Chiral Metal Complexes.
9.* Changes in Tetradentate Stereochemistry Involving a Λ-α to Δ-α Rearrangement: a New Form of Octahedral Inversion

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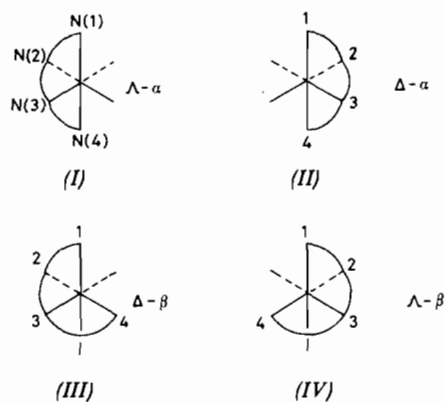*School of Chemistry, Macquarie University, North Ryde 2113, N.S.W., Australia*

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When Λ-α-[Co(R-picpn)Cl₂]ClO₄ (R-picpn = (3R)-3-methyl-1,6-di(2-pyridyl)-2,5-diazahexane) is reacted with sodium oxalate in aqueous solution, the complex Λ-α-[Co(R-picpn)(ox)]ClO₄ is obtained. This reaction represents a total inversion of absolute configuration with respect to the metal centre. When isolated as the iodide salt, [Co(R-picpn)(ox)]I·1.5H₂O, the cationic product is obtained as a mixture of Δ-α and Λ-β diastereoisomers with a minor quantity of the Λ-α form. These isomeric ratios appear to be influenced by differences in reaction conditions, including exposure to light.
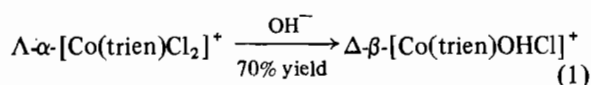
Introduction

Unlike reactions involving substitution at tetrahedral atomic centres, those resulting in inversion of absolute configuration of octahedral coordination complexes are few in number. Most of these inversions have involved species containing bidentate ligands such as en†, phen or an α-amino acid [2–4], although some examples are known of Co(III) complexes with nitrogen-donor linear tetradentates [5].

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*Part 8 is reference [1].

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†en = 1,2-diaminoethane, phen = 1,10-phenanthroline, trien = 1,4,7,10-tetraazadecane, R-picpn = (3R)-3-methyl-1,6-di(2-pyridyl)-2,5-diazahexane, R-(−)-pn = R-1,2-diaminopropane, S,S-peaen = (2S,7S)-2,7-di(20pyridyl)-3,6-diazaoctane, ox = oxalate dianion.

When the simplest such ligand, trien, coordinates with *cis*-topology, several isomers may result. These are shown in (I)–(IV) below. The absolute configuration of N(3) in the β-isomers may be either *R* or
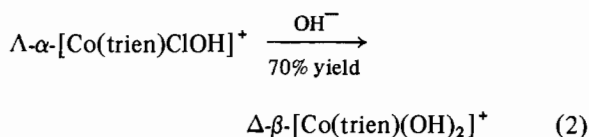

(I)   *(II)*   *(III)*   *(IV)*

S, but the configuration of N(2) in each is determined by the absolute configuration of the complex. Substitution on the ligand or completion of the coordination sphere with non-equivalent unidentates or an asymmetric bidentate would each serve to further increase the number of possible isomers. Reactions of *cis*-[Co(trien)Cl₂]⁺ with certain nucleophiles, as shown in (1) and (2) proceed with inversion of configuration with respect to the metal centre under appropriate conditions [6]. These reactions involve changes in topology of the kind

$$\Lambda\text{-}\alpha\text{-}[Co(trien)Cl_2]^+ \xrightarrow[\text{70\% yield}]{OH^-} \Delta\text{-}\beta\text{-}[Co(trien)OHCl]^+$$

(1)

$$\Lambda\text{-}\alpha\text{-}[Co(trien)ClOH]^+ \xrightarrow[\text{70\% yield}]{OH^-}$$

$$\Delta\text{-}\beta\text{-}[Co(trien)(OH)_2]^+ \qquad (2)$$

(I) → (III) and may be viewed as examples of a simple octahedral edge-displacement mechanism [7].

An inversion involving the transformation (I) → (II) would represent a more radical redistribution of the coordination sphere. In this paper we wish to report the first example of such an inversion in the reaction (3) of a Co(III) complex of R-picpn (V).

$$\Lambda\text{-}\alpha\text{-}[Co(R\text{-}picpn)Cl_2]^+ \xrightarrow{ox} \Delta\text{-}\alpha\text{-}[Co(R\text{-}picpn)(ox)]^+$$
$$(3)$$

(V)
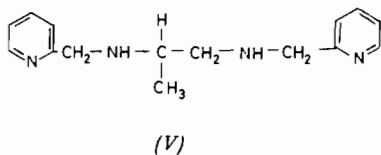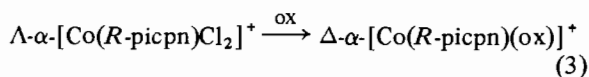
Experimental

Analyses were carried out by Mrs. A. Dams in the Department of Chemistry, University College, Cardiff. Electronic and circular dichroism spectra were recorded using a Pye-Unicam SP8000 spectrophotometer and a Jobin-Yvon Dichrographe III, respectively. Optical rotations were measured using a Thorn Automation NPL 243 polarimeter. 360 MHz ^{1}H nmr spectra were recorded at 298 K using a Bruker WM-360 spectrometer. Chemical shifts are reported relative to the solvent impurity peak for spectra recorded in d_6-DMSO (δ 2.62) or d_4-methanol (δ 3.30) when added as internal reference for spectra recorded in D_2O solution (CD$_3$OD 10% v/v).

R-(−)-pn was isolated by resolving racemic 1,2-diaminopropane using the method of Dwyer et al., [8]. ([α]$_D$ −34.1° in dry benzene; Lit: −34.8 ± 0.4° from ref. [8]). R-picpn was synthesised using the method of Goodwin and Lyons [9].

Λ-α-[Co(R-picpn)Cl₂]ClO₄

This complex was synthesised using a method similar to that of Cragel and Brubaker [10]. A solution of R-picpn (36.6 g, 0.143 mol) and CoCl$_2$· 6H$_2$O (34.0 g, 0.143 mol) in H$_2$O (500 cm^3) together with conc. HCl (1 cm^3) was oxidized in a stream of air at room temperature during 15 hours. To the resultant red-brown reaction mixture was added slowly with stirring conc. HCl (20 cm^3) and then conc. HClO$_4$ (40 cm^3) under the same conditions. The red reaction mixture was filtered, reduced in

volume to 500 cm^3 on a steam bath and then cooled to room temperature. The blue-violet crystalline product which had formed was collected at the pump, washed with water, then acetone and air-dried [Yield: 14.6 g. Anal. Found: C, 37.1; H, 4.2; N, 11.6%. Calc. for C$_{15}$H$_{20}$N$_4$O$_4$Cl$_3$Co: C, 37.1; H, 4.1; N, 11.5%].

The filtrate was further evaporated to 200 cm^3 on the steam bath, then cooled to room temperature when a further crop of crystals was obtained [Yield: 2.9 g]. To the filtrate was added 20 cm^3 of EtOH and the reaction mixture was allowed to stand at room temperature for 4 hours. The solid product which had formed was filtered and washed as described above [Yield: 2.6 g]. The filtrate was left in the refrigerator overnight to yield another crystalline fraction [Yield: 2.8 g]. The supernatant was reduced on the steam bath to a volume of 150 cm^3, cooled to room temperature and then placed in an ice bath. The resultant crystals were isolated as described above [Yield: 6.6 g]. All of these blue-violet products had identical electronic and CD spectra and all gave satisfactory elemental analyses [Total yield: 29.5 g, 42.6%]. Subsequently fractions of a red-violet isomer were isolated from the remaining filtrate. These had somewhat different chiroptical properties [11] indicating that the Λ-α-diastereoisomer is obtained as a result of its lower solubility under these preparative conditions.

Δ-α-[Co(R-picpn)(ox)]ClO₄

To a suspension of Λ-α-[Co(R-picpn)Cl$_2$]ClO$_4$ (1.84 g, 3.65 × 10^{-3} mol) in H$_2$O (40 cm^3) was added sodium oxalate (0.49 g, 3.65 × 10^{-3} mol) and the reaction mixture was heated on a water bath for two hours during which time the solids dissolved to yield a red-orange solution. This reaction solution was filtered, cooled to room temperature and allowed to stand for 48 hours. Large orange prisms of the product slowly crystallized. These were collected at the pump, washed with ice-cold water and dried at room temperature in an air stream [Yield: 1.65 g, 86.5%. Anal. Found: C 40.4; H, 4.2; N, 11.2%. Calc. for C$_{17}$H$_{20}$N$_4$O$_8$ClCO: C, 40.6; H, 4.0; N, 11.1%]. The CD and electronic spectra of the filtrate were the same as those of the solid product in aqueous solution.

[Co(R-picpn)(ox)]I·1.5H₂O

This material was prepared using a modified version of the method of Cragel and Brubaker [10]. To a suspension of Λ-α-[Co(R-picpn)Cl$_2$] ClO$_4$ (1.0 g, 1.985 × 10^{-3} mol) in H$_2$O (40 cm^3) was added potassium oxalate monohydrate (0.366 g, 1.985 × 10^{-3} mol) and the reaction mixture was heated on a water bath during 2 hours when all solids had dissolved. Sodium iodide (0.495 g, 3.3 × 10^{-3} mol) was added, the reaction solution reduced to 10

TABLE I. Electronic and CD Spectral Data for the Complexes.

Complex	Ref.	$10^{-3} \epsilon/dm^2\,mol^{-1}$ [a]	$\Delta\epsilon/dm^2\,mol^{-1}$ [a]
Δ-α-[Co(S-picpn)Cl₂]ClO₄	[10]	1.41 (544)[c]	+10 (600)[c,d] −12.5 (520)[c,d] −3 (400)[c,d]
Δ-α-[Co(S-picpn)Cl₂]ClO₄[e]	[13]	1.26 (539) 1.35 (384)	+16.7 (600) −16.5 (520) −4.1 (408) +23.4 (328)
Λ-α-[Co(R-picpn)Cl₂]ClO₄[f]	b	1.18 (536) 1.25 (388)	−14.4 (600) +16.2 (518) +4.4 (407) −25.4 (328) +153.6 (283) −297.3 (261)
Δ-α-[Co(R-picpn)(ox)]ClO₄[g]	b	1.63 (487) 2.24 (354) 253.2 (236)	−46.0 (503) −7.0 (377) +379.7 (265)
Δ-α-[Co(R-picpn)(ox)]ClO₄[c]	b	1.86 (490) 2.57 (356)	−35.1 (510) −8.7 (377) +262.2 (265)
Λ-α-[Co(S,S-peaen)(ox)]ClO₄[g,h]	[21]	1.52 (494) 2.19 (335)	+30.7 (503) +4.5 (386) −277 (265)

[a]Figures in brackets are λ_{max} for the electronic spectra and extrema in the CD spectra. [b]This work. [c]In MeOH. [d]Taken from figure in ref. [10]. [e]In 0.1 mol dm⁻³ HCl. [f]In 1.0 mol dm⁻³ HCl. [g]In H₂O. [h]Taken from figure in ref. [21].

cm³ at 40 °C, and 20 cm³ EtOH added. After cooling the mixture to room temperature, any solid KClO₄ was filtered off and the supernatant reduced to dryness at 40 °C. The residue was taken up in 75 cm³ of boiling ethanol, filtered and cooled, and the resulting orange crystalline material was collected at the pump, washed with ice-cold water, then ethanol and air dried [*Yield*: 0.60 g, 54.2%. *Anal.* Found: C, 36.6; H, 4.3; N, 10.1%. Calc. for C₁₇H₂₃-N₄O₅‚₅I Co: C, 36.6; H, 4.2; N, 10.1%]. A second fraction was isolated by taking the supernatant from the above preparation, reducing it to dryness at 40 °C, redissolving the residue in absolute alcohol (30 cm³) and adding an equal volume of diethylether. Orange crystals separated which were collected at the pump, washed with ether and dried under suction [*Yield*: 0.35 g, 31.6%. *Anal.* Found: C, 36.4; H, 4.2; N, 10.5%].

Results and Discussion

No details were given of the preparation of the isomer of [Co(R-picpn)Cl₂]⁺ used in a previous study on stereoselective coordination of the ligand [12], but its reported CD spectrum is enantiomorphous to that of the isomer isolated and assigned as Λ-β of [Co(S-picpn)Cl₂]ClO₄ by Cragel and Brubaker [10].

Subsequently other workers [13] have shown the latter salt to be isomorphous with Δ-α-[Cr(S-picpn)-Cl₂]ClO₄ [13], whose coordination geometry and absolute configuration have been established crystallographically [14].

CD and electronic spectral data for Δ-α-[Co(S-picpn)Cl₂]⁺, [13], and the [Co(R-picpn)Cl₂]ClO₄ isomer prepared in this present study are given in Table I. The obvious enantiomorphic relationship between these two species would be expected since the picpn ligands were prepared from the opposite hands of 1,2-diaminopropane. Thus it emerges that the complex obtained in this study is in fact Λ-α-[Co(R-picpn)Cl₂]ClO₄. We wish to reiterate that this diastereoisomer is not necessarily the most stable isomer, but is, however, the least soluble one isolated from a mixture of species.

Proton nmr measurements in d₆-DMSO solution at 298 K confirm the α-topology of the complex. An α-isomer has a pseudo-twofold rotation axis and both H(6) and H(6') protons will be deshielded, (*VI*). This is in contrast to a β-isomer, (*VII*), for which the H(6') proton of one pyridyl ring is oriented towards the π-cloud of the second pyridyl group and thus would be expected to occur at higher field in the proton spectrum. Spectral data for Λ-α-[Co(R-picpn)-Cl₂]ClO₄ are given in Table II, with the numbering scheme for the protons shown in (*VI*). Both H(6) and

TABLE II. 360 MHz ^{1}H NMR Data for the α-Complexes.[a]

	Λ-α[Co(R-picpnCl$_2$]ClO$_4$[b]		Δ-α[Co(R-picpn)(ox)]ClO$_4$[c]	
H(3)	d*	7.79[d]	d	7.81[d]
H(4)	t	8.26[e]	t	8.18[e]
H(5)	t	7.83[f]	t	7.70[f]
H(6)	d	9.44[g]	d	8.57[g]
H(3')	d	7.84[d]	d	7.79[d]
H(4')	t	8.24[e]	t	8.17[e]
H(5')	t	7.85[f]	t	7.70[f]
H(6')	d	9.45[g]	d	8.57[g]
H(11)	d	4.28[h]	d	4.16[h]
H(12)	dd	4.69[i]	d	4.91[i]
H(21)	dd	7.35[j]	exchanged	
H(31)	m	2.67[k]	m	2.67
CH$_3$	d	1.27	d	1.22
H(41)	dd	2.52	dd	3.07
H(42)	m	2.17	t(dd)	2.19
H(51)	dd	7.46[j]	exchanged	
H(61)	d	4.21[h]	d	4.26[h]
H(62)	dd	4.99[i]	d	5.01[i]
J$_{31,CH_3}$		7.21		6.23
J$_{31,41}$		4.00		4.57
J$_{31,42}$		12.25		12.80
J$_{41,42}$		−13.35		−13.20
J$_{21,31}$ = J$_{42,51}$		4.05		
J$_{12,21}$ = J$_{52,62}$		8.60		
J$_{61,62}$ = J$_{11,12}$		17.10		16.26
J$_{51,61}$ = J$_{11,21}$		~0.0		

[a]Chemical shifts ± 0.01 ppm, coupling constants ± 0.05 Hz.   [b]10^{-2} mol dm^{-3} solution in d$_6$-DMSO.   [c]Saturated solution in 10:1 (v/v) D$_2$O:d$_4$-methanol. All spectra recorded at 298 K.   [d-j]We do not distinguish between these pairs of resonances.
[k]Partially obscured by DMSO peak.   *d = doublet, t = triplet, m = multiplet, dd = doublet of doublets.
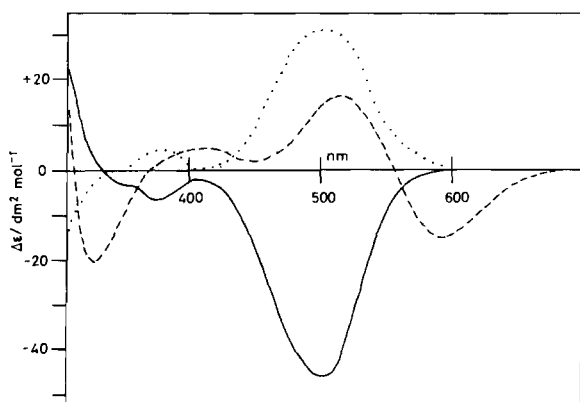

Fig. 1. Visible CD spectra of (------) Λ-α-[Co(R-picpn)Cl$_2$]$^+$ in 1.0 mol dm^{-3} aqueous HCl, (———) Δ-α-[Co(R-picpn)-(ox)]$^+$ in H$_2$O and (······) Λ-α-[Co(S,S-peaen)(ox)]$^+$ in H$_2$O taken from ref. [21].

H(6') proton resonances occur at low field with comparable chemical shifts, indicative of the α-topology. Coupling constants between protons in the aliphatic backbone of the tetradentate are consistent with those predicted using the Karplus relationship provided the methyl group of the central chelate ring lies in an equatorial position. In this solution the N-hydrogen atoms did not exchange during the course of the nmr experiment.

The CD spectrum in aqueous solution of (−)$_{500}^{CD}$-[Co(R-picpn)(ox)]ClO$_4$ is shown in Fig. 1 together with that of Λ-α-[Co(R-picpn)Cl$_2$]ClO$_4$. This spectrum is closely enantiomorphic to that reported for the S-picpn analogue in aqueous solution [10]. The ^{1}H nmr spectrum of the (−)$_{500}^{CD}$-oxalate complex of Co(III) with R-picpn (Table II, Fig. 2) also shows it to be an α-isomer. Both H(6) and H(6') resonances occur at low field and are not resolved even at 360 MHz in D$_2$O solution. The
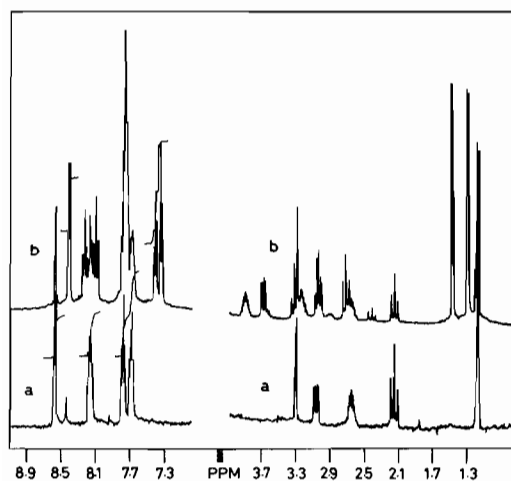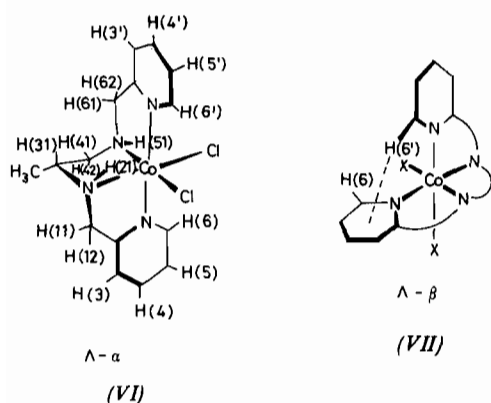
Fig. 2. 360 MHz ^{1}H nmr spectra of (a) Δ-α-[Co(R-picpn)-(ox)]ClO4 in D2O and (b) [Co(R-picpn)(ox)]I·1.5H2O; first crystalline crop in D2O.

N-hydrogen atoms are seen to have fully exchanged. The question then remains as to the absolute configuration of the α-[Co(R-picpn)(ox)]ClO4 complex.

Electronic and circular dichroism spectral details are given for the complex in Table I. The visible CD spectrum is dominated by a single band of negative sign. This is very similar to the circular dichroism spectrum of Δ-[Co(en)2(ox)]+, which also shows such a CD spectral pattern [15] with the band assigned to the composite $^1A_1 \rightarrow A_2(E_a) + {}^1B_2(E_a) + {}^1B_1(A_2)$ transition in point group C_2. Indeed the sign of the low-energy A → E transition has been used frequently to assign the absolute configuration of related species [16]. The absolute configurations of both Δ- and Λ-[Co(en)2(ox)]+ have been established crystallographically [17, 18]. Similar CD spectral features are reported for Λ-[Co(en)2(CN)2]+ whose absolute configuration is also known [15, 19]. A like CD spectrum, positive in the visible range has also been assigned to Λ-α-[Co(trien)(ox)]+, [20].

Moreover, of particular relevance to this study is the work of Suzuki *et al.*, [21], who prepared (+)-α-[Co(S,S-peaen)(ox)]+. The structure of the ligand is shown in (*VIII*). The CD spectrum of the complex

(VIII)
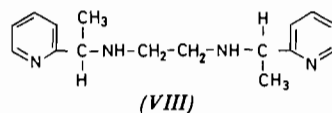
is shown for comparison in Fig. 1. In the visible region the circular dichroism is seen to be dominated by a positive transition and indeed is almost enantiomorphic to that of the complex $(-)_{500}{}^{CD}$-[Co(R-picpn)(ox)]ClO4. The absolute configuration of the S,S-peaen complex has been determined crystallographically as Λ [22]. Thus it becomes obvious that the complex isolated in this study is Δ-α-[Co(R-picpn)(ox)]ClO4, which has formed as a result of the unusual inversion process shown in (3) above.

It is of some interest that the $(-)_{500}{}^{CD}$-Λ-α-oxalate salt of Suzuki *et al.*, was prepared from $(+)_{600}{}^{CD}$-[Co(S,S-peaen)Cl2]ClO4·1.5H2O. Although this dichloride salt displays a CD spectrum opposite in sign to that of Λ-α-[Co(R-picpn)Cl2]+ and related Λ-species [23, 24], it was nevertheless assigned the Λ-configuration. It would appear that this is in fact the Δ-α-diastereoisomer, and that the inversion process thus involved in the formation of the oxalate derivative was not recognised as such by those workers.

The compound [Co(S-picpn)(ox)]I of Cragel and Brubaker [10] gave a CD spectrum which is almost enantiomophric with our complex Δ-α-[Co(R-picpn)(ox)]ClO4 in aqueous solution. However, their compound, in fresh alcoholic solution, displayed a marked change in chiroptical properties. We do not observe this to be so with our perchlorate salt. Some spectral differences are noticeable in methanol solution (Table I) but these are in no way unusual [25]. However, the CD spectrum (Table III) of our iodide complex, although opposite in sign, is comparable to that of Cragel and Brubaker's in MeOH. Similar spectra are obtained for aqueous solutions, which are stable if kept in the dark. Some photoreaction, the nature of which has not been investigated, occurs if solutions of this iodide salt are exposed to light.

We are able to show that our iodide compound is not a single diastereoisomer, but a mixture of four. The proton nmr spectrum of the first crystalline fraction of [Co(R-picpn)(ox)]I·1.5H2O is shown in Fig. 2 and spectral details are given in Table IV. Each isomer displays a doublet signal for the methyl group, but these are not in equal ratio. The doublet at highest field (δ 1.22) is seen to correspond with that of the isolated species Δ-α-[Co(R-picpn)(ox)]+ and the corresponding signal of a minor isomer occurs

TABLE III. Electronic and CD Spectral Details in the Visible Region for the Isomers $[Co(picpn)(ox)]I \cdot nH_2O$.

Complex	$\epsilon/dm^2 \ mol^{-1}$ [a]	$\Delta\epsilon/dm^2 \ mol^{-1}$ [a]
$[Co(S\text{-picpn})(ox)]I$ [b]	2110 (495)	+1.0 (550) [c]
	2310 (362)	−10.4 (486)
		+6.5 (368)
$[Co(R\text{-picpn})(ox)]I \cdot 1.5H_2O$ [d]	1660 (489)	−0.6 (549)
	3500 (354)	+8.8 (487)
		−3.5 (367)
$[Co(R\text{-picpn})(ox)]I \cdot 1.5H_2O$ [e]	1790 (486)	−0.6 (547)
	2950 (350)	+7.5 (482)
		−3.4 (361)

[a]Figures in brackets are λ_{max} for the electronic spectra and extrema in the CD spectra.   [b]Ref. [10].   [c]$\Delta\epsilon$ values taken from figure in ref. [10]. Solution of salt in methanol.   [d]First crystalline fraction in MeOH.   [e]First crystalline fraction in H_2O.

TABLE IV. 360 MHz ^1H NMR Data[a] for the $[Co(R\text{-picpn})(ox)]I \cdot 1.5H_2O$ Isomers.[b]

		$\Lambda\text{-}\alpha$	$\Lambda\text{-}\beta_A$	$\Lambda\text{-}\beta_B$
CH_3	d[c]	1.25	1.34	1.52
H(31)	m	2.92	3.89	3.25
H(41)	dd	2.73	3.68	3.04
H(42)	t(dd)	2.44	2.73	3.33
J_{31,CH_3}		6.66	6.48	6.17
$J_{31,41}$		4.40	4.05	3.42
$J_{31,42}$		13.27	12.92	13.28
$J_{41,42}$		−14.03	−13.10	−11.48
H(6)	d	8.57	8.42	8.42
H(6')	d	8.57	7.38	7.38

[a]Recorded in a saturated solution in 10:1 (v/v) D_2O:d_4-methanol at 298 K. Chemical shifts ± 0.01 ppm, coupling constants ± 0.05 Hz. All N–H protons are exchanged. [b]Protons are numbered according to (VI) and (VII).   [c]d = doublet, t = triplet, m = multiplet, dd = doublet of doublets.

close by. Integration of both these methyl signals, and comparison with the integral of the low-field H(6) and H(6') protons, indicates that this minor product is also an α-isomer and therefore must be $\Lambda\text{-}\alpha\text{-}[Co(R\text{-picpn})(ox)]^+$.

We have been able to assign all the resonances in the aliphatic region (Table IV) arising from the R-pn residues using spin-decoupling techniques. With the second fraction of $[Co(R\text{-picpn})(ox)]I \cdot 1.5H_2O$ no signals corresponding to the $\Lambda\text{-}\alpha$-isomer were observed. Attempts to separate the remaining three isomers by fractional crystallization in the dark were unsuccessful, although we have been able to isolate the two main isomers in the mixture using ion-exchange chromatography (CM-Sephadex® C-25; elution with 0.05 mol dm^{-3} $NaClO_4$ in the dark). No separation

of these two species was evident however. CD spectra of all fractions containing the two isomers were dominated by a strong positive transition in the visible region.

Reference to the aromatic region of the 360 MHz ^1H nmr spectrum (Table IV, Fig. 2) shows that for these two species the signals for the H(6) and the H(6') protons are well separated. Both α-isomers have identical chemical shifts at low-field for these two protons; therefore we conclude that these two main isomers are β-forms, and the CD spectral results, although necessarily of a qualititative nature, suggest that they both have Λ absolute configuration. Two such isomers are possible because of the inequivalence of the two halves of the R-picpn ligand, with N(2) and N(3) each adopting the S-configuration, (VIII). Thus it would seem that the spectral changes observed by Cragel and Brubaker [10] reflect an isomeric reequilibration in the presence of light.

The first crystalline fraction isolated of $[Co(R\text{-picpn})(ox)]I \cdot 1.5H_2O$ shows the ratio of diastereoisomers $\Delta\text{-}\alpha$: $\Lambda\text{-}\alpha$: $\Lambda\text{-}\beta_A$: $\Lambda\text{-}\beta_B$ to be 0.69:0.25:1.0:1.0: by integration of the methyl resonances. While we do not suggest that these ratios necessarily reflect equilibrium concentrations, with the $\Delta\text{-}\alpha$-isomer appearing to be the most thermodynamically stable one in aqueous solution, it is worthy of note that, since the β-isomers are predominant in the above mixture, their formation demonstrates another form of isomerization as represented by eqn. (4). This is equivalent to the transformation (I) → (IV).

$$\Lambda\text{-}\alpha\text{-}[Co(R\text{-picpn})Cl_2]^+ \xrightarrow{\text{ox}} \Lambda\text{-}\beta\text{-}[Co(R\text{-picpn})(ox)]^+$$

(4)
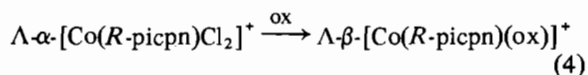
Hence it becomes obvious that the R-picpn ligand is readily able to adopt a variety of conformations which are dependent upon the reaction conditions employed. The presence of several isomers in the isolated iodide salt no doubt reflects the differing methods of preparation of the perchlorate and

iodide complexes. For the reactions represented in (3) and (4) complex mechanisms must be involved, and we are directing our investigations towards their elucidation. In addition we are investigating the geometries which may be enforced on such tetradentates through the discriminatory effects of asymmetric bidentate coordination in the remaining coordination positions.

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