The active anion was removed from the diastereoisomeride using the anion exchange resin procedure described previously.[24] ORD, CD and visible absorption spectra were measured for the cation in the column effluent using a JASCO ORD/CD/UV-5 recording spectropolarimeter and the Co(III) concentration was determined by $S_2O_8^{2-}$ decomposition.[25] Aqua complexes were generated by addition of Hg^{2+} (as the solid nitrate or acetate salts) to solutions of the chloro complexes of known concentration in 0.1 *F* $HClO_4$, and the chiroptical parameters were determined after 24 hr at room temperature.[6] These procedures were duplicated for all diastereoisomeride crops to obtain the mean spectral parameters for the most active samples quoted in Tables IV–VII.

Every effort has been made to obtain "complete resolution" of these chloro complexes, and most of the resolution procedures have been carried out separately by both authors. However, it is obvious from the chiroptical parameters (Tables IV–VII) that the complexes with A = nBuNH$_2$ (and probably A = 4-Me-py) are only partially resolved.

Attempts were also made to resolve some $CoCl(en)_2(A)^{2+}$ ions (A = py, $EtNH_2$, n-BuNH$_2$) using Sephadex.[26–28] About 200 mg of the racemic complex was dissolved in 30 ml of water and absorbed on a SE–Sephedex C-25, 40–120 μ, 10 cm × 2.5 cm column. A 0.2 *F* sodium (+)-tartrate solution was used as an eluting agent with a flow rate of *ca.* 1 ml/min, and 7 ml aliquots of the coloured effluent were collected. Visible absorption and CD spectra were recorded for 14 samples and the CD parameters calculated from the known[6] spectral parameters. For A = py, partial resolution was obtained and the following data in the order, (fraction number), $[10^{-1}\Delta\varepsilon]_{465}$ shows the results: (1), +1.15; (2), +0.45; (3), +0.20; (4), +0.08; (5), +0.02; (6), –0.03; (7), –0.06; (8), –0.09; (9), –0.11; (10), –0.13; (11), –0.18; (12), –0.27; (13), –0.35; (14), –0.33.

TABLE I. Resolution Procedures for (±)-*cis*-$[CoCl(en)_2(A)]Cl_2$. Yield of Diastereoisomeride and Sign of Rotation of the Active Cation at 589 nm.

A	Crop 1	Crop 2	Crop 3	Resolving Agent[b]
$MeNH_2$	1.0g (20 min) (+)	0.9g (ClO_4^-) (–)[c]		1
$EtNH_2$[d]	1.9g (2 day) (+)	0.4g (1 week) inactive	0.9g (NO_3^-)[e] inactive	1
nBuNH$_2$	0.3 g (1 day) (–)	inactive	inactive	2
4-Me-py[f]	0.8 g (1 day) (+)	0.4 g (1 week) (+)	0.3 g (NO_3^-)[e] (inactive)	2
*iso*quin[g]	0.3 g (hot) (–)	0.4 g (cold) (–)	0.8 g (1 week) (+)	2
imid	0.05 g (1 day) (+)	0.9 g (2 day) (+)	0.6 g (5 day) (–)[h]	1
bzimid	1.2 g (1 day) (–)	0.3 g (1 week) (+)		1

[a] Chloropentaamine chloride (2 g) in water (10 ml) at room temperature plus resolving agent (5 g). [b] Resolving agents; Na[(+)SbOT] = 1, Na[(+)AsOT] = 2. [c] Excess $NaClO_4 \cdot H_2O$ (3 g) added to filtrate after the removal of the less-soluble diastereoisomeride. [d] Double scale. [e] Excess $NaNO_3$ (8 g) added to filtrate after the removal of the less-soluble diastereoisomeride. [f] In 80 ml of 40° C water. [g] At 40° C initially. [h] Crop 4; 0.2 g (1 week) (–). Crop 5; 0.3 g (NO_3^-) (inactive)[e].

$[10^{-1}\Delta\varepsilon]_{465} = 10M^{-1}$ cm^{-1} for the most active sample obtained by diasteroisomeride resolution. With A = EtNH$_2$, nBuNH$_2$, no resolution from Sephadex was achieved.

Racemisation Kinetics

The techniques and procedures described previously[20] were used.

Results and Discussion

The resolution of seven CoCl(en)$_2$(A)$^{2+}$ complexes assigns the *cis* configuration to the racemic analogues. The visible absorption, ORD and CD spectral parameters are listed in Tables II, IV and V and Figures 1 and 2 give plots of $[M]_\lambda$ and $[\Delta\varepsilon]_\lambda$ *vs.* wavelength. Tables III, VI and VII and Figures 3 and 4 present similar data for the corresponding active aqua ions. Although the conventional method of diastereoisomeride formation has been used for the resolution of the chloro complexes, *cis*-CoCl(en)$_2$py^{2+} was also partially resolved on Sephedex using Na$_2$(+)tartrate as the eluting solution. However, the resolution achieved was only one tenth that of thc most active diastereoisomeride and for A = EtNH$_2$ or *n*BuNH$_2$, no resolution was observed under the conditions used.

Table VIII lists the absolute configurations assigned to the less soluble diastereoisomeride for the particular resolving agents used. In no case does the less soluble diastereoisomeride give a unique absolute configuration. This provides further evidence that the application of "the method of less soluble diastereoisomerides",[29–32] without checks for isomorphism, will lead to an erroneous absolute configuration.

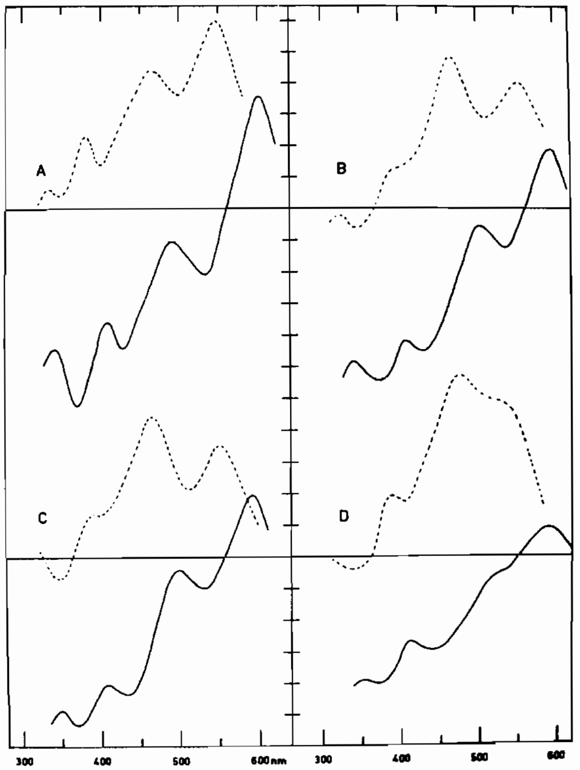

Figure 1. ORD —— and CD ----- spectra of (+)-Λ-CoCl(en)$_2$(NH$_3$)$^{2+}$ (A), (+)-CoCl(en)$_2$(MeNH$_2$)$^{2+}$ (B), (+)-CoCl(en)$_2$(EtNH$_2$)$^{2+}$ (C) and (+)-CoCl(en)$_2$(BzNH$_2$)$^{2+}$ (D) in 0.1*F* HClO$_4$ (B, C, D). Data for A(ORD) were taken from Ref. 30 and for A(CD) from Ref. 18. For ORD each ordinate division corresponds to $[M]_\lambda = \pm 200$ deg M^{-1} m^{-1}, except for D, where each division corresponds to ±400 deg M^{-1} m^{-1}. For CD each ordinate division corresponds to $[\Delta\varepsilon]_\lambda = \pm 0.05M^{-1}$ cm^{-1}.

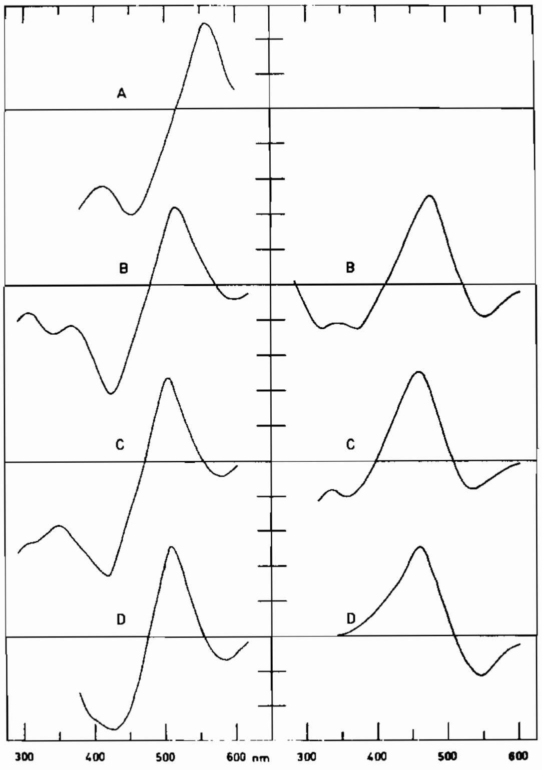

Figure 2. ORD (left hand column) and CD (right hand column) spectra of Λ-(+)-CoCl(en)$_2$(OH$_2$)$^{2+}$ (A),[30] (–)-CoCl(en)$_2$(benzimidazole)$^{2+}$ (B), (–)-CoCl(en)$_2$(imidazole)$^{2+}$ (C) and (–)-CoCl(en)$_2$(pyridine)$^{2+}$ (D) in 0.1 *F* HClO$_4$ at 20–23° C. For ORD, each ordinate division corresponds to [M] = ±1000 deg M^{-1} m^{-1} except A and B where each division corresponds to ±500 and ±2000 respectively. For CD, each ordinate division corresponds to $[\Delta\varepsilon] = \pm 0.4M^{-1}$ cm^{-1} except for B, where each division corresponds to $[\Delta\varepsilon] = \pm 0.8$.

TABLE II. Visible Absorption Spectral Parameters for Some *cis*-$CoCl(en)_2(A)^{2+}$ Cations in Dilute $HClO_4$ at 20–23° C.

A	This Work			Literature		Ref.
	max	min	max	max	max	
NH_3				526 (58)	364 (66)	18
$MeNH_2$	532 (62)	422 (10)	368 (67.5)	530 (63)	370 (69)	3
$EtNH_2$	530 (74)	420 (17)	368 (81)	530 (64)	360 (67)	3
n$BuNH_2$	528 (75)	421 (18)	368 (83)	528 (79)		3
aniline				518 (93)		6
benzylamine				528 (74)	367 (90)	6
pyridine				525 (76)	369 (81)	6
4-Me-py	520 (77)	422 (21)	369 (84)	535 (82)	376 (87)	15
*iso*quinoline	517 (83)	422 (24)				
imidazole	520 (78.5)	430 (23)	360 (95)			
benzimidazole	520 (82.2)	430 (29)	365sh (125)			

TABLE III. Visible Absorption Spectral Parameters for Some *cis*-$Co(en)_2(A)(OH_2)^{3+}$ Cations in Dilute $HClO_4$ at 20–23° C.

A	This Work			Literature		Ref.
	max	min	max	max	max	
NH_3				485 (65)	351 (72)	18
$MeNH_2$	490 (61.3)	416 (8)	352 (56)	490 (60)		3
$EtNH_2$	488 (74)	405 (15)	350 (71)	490 (66)	350 (65)	3
n$BuNH_2$	489 (76)	407 (18)	352 (74)	488 (81)		3
aniline				480 (140)		6
benzylamine				488 (77)		6
pyridine				482 (78)	351 (68)	6
4-Me-py	483 (79.5)	407 (17.5)	354 (70)			
*iso*quinoline	482 (94)	409 (23)				
imidazole	475 (90.3)	404 (28)	355sh (99)			
benzimidazole	486 (93.3)	416 (27.6)				

TABLE IV. ORD Spectral Parameters for some Λ-*cis*-$CoCl(en)_2(A)^{2+}$ Cations in Dilute $HClO_4$ at 20–23° C.

A	$[H^+]$	(λ), nm $[M]_\lambda$, deg $M^{-1}m^{-1}$									Ref.
OH_2			(589) +		(555) +1220	(520) 0	(455) –1500	(416) –1100			30
bzimid	0.1	(600) –821	(589) –755	(572) 0	(516) +4390	(481) 0	(426) –6160	(360) –2330	(339) –2730	(310) –1575	
imid	0.1	(589) –322	(578) –413	(554) 0	(506) +2360	(473) 0	(420) –3260	(352) –1810	(314sh) –2270		
py	0.1	(594) –692	(589) –681	(561) 0	(511) +2540	(475) 0	(431) –2670	(395sh) –2330			6
4-Me-py	0.1	(590) –221	(589) –217	(557) 0	(506) +805	(471) 0	(426) –863	(375) –720			
*iso*quin	0.1	(592) –628	(589) –622	(556) 0	(509) +1655	(476) 0	(428) –2080	(388) –1815			
NH_3		(602) +710		(560) 0	(535) –420	(493) –210	(430) –880	(410) –720	(370) –1250	(345) –890	30
$MeNH_2$	0.1	(595) +377	(589) +365	(562) 0	(535) –251	(502) –117	(430) –900	(405) –835	(375) –1092	(350) –970	
$EtNH_2$	0.1	(594) +387	(589) +384	(557) 0	(533) –200	(500) –80	(434) –870	(407) –808	(370) –1070	(348) –972	
n$BuNH_2$	0.1	(594) +70	(589) +66	(555) 0	(530) –75	(505) –24	(432) –216	(405) –173	(370) –252	(348) –228	
aniline	0.1	(596) +266	(589) +247	(556) 0	(520sh) –328		(444) –374				6
$BzNH_2$	0.1		(589) +362	(550) 0	(530sh) –198		(440) –1180	(410) –1080	(370) –1610	(352) –1560	6

TABLE V. CD Spectral Parameters for Some Λ-*cis*-$CoCl(en)_2(A)^{2+}$ Cations in Dilute $HClO_4$ at 20–23° C.

A	$[H^+]$	(λ), nm $\Delta\varepsilon$, $M^{-1}cm^{-1}$								Ref.
bzimid	0.1	(550) –0.770	(519) 0	(476) +2.09	(412) 0	(372) –0.975	(346) –0.897	(320) –1.00	(286) 0	
imid	0.1	(533) –0.319	(507) 0	(458) +1.07	(398) 0	(357) +0.393	(328) –0.325			
py	0.1	(541) –0.476	(508) 0	(464) +1.03						6
4-Me-py	0.1	(540) –0.153	(509) 0	(462) +0.338	(367) 0	(360) –0.004	(351) 0			
*iso*quin	0.1	(542) –0.371	(509) 0	(464) +0.723	(386) 0	(350) +0.097				
NH_3		(547) +0.30	(500) +0.18	(466) +0.22	(400) +0.07	(383) +0.09	(350) +0.02	(335) +0.03	(320) 0	18
$MeNH_2$	0.1	(555) +0.209	(512) +0.143	(465) +0.239	(390sh) +0.059		(368) 0	(346) –0.031	(325) –0.011	
$EtNH_2$	0.1	(552) +0.176	(512) +0.107	(466) +0.219	(400) +0.067	(390) +0.069	(364) 0	(350) –0.033	(324) 0	
n$BuNH_2$	0.1	(552) +0.055	(512) +0.038	(467) +0.059	(405) +0.017	(385) +0.019	(364) 0	(350) –0.009	(334) 0	
aniline	0.1	(550) +0.156		(470sh) +0.088						6
$BzNH_2$	0.1	(530sh) +0.244		(475) +0.286	(405) +0.086	(388) +0.094	(361) 0	(345) –0.020		6

TABLE VI. ORD Spectral Parameters for Some Λ-cis-$Co(en)_2(A)(OH_2)^{3+}$ Cations in Dilute $HClO_4$ at 20–23° C.

A	H^+	(λ), nm $[M]_\lambda$, deg M^{-1} m^{-1}										Ref.
OH_2	1.5		(589) +35			(520) +1180	(480) 0	(445) −1330	(390) −703	(360sh) −818		30
bzimid	0.1	(594) 0	(589) −73	(580) −110	(572) 0	(506) +7870	(469) 0	(431) −6250		(350) 0		
imid	0.1		(589) +52			(497) +3630	(462) 0	(424) −3350	(380sh) −2410	(327) −276		
py	0.1		(589) +43			(505) +3730	(466) 0	(430) −2970	(394sh) −2100	(338) −343		6
4-Me-py	0.1		(589) −51	(580) −59	(562) 0	(500) +1130	(463) 0	(424) −985	(380) −740	(335) −187		
*iso*quin	0.1		(589) +155	(581) +137		(502) +2520	(466) 0	(430) −2080	(390sh) −1560			
NH_3						(564) +724	(526) 0	(440) −1408	(389) −1200	(360) −1600	(330) −1216	30
$MeNH_2$	0.1		(589) +129			(554) +199	(509) 0	(430) −930	(395) −832	(350sh) −1250		
$EtNH_2$	0.1		(589) +164			(550) +249	(511) 0	(428) −792	(396) −673	(350sh) −1125		
n$BuNH_2$	0.1		(589) +38			(555) +33		(433) −256	(402) −161	(344sh) −327		
aniline	0.1		(589) +198			(570) +234	(530) 0	(438) −980	(410) −850			6
$BzNH_2$	0.1		(589) +148			(550) +296	(514) 0	(442) −1310	(400) −1210	(356) −1830		6

TABLE VII. CD Spectral Parameters for Some Λ-*cis*-$Co(en)_2(A)(OH_2)^{3+}$ Cations in Dilute $HClO_4$ at 20–23° C.

A	H^+	(λ), nm Δε, M^{-1} cm^{-1}						Ref.
OH_2	1.5	(555) −0.232	(525) 0	(478) +0.735	(374) +0.085	(340sh) +0.069	(295) 0	36
bzimid	0.1	(534) −0.937	(508) 0	(463) +3.04	(400) 0	(356) −0.900	(304) 0	
imid	0.1	(526) −0.403	(501) 0	(455) +1.53	(389) 0	(346) −0.436		
py	0.1	(531) −0.410	(505) 0	(458) +1.38	(381) 0	(350) −0.268		6
4-Me-py	0.1	(532) −0.132	(505) 0	(456) +0.473	(383) 0	(353) −0.094	(309) 0	
*iso*quin	0.1	(533) −0.232	(508) 0	(460) +1.155	(391) 0	(358) −0.258		
NH_3	0.1	(515) +0.31	(472sh) +0.18	(400) +0.05	(377) +0.09	(340) +0.01	(325) +0.03	18
$MeNH_2$	0.1		(470) +0.231	(396) +0.043	(370) +0.065	(320sh) +0.022	(295) 0	
$EtNH_2$	0.1		(482) +0.222	(396) +0.047	(370) +0.069	(336) +0.029	(328) +0.031	
n$BuNH_2$	0.1		(487) +0.055	(400) +0.010	(370) +0.018			
aniline	0.1		(496) +0.241					6
$BzNH_2$	0.1		(484) +0.367	(400) +0.060	(365) +0.090			6

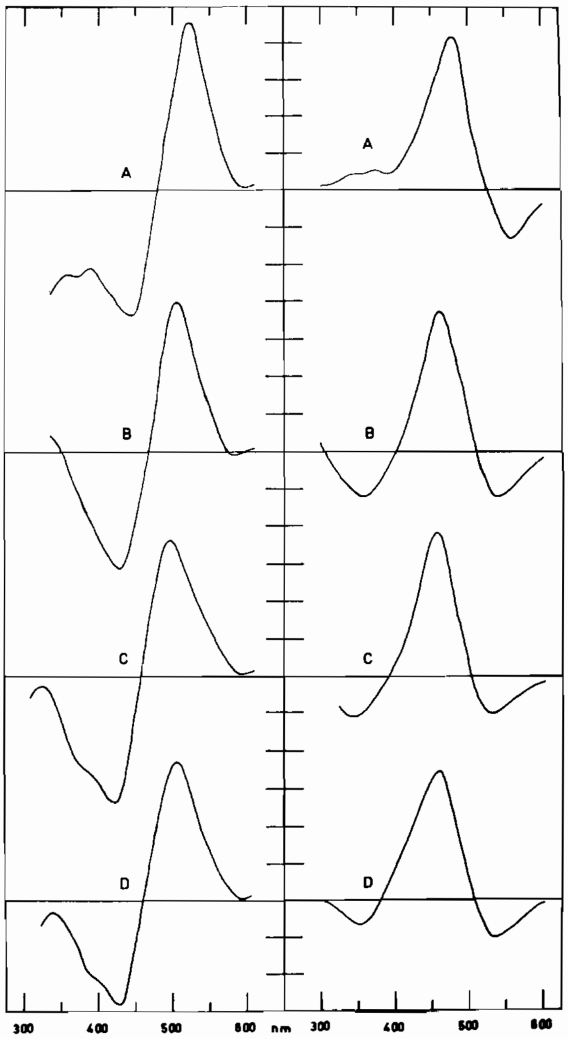

Figure 3. ORD (left hand column) and CD (right hand column) spectra of Λ-(+)-$Co(en)_2(OH_2)_2^{3+}$ (A),[36] (−)-$Co(en)_2$(benzimidazole)$(OH_2)^{3+}$ (B), (+)-$Co(en)_2$(imidazole)$(OH_2)^{3+}$ (C) and (+)-$Co(en)_2(py)(OH_2)^{3+}$ (D) in 0.1*F* $HClO_4$ containing Hg^{2+} at 20–23° C. For ORD, each ordinate division corresponds to [M] = ±1000 deg M^{-1} m^{-1}, except for A and B, where each division corresponds to ±500 and ±2000, respectively. For CD, each ordinate division corresponds to $\Delta\varepsilon$ = ±0.4M^{-1} cm^{-1}, except for A and B, where each division corresponds to ±0.2 and ±0.8, respectively.

Visible Absorption Spectra

These are typical of pentaaminecobalt(III) chloro or aqua complexes (Tables II and III) and are characterised by a band at about 525 nm (usually with a more or less pronounced shoulder on the low wavelength side) for the chloro species and a more symmetrical band at about 490 nm for the aqua ions. Most of the chloro complexes are also characterised by an absorption band at about 370 nm, but in some cases (A = benzimidazole) this appears as a shoulder on the u.v. charge transfer band. As this band moves further towards the u.v. (to about 355 nm) in the aqua ions,

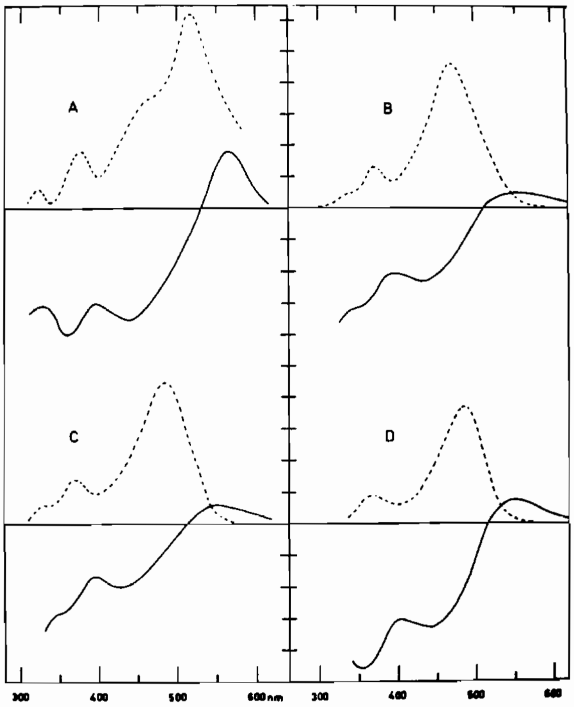

Figure 4. ORD —— and CD ----- spectra of (+)-Λ-$Co(en)_2(NH_3)(OH_2)^{2+}$ (A), (+)-$Co(en)_2(MeNH_2)(OH_2)^{3+}$ (B), (+)-$Co(en)_2(EtNH_2)(OH_2)^{3+}$ (C) and (+)-$Co(en)_2(BzNH_2)(OH_2)^{3+}$ D in 0.1*F* $HClO_4$ (B, C, D). Data for A(ORD) were taken from Ref. 30 and for A(CD) from Ref. 18. For ORD, each ordinate division corresponds to $[M]_\lambda$ = ±400 deg M^{-1} m^{-1}. For CD each ordinate division corresponds to $[\Delta\varepsilon]_\lambda$ = ±0.05M^{-1} cm^{-1} except for D, where each division corresponds to ±0.1M^{-1} cm^{-1}.

TABLE VIII. Sign of Rotation at the Na_D Line and Absolute Configuration of the Less Soluble Diastereoisomerides of Some *cis*-$CoCl(en)_2A^{2+}$ Salts.

Resolving Agent	Λ	Δ
NH_4(+)BCS	(+)-NH_3[30]	(−)-aniline[6] (−)-benzylamine[6]
K(+)SbOT	(+)-benzylamine[6] (−)-pyridine[6]	(−)-NH_3[31]
Na(+)SbOT	(−)-benzimidazole	(−)-$MeNH_2$ (−)-*n*$BuNH_2$ (+)-pyridine (+)-imidazole
Na(+)AsOT	(+)-$EtNH_2$ (+)-benzylamine (−)-isoquinoline	(+)-γ-picoline

it is occasionally masked completely for these species. Thus, within the visible region, there is no evidence for interaction between the π-orbitals of the aromatic ring system and the partly filled shell of the central Co(III) in the systems where such interaction is possible. It is interesting to note that for the visible chiroptical parameters, the intensities observed for the aqua ions are generally greater than those of the corresponding chloro species.

ORD and CD Spectra

Chloro Complexes

The ORD spectrum of the parent complex, A = NH_3, has been recorded by Matheiu[33] and by Garbett and Gillard,[30] while the CD spectrum has been recorded by Norman.[18] Their data are reproduced in Figure 1A and Tables IV and V. The absolute configuration of the $(+)$-$CoCl(en)_2(NH_3)^{2+}$ ion has been assigned as Λ (previously D)* on the basis of both chemical interconversions[30] and spectroscopic considerations.[18]

It is apparent from an inspection of the data in Tables IV and V and by comparing the ORD and CD spectra presented in Figure 1, that the $(+)_{589}$ isomers of the complexes with A = $MeNH_2$, $EtNH_2$, *n*$BuNH_2$, and $BzNH_2$, have absolute configurations similar to $(+)$-$CoCl(en)_2(NH_3)^{2+}$ (*i.e.* Λ). These are complexes where the amine ligand is bonded through a primary amino nitrogen atom. It is also apparent that the ORD and CD spectra of complexes containing A = py, 4-Me-py, *iso*quin, imid or bzimid (Figure 2, Tables IV and V) are related to one another, but are difficult to correlate with the spectra for complexes with primary amines. This class of complex contains tertiary nitrogen donor atoms where the nitrogen is associated with the π-system of an aromatic ring.

We suggest, however, that these spectra may be correlated with, and are similar to, the ORD spectrum of $(+)$-$CoCl(en)_2(OH_2)^{2+}$ (Figure 2A) which has been assigned the Λ absolute configuration by Garbett and Gillard[30] and MacDermott and Sargeson[34] (the correlation is even more marked when the ORD or CD spectrum of Λ-$(+)$-$Co(en)_2(OH_2)_2^{3+}$ are compared with the ORD or CD spectra of $(+)_{500}$-$Co(en)_2(A)(OH_2)^{3+}$, A = tertiary amine, see later). If this is the case, the $(-)_{589}$ isomers of $CoCl(en)_2(A)^{2+}$, A = tertiary aromatic amine, can be assigned to the Λ absolute configuration.

In addition, for both classes of amines, the dominant CD band (*ca.* 520 nm) in the region of the first absorption maxima is positive, for the isomers listed in Table V. There seems to be a general consensus of opinion,[35] that a dominant positive CD in this region results from the orientation of non-adjacent pairs of chelate rings in the same way as they occur in Λ-$(+)$-$Co(en)_3^{3+}$.

Aqua Complexes

Inspection of Figures 3 and 4 and Tables VI and VII shows that the ORD and CD spectra of the active *cis*-$Co(en)_2(A)(OH_2)^{3+}$ ions again fall into the above two classes. The $(+)_{589}$ isomers for A = $MeNH_2$, $EtNH_2$, *n*$BuNH_2$, and $BzNH_2$ are assigned the Λ configuration on the basis of the similarity of their ORD and CD spectra with those of Λ-$(+)$-$Co(en)_2(NH_3)(OH_2)^{3+}$.[18] on the other hand, the ORD and CD spectra of the aqua complexes with A = tertiary aromatic amine are more readily related to the analogous spectra of Λ-$(+)$-$Co(en)_2(OH_2)_2^{3+}$ [36] and the $(+)_{500}$ isomers* are assigned to this configuration.

Bonding Effects

We now come to the question as to the origin of these chiroptical effects for the two classes of amines. Bosnich and Harrowfield[37] have pointed out the optical activity shown by *d–d* electronic excitations of transition metal ions can be attributed to three sources: the configurational, the conformational and the vicinal effects. Such a view is essentially based on symmetry considerations. Alternatively, Katzin and Eliezer[38] suggest that the factors effecting electron distribution in the bonds to the metal ion are the most significant ones. Unfortunately, despite a considerable body of information,[38,39] the CD spectra (and consequently, the ORD spectra) of *cis*-$Co(XY)(en)_2^{n+}$ complexes remain difficult to interpret.[39]

Within the present systems, we have essentially the same $CoXN_5^{n+}$ chromophore, as evidenced from the visible absorption spectra and hence essentially the same symmetry for the complexes. We thus suggest, following Katzin and Eliezer,[38] that the difference in ORD and CD spectra between the primary and tertiary amines is due to electronic effects. The major difference in electron distribution between the two classes of amines is that for primary amines, the bonding is restricted to the σ type, whereas for the tertiary amines, some π-bonding with cobalt(III) is possible. On the other hand, it may be argued that the differences are due to inductive effects. However, there does not appear to be a correlation between the ORD or CD

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* For a description of the Λ and Δ arrangements of the chelate rings in *cis*-$M(en)_2XY^{n+}$ complexes see Figure 3 in Reference 24 and "Nomenclature of Absolute Configurations Based on the Octahedron", *Inorg. Chem., 9,* 1 (1970). Where no wavelength subscript follows the sign of rotation, the wavelength is assumed to be 589 nm.

* This wavelength is used because of the variable sign of rotation at 589 nm for these aqua ions with related absolute configurations. If the rotation at 589 nm is used, the $(-)_{589}$ isomers with A = bzimid and 4-Me-py and the $(+)_{589}$ isomers with A = py, *iso*quin and imid all have the same Λ absolute configuration.

and base strength of the amine, but rather the presence or absence of a π-electron system. It is thus tempting to assume that the aromatic hetrocyclic amines are producing "anomolous" ORD and CD spectra. It is important to realise, however, that the "amino type" nitrogen is one of the few donor atoms which does not have any other vacant or fillcd orbitals available for potential π-bonding. This may well be the reason for the similarity of the CD spectra of many CoN_6^{3+} (N = amino nitrogen) complexes.[38,40,41] If this amino nitrogen effect is dominent, we would expect the ORD and CD spectra of all $CoClN_5^{2+}$ (N = amino nitrogen) complexes to be similar to those of $CoCl(en)_2(NH_3)^{2+}$. The ORD and CD spectra of (–)-Δ*-CoCl(tetren)$^{2+}$ have been published[35,42] but the similarity between these and the analogous spectra of $CoCl(en)_2(RNH_2)^{2+}$ reported here is not marked. However, the spectra of CoCl(tetren)$^{2+}$ are almost certainly composite, being made up of contributions from both configurational (chelate rings) and conformational (asymmetric *sec* NH proton) effects, and comparisons between the two systems are probably not valid.

Even so, it is probably an oversimplification to try to explain trends in ORD or CD spectra solely in bonding or symmetry terms, but rather a combination of both effects appears necessary. Nevertheless, within the range of complexes studies here, bonding effects are clearly demonstrated.

Racemisation Kinetics for the Aqua Ions

The rates of racemisation for the active *cis*-$Co(en)_2(A)(OH_2)^{3+}$ ions (A = $MeNH_2$, $EtNH_2$, imid) have been measured spectropolarimetrically in 0.1 *F* $HClO_4$ at various temperatures. Table IX lists the observed peuso first order rate constants obtained and Table X, the activation parameters calculated from these data. Previously determined activation parameters for A = NH_3,[19] py,[20] $BzNH_2$[20] are also included. The reactions are characterised by relatively high activation energies and large positive activation entropies. In view of the similarity of the activation parameters for A = $MeNH_2$, $EtNH_2$, $BzNH_2$, py, imid, it is possible that the energy of activation for A = NH_3[19] is too low.

Under the acid conditions used, there was no evidence for loss of optical activity by any other path than racemisation, and the absorption spectra throughout corresponded to the *cis*-$Co(en)_2(A)(OH_2)^{3+}$ ion. The mechanism of these racemisation processes has been discussed previously.[20]

TABLE IX. Pseudo First-order Rate Constants for the Racemisation of Some Active *cis*-$Co(en)_2(A)(OH_2)^{3+}$ Cations in 0.1*F* $HClO_4$.

A	T °C	10^5k (sec^{-1})	10^5k_{calc}[a] (sec^{-1})
imid	73.9	1.70 ± 0.08	1.69
	77.0	2.61 ± 0.13	2.70
	80.0	4.24 ± 0.2	4.23
	82.9	7.03 ± 0.35	6.48
	85.9	10.1 ± 0.5	9.99
	89.0	14.8 ± 0.7	15.5
$MeNH_2$	70.0	0.64 ± 0.03	0.65
	80.0	3.10 ± 0.15	3.03
	81.6	4.02 ± 0.2	3.85
	84.2	5.52 ± 0.25	5.66
	86.8	7.80 ± 0.4	8.26
	89.9	12.6 ± 0.6	12.9
	92.4	19.1 ± 0.95	18.4
$EtNH_2$	78.0	2.50 ± 0.12	2.55
	80.9	4.04 ± 0.2	3.94
	84.9	7.39 ± 0.37	7.10
	88.0	11.4 ± 0.57	11.1
	90.9	16.3 ± 0.8	16.7

[a] Calcd. using the kinetic parameters listed in Table X.

Acknowledgements

We thank the New Zealand Universities Grants Committee for providing funds to purchase instruments used in this research.

TABLE X. Activation Parameters for the Racemisation of Some *cis*-$Co(X)(en)_2(A)^{n+}$ Ions in Aqueous Acidic Solution.

A	H^+ (*F*)	10^9 k(25° C) (sec^{-1})	E_a (kJ mol^{-1})	logPZ (sec^{-1})	ΔS_{298} (JK^{-1} mol)	Ref.
NH_3	0.1	22.5	118 ± 3	13.09	−2.5 ± 6	19
$MeNH_2$	0.1	1.7	156 ± 2	18.52	+101 ± 4	
$EtNH_2$	0.1	2.0	155 ± 3	18.48	+100 ± 6	
$BzNH_2$	0.1	2.0	157 ± 4	18.93	+109 ± 8	20
imid	0.1	2.74	153 ± 5	18.33	+97 ± 10	
py	0.1	4.3	164 ± 2	20.43	+138 ± 6	20

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* Hawkins (Reference 32, p. 355–6) regards this assignment as not proven, but subsequent X-ray analysis[35] has shown it to be correct.

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