Note

Chiral metal complexes
40*. The sterically mediated hydrolysis of a coordinated imine

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(Received July 19, 1993; revised March 8, 1994)

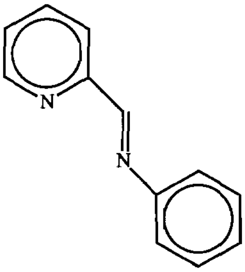
Abstract

Reaction of pyridine-2-carboxaldehyde-*N*-phenylimine (pcp), with Λ-β-[Co(*R*,*R*-picchxn)Cl_2]$^+$ in aqueous solution (*R*,*R*-picchxn = *N*,*N*′-di(2-picolyl)-1*R*,2*R*-diaminocyclohexane) results in the formation of a Λ-β-[Co(*R*,*R*-picchxn)(pcp)]$^{3+}$ species, as one of two major products. The other species is the ternary complex containing the anionic hydrolysis product hydroxy(2-pyridyl)methanol (hpm), Λ-β_2-[Co(*R*,*R*-picchxn)-(hpm)]$^{2+}$, which was crystallized as its diperchlorate monohydrate salt, and its structure determined by single-crystal X-ray diffraction. Λ-β_2-[Co(*R*,*R*-picchxn)(hpm)]$(ClO_4)_2 \cdot H_2O$ is orthorhombic, $a = 9.171(2)$, $b = 17.771(3)$, $c = 17.785(4)$ Å, space group $P2_12_12_1$, with $Z = 4$. The structure was refined to a final R value of 0.061 for 1822 unique reflections with $I > 3\sigma(I)$. This shows that, in this compound, hpm coordinates stereospecifically (*R*) to Co in the solid state. However, two diastereoisomers are observed using NMR methods when the complex is dissolved in dmso. The study illustrates the need to take into account the existence of derived diol species in metal–aldehyde systems.

Key words: Crystal structures; Cobalt complexes; Chiral ligand complexes; Imine complexes; Hydrolysis

Introduction

For some time we have been interested in exploring sources of chiral discriminations in complexes containing optically active ligands [1]. In this connection, our attention generally has focussed on complexes containing a chiral tetradentate ligand, with studies being directed towards the various discriminatory interactions which attend the further coordination of a bidentate in the remaining sites of an octahedral coordination sphere [2]. During the course of these studies, we examined the reaction of pyridine-2-carboxaldehyde-*N*-phenylimine (pcp) (**1**) with Λ-β-[Co(*R*,*R*-picchxn)Cl_2]$^+$ in aqueous solution (where *R*,*R*-picchxn is *N*,*N*′-di(2-picolyl)-1*R*,2*R*-diaminocyclohexane). It was hoped that methods could be devised to react the coordinated forms of **1** stereospecifically to produce new chiral products, or to reduce it (as a precursor archetype) in ways similar to those employed in a related successful synthesis of chiral proline [3, 4].



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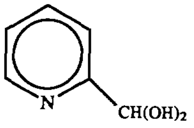

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Under mild conditions, the synthetic reaction was shown to yield one isomer of Λ-β-[Co(*R*,*R*-picchxn)(pcp)]$^{3+}$, stereospecifically, as one of two major products. The other compound isolated, and whose structure has been unambiguously established by the X-ray crystallographic study reported herein, is a ternary complex containing a hydrolysis product of pcp†† (followed by hydration), namely the anion of hydroxy(2-pyridyl)methanol (hpm) (**2**). These results provide structural evidence for the existence of such species when aldehydes are reacted with metal ions in protic solvents [6, 7].

Experimental

Electronic and CD spectra were recorded using a Perkin Elmer Lambda 5 spectrophotometer and a Jobin-Yvon Dichrographe III, respectively. High-resolution

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*For Part 39 see ref. 1.

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††Initial investigations [5] suggested that this complex contained a hydrolyzed imine function, but it has been subsequently demonstrated that it in fact contains a hydrolyzed aldehyde.

0020-1693/94/$07.00
SSDI 0020-1693(94)03976-U

NMR spectra were recorded at 21 °C using a Bruker WM 360 spectrometer, and available Bruker software, with TMS or DSS as internal standards. Elemental analyses were carried out by Mrs A. Dams of the School of Chemistry, Cardiff.

Pcp (**1**) was prepared following the method of Chan and Lees, see ref. 5, using freshly distilled aniline and pyridine-2-carboxaldehyde, when a pale yellow oil was obtained. The crude product was vacuum distilled (114–116 °C, 2.5 mmHg) to yield a colourless liquid which solidified on standing at room temperature and was NMR pure.

Λ-[Co(R,R-picchxn)(pcp)](ClO$_4$)$_3$·H$_2$O and Λ-β$_2$-[Co(R,R-picchxn)(hmp)](ClO$_4$)$_2$·H$_2$O

Λ-*β*-[Co(*R*,*R*-picchxn)Cl$_2$]ClO$_4$·0.5H$_2$O [8] (2.24 g, 4.2 mmol) and pcp (1.53 g, 8.4 mmol) were added to H$_2$O/MeOH (90/10 vol./vol., 100 cm^3) and the reaction mixture was stirred for 2 days at ambient temperature. The resulting organic solution was filtered, diluted to 400 cm^3 with H$_2$O, and applied to a CM Sephadex C-25 column (70×1.5 cm) in the Na$^+$ cycle. The column was washed with H$_2$O, then eluted with 0.5 M aqueous NaCl. Two orange bands developed, separated by a brown band. Both orange bands were collected in fractions using an LKB Ultrorac II fraction collector, and measurements of electronic and CD spectra of the fractions suggested that each band contained a single diastereoisomer (in view of the constant $\Delta A/A$ ratios obtained). Fractions from the slower moving bright orange band were combined, saturated aqueous NaClO$_4$ was added, and the solution was reduced to small volume under reduced pressure at room temperature. The acidular orange crystals of *Λ*-*β*-[Co(*R*,*R*-picchxn)(pcp)](ClO$_4$)$_3$·H$_2$O that formed were collected at the pump, washed with ice-cold water and air dried. Yield 0.98 g (27%). *Anal.* Calc. for $C_{30}H_{36}N_6Cl_3O_{13}Co$: C, 42.2; H, 4.2; N, 9.8. Found: C, 42.0; H, 4.0; N, 9.2%. Characteristic spectroscopic data (in H$_2$O): $\epsilon_{480} = 302$ M^{-1} cm^{-1} (maximum), $\Delta\epsilon_{537,487} = +0.07, +2.09$ M^{-1} cm^{-1}, respectively (extrema).

Eluted fractions from the column containing the faster moving deep orange band were also combined and treated in the same manner as above. Overnight, large, deep red crystals formed. These were collected at the pump and dried on absorbent paper. The compound is very soluble in H$_2$O. Yield 0.12 g (4.1%). *Anal.* Calc. for $C_{24}H_{32}N_5Cl_2O_{11}Co$: C, 41.4; H, 4.6; N, 10.1. Found: C, 41.3; H, 4.5; N, 10.0%. It was subsequently shown that although these crystals did contain only one diastereoisomer, aqueous solutions prepared from them contained two diastereoisomers in equilibrium, which gives the impression from spectroscopic measurements that a single species was obtained from the column (*vide infra*). Thus spectroscopic data given below refer only to maxima and extrema in the electronic and CD spectra of aqueous solutions, respectively: ϵ_{max}: 474, 350 nm; $\Delta\epsilon_{max}$: 555 (−ve), 484 nm (+ve). The successful solution of the single-crystal X-ray structure of the compound showed the crystals to contain, exclusively, *Λ*-*β*$_2$-[Co(*R*,*R*-picchxn)(*R*-hpm)](ClO$_4$)$_2$·H$_2$O. Furthermore, it is important to note that the CD spectrum of the product dissolved in H$_2$O is identical, in terms of extrema and null points, to the solution from which it crystallized, in accord with equilibrium being established in the solution of the diastereoisomeric complex.

The oily residue from the crude reaction mixture was extracted with diethyl ether, the extract filtered and dried over sodium sulfate, and reduced to a viscous pale yellow oil. ^{1}H NMR measurements on this oil in CDCl$_3$ showed that it contained both unreacted pcp, and aniline, by reference to authentic samples.

Crystal and molecular structure of Λ-β$_2$-[Co(R,R-picchxn)(R-hpm)](ClO$_4$)$_2$·H$_2$O

Crystal data. $C_{24}H_{32}N_5O_{11}Cl_2Co$, $M_r = 696.4$, orthorhombic, $a = 9.171(2)$, $b = 17.771(3)$, $c = 17.785(4)$ Å, $U = 2898.6$ Å^3, $Z = 4$, $D_c = 1.593$, $D_m = 1.58$ (by flotation), $F(000) = 1440$, μ(Mo Kα) = 8.7 cm^{-1}, space group $P2_12_12_1$ (No. 19).

Unit cell data were established from precession photographs and were measured accurately by means of a Nicolet XRD P3 four-circle diffractometer [9] using graphite-monochromatized Mo Kα radiation. The $\theta/2\theta$ scan technique was used to collect reflection intensities in the range $4.0 < 2\theta < 52.0°$ with the crystal temperature being maintained at 19 °C. The crystal used for data collection was a pentagonal plate, lying on (010), of size $0.4 \times 0.4 \times 0.12$ mm. Intensities were corrected for absorption ($T_{max} = 0.962$, $T_{min} = 0.890$), and for Lorentz and polarization effects. Of the 3120 independent reflections measured, 1822 had $I > 3\sigma(I)$ and these were used for the structure determination.

The structure was solved by the heavy atom method and initially refined by full-matrix least-squares calculations in which the function minimized was $\Sigma w\Delta^2$. After several cycles of refinement, the positions of the hydrogen atoms were calculated assuming the appropriate geometries to which they are attached with bond lengths of 1.0 Å and they were assigned $B = 2.0$ Å^2; that of the uncoordinated OH group was located from a difference Fourier map, and its position idealized. The final structure refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms in which the weights used were $w = (5 + 0.01|F_o| + 0.001|F_o|^2)^{-1}$. When the maximum shift in any parameter was less than 0.1σ the refinement process was terminated. The final value for R was 0.061 and R' $\{= (\Sigma w(F_o - F_c)^2/\Sigma w|F_o|^2)^{0.5}\}$ was 0.075. A final difference Fourier map showed no unusual features.

Calculations were carried out on a FACOM M350S computer using programs written by F.S.S. Neutral atom scattering factors, with corrections being applied for anomalous dispersion, were taken from International Tables for X-ray Crystallography [10] (see also 'Supplementary material').

Results and discussion

Crystal and molecular structure of Λ-β$_2$-[Co(R,R-picchxn)(R-hpm)](ClO$_4$)$_2$·H$_2$O

A stereo view [11] of the complex cation showing the atom labelling scheme is shown in Fig. 1. Final atomic coordinates for the non-hydrogen atoms and a list of selected bond lengths and angles are given in Tables 1 and 2, respectively.

The geometry about the cobalt centre is Λ-β$_2$*, with both secondary nitrogens of the tetradentate adopting an *R* absolute configuration. The tetrahedral acyclic carbon of hpm, C(36) (which is chiral upon coordination) has the *R* configuration, and the two C–O distances are in accord with single bond character. Hpm exists in the structure as the anion of the *geminal* diol 2, whose coordination via the anionic oxygen atom leads to the overall +2 charge for the cation, consistent with its chromatographic behaviour.

There are no unusually short contacts in the crystal structure. Hydrogen bonds link the perchlorate anions, the lattice water molecule and the two secondary amines of the tetradentate (Table 3). An additional hydrogen bond is observed between the lattice water molecule and the uncoordinated OH group of the anionic diol, which may assist in stabilizing the structural form of the bidentate observed in the solid state.

Reaction chemistry

The facile hydrolysis of pcp to form the hpm complex could be contrasted with its stability (and that of its analogues) in aqueous solution in binary Fe(II) complexes [13]. It could be the case that the greater charge on Co(III) relative to Fe(II) contributes to the increased instability of the imine bond through depletion of electron density at the imine carbon atom via an inductive mechanism, thus activating the carbon towards nucleophilic attack by OH$^-$ or H$_2$O. Such nucleophilic attack is common in classical organic chemistry [14], and a number of precedents are found in the literature for coordinated imines. Busch and Bailar reported [15] that water adds across both imines of a tetradentate di-Schiff base coordinated to Cu(II), and complete hydration of one of the C=N bonds of a diimine macrocyclic ligand incorporating a 2,6-diacetylpyridine fragment has been observed [16]. In addition, alcohols attack coordinated imines to form stable complexes of resulting aminoethers [16–18]. Molecular modelling based on the crystal structure strongly suggests that the imine of pcp would be severely strained in the Λ-β$_1$ complex; its hydrolysis would result in the Λ-β$_2$ hpm complex without rearrangement of the coordination sphere (note that the priority rules are such that the change actually involves no site shift of the coordinated pyridine nitrogen atom). In Λ-β$_1$-[Co(*R*,*R*-picchxn)(pcp)]$^{3+}$ the phenyl group of the bidentate would encounter a number of several non-bonded interactions with hydrogen atoms of the cyclohexane ring of the tetradentate. Hence the hydrolysis of the imine could be seen as a natural consequence of reactivity forced on the group by steric effects. Such steric effects would be absent in the corresponding Λ-β$_2$ complex of pcp. The importance of coordination for the ligand hydrolysis is evidenced by the fact that no such reaction occurs for the free pcp ligand under analogous conditions.

As noted above, reaction of pcp with Λ-β-[Co(*R*,*R*-picchxn)Cl$_2$]$^+$ gives only one isomer containing unhydrolyzed pcp, Λ-β-[Co(*R*,*R*-picchxn)(pcp)]$^{3+}$. No single-crystal structure analysis of it has been undertaken,

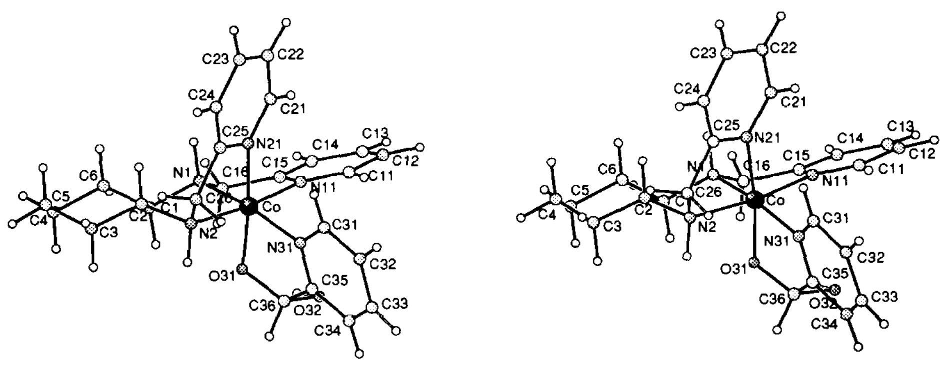

Fig. 1. A stereo view [11] of the Λ-β$_2$-[Co(*R*,*R*-picchxn)(*R*-hpm)]$^{2+}$ complex cation showing the atom labelling.

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*For a discussion of the nomenclature for these geometric isomers, see ref. 12.

TABLE 1. Final atomic coordinates (fractional×10^4) for non-hydrogen atoms with e.s.d.s in parentheses for Λ-β_2-[Co(R,R-picchxn)(R-hpm)]$(\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$

	x/a	*y/b*	*z/c*
Co	908(2)	2312(2)	2237(1)
N(11)	1934(10)	1363(5)	2261(7)
N(21)	2237(10)	2854(5)	2913(5)
N(1)	2070(10)	2493(5)	1350(5)
N(2)	108(10)	3313(6)	2096(5)
N(31)	−491(11)	2020(5)	3016(5)
O(31)	−480(9)	1932(5)	1583(5)
O(32)	−975(14)	678(6)	1788(6)
C(31)	−510(15)	2185(8)	3756(7)
C(32)	−1588(22)	1904(10)	4221(9)
C(33)	−2691(20)	1457(10)	3913(11)
C(34)	−2632(16)	1291(9)	3171(11)
C(35)	−1568(15)	1584(8)	2715(10)
C(36)	−1429(16)	1439(7)	1893(10)
C(11)	2090(14)	905(7)	2840(8)
C(12)	2846(16)	233(7)	2805(10)
C(13)	3407(17)	33(7)	2103(10)
C(14)	3278(18)	523(8)	1515(9)
C(15)	2542(13)	1196(7)	1596(8)
C(16)	2327(15)	1764(8)	974(8)
C(1)	1322(13)	3062(7)	895(7)
C(2)	932(14)	3684(6)	1455(6)
C(3)	121(16)	4334(8)	1080(8)
C(4)	1049(19)	4628(8)	448(8)
C(5)	1377(17)	4020(9)	−132(9)
C(6)	2201(16)	3379(8)	237(7)
C(21)	3536(13)	2621(7)	3174(6)
C(22)	4389(15)	3052(8)	3648(7)
C(23)	3917(18)	3750(8)	3851(8)
C(24)	2567(17)	3995(7)	3590(8)
C(25)	1748(15)	3542(6)	3118(7)
C(26)	288(13)	3752(6)	2792(8)
Cl(1)	5908(5)	3214(2)	1564(2)
O(1a)	6916(10)	3237(6)	2162(7)
O(1b)	4715(11)	3689(7)	1737(7)
O(1c)	5384(11)	2466(6)	1484(8)
O(1d)	6616(15)	3430(10)	899(7)
Cl(2)	2897(6)	1159(3)	5016(3)
O(2a)	2419(22)	451(9)	4740(10)
O(2b)	2566(26)	1187(11)	5756(9)
O(2c)	4248(19)	1162(16)	5021(20)
O(2d)	2345(40)	1751(12)	4634(13)
O(w)	−129(19)	384(11)	262(10)

TABLE 2. Bond lengths and angles with e.s.d.s in parentheses for Λ-β_2-[Co(R,R-picchxn)(R-hpm)]$(\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$

Distances (Å)			
Co–N(11)	1.932(9)	Co–N(1)	1.930(10)
Co–N(21)	1.965(9)	Co–N(2)	1.940(10)
Co–N(31)	1.959(10)	Co–O(31)	1.852(8)
O(31)–C(36)	1.353(15)	O(32)–C(36)	1.427(16)
C(1)–C(2)	1.529(16)	C(4)–C(5)	1.523(21)
C(2)–C(3)	1.528(17)	C(5)–C(6)	1.517(19)
C(3)–C(4)	1.504(19)	C(6)–C(1)	1.529(17)

	$n=1$	$n=2$	$n=3$
N(n1)–C(n1)	1.319(16)	1.344(14)	1.348(15)
N(n1)–C(n5)	1.341(16)	1.352(14)	1.365(18)
C(n1)–C(n2)	1.383(16)	1.382(17)	1.382(20)
C(n2)–C(n3)	1.396(21)	1.362(19)	1.399(25)
C(n3)–C(n4)	1.365(20)	1.393(20)	1.353(24)
C(n4)–C(n5)	1.381(18)	1.385(17)	1.372(19)
C(n5)–C(n6)	1.511(18)	1.506(17)	1.490(21)
C(n6)–N(n)	1.476(15)	1.473(15)	
N(n)–C(n)	1.466(14)	1.518(15)	

Angles (°)			
N(11)–Co–N(1)	84.0(4)	N(11)–Co–N(2)	170.9(4)
N(21)–Co–N(2)	82.2(4)	N(21)–Co–O(31)	171.8(4)
N(1)–Co–N(2)	87.2(4)	N(1)–Co–N(31)	169.7(4)
O(31)–Co–N(31)	84.1(4)	N(21)–Co–N(31)	95.9(4)
N(11)–Co–O(31)	91.7(4)	N(1)–Co–O(31)	85.8(4)
N(11)–Co–N(31)	94.1(4)	N(2)–Co–O(31)	89.6(4)
N(21)–Co–N(11)	96.4(4)	N(2)–Co–N(31)	95.0(4)
N(21)–Co–N(1)	94.4(4)	N(2)–C(2)–C(1)	106.9(9)
Co–O(31)–C(36)	115.0(9)	N(2)–C(2)–C(3)	112.1(10)
C(35)–C(36)–O(31)	110.0(12)	C(1)–C(2)–C(3)	114.4(11)
C(35)–C(36)–O(32)	108.5(13)	C(2)–C(3)–C(4)	108.3(12)
O(31)–C(36)–O(32)	111.9(12)	C(3)–C(4)–C(5)	111.8(12)
N(1)–C(1)–C(2)	104.4(9)	C(4)–C(5)–C(6)	109.7(12)
N(1)–C(1)–C(6)	115.5(10)	C(5)–C(6)–C(1)	110.2(11)
C(2)–C(1)–C(6)	110.8(10)		

	$n=1$	$n=2$	$n=3$
Co–N(n1)–C(n1)	127.5(9)	127.6(8)	129.9(9)
Co–N(n1)–C(n5)	112.1(8)	113.7(8)	110.3(9)
C(n1)–N(n1)–C(n5)	120.4(10)	118.7(11)	119.8(12)
N(n1)–C(n1)–C(n2)	123.5(14)	122.8(12)	121.0(14)
C(n1)–C(n2)–C(n3)	116.4(13)	119.1(13)	119.2(15)
C(n2)–C(n3)–C(n4)	119.4(12)	118.6(13)	118.5(16)
C(n3)–C(n4)–C(n5)	121.0(13)	120.2(12)	121.5(17)
C(n4)–C(n5)–N(n1)	119.1(12)	120.6(12)	119.9(16)
C(n4)–C(n5)–C(n6)	124.5(12)	124.8(11)	125.1(16)
N(n1)–C(n5)–C(n6)	116.3(10)	114.6(11)	114.9(12)
C(n5)–C(n6)–N(n)	106.0(10)	106.9(9)	
C(n6)–N(n)–C(n)	115.5(9)	110.2(9)	
C(n6)–N(n)–Co	108.2(7)	109.6(7)	
C(n)–N(n)–Co	107.9(7)	107.8(7)	

but CD spectra (see ‘Experimental’) show that the complex has absolute configuration Λ. Its ^{1}H NMR spectrum shows three high-field doublets which integrate for one proton each (δ 7.31, 6.96 and 5.99 ppm, in dmso-d$_6$), and which cannot be due to N–*H* resonances (8.28, 8.47 ppm) or methylene hydrogen atoms of the picolyl groups (3.61, 3.78, 4.30, 4.40 ppm). If they were due to three shielded pyridyl H atoms (those *ortho* to the nitrogen atoms), the only possible arrangement of the three pyridyl rings in the complex would be *fac*, and this would identify the complex as the β_1 isomer.

The behaviour of Λ-β_2-[Co(R,R-picchxn)(R-hpm)]$(\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ dissolved in dmso is somewhat more complicated. This is not surprising in view of the known chemistry of pyridine-2-carboxaldehyde [19, 20], which may act as a unidentate or a bidentate through the pyridine nitrogen and carbonyl oxygen atoms. The latter mode of coordination may involve the free aldehyde

TABLE 3. Contact distances (Å) with e.s.d.s in parentheses for Λ-β_2-[Co(R,R-picchxn)(R-hpm)]$(ClO_4)_2 \cdot H_2O$

Proposed hydrogen bonding[a]			
O(32)–H(O32)...O(w)	2.87(2)	[b]N(1)–H(N1)...O(1c)	3.05(1)
N(2)–H(N2)...O(1a^{I})	2.93(1)	...O(1b)	3.30(1)
		[b]O(w)–H(wa)...O(2a^{II})	3.04(3)
		...O(2c^{II})	2.90(4)
Intermolecular distances <3.3 Å			
C(31)...O(2d)	3.14(3)	C(21)...O(2d)	3.21(3)
C(16)...O(1c)	3.20(2)	C(32)...O(2d^{III})	3.29(3)

[a] Roman number superscripts refer to the following equivalent positions relative to x, y, z: I, $x-1, y, z$; II, $\frac{1}{2}-x, -y, \frac{1}{2}+z$; III, $x-\frac{1}{2}, \frac{1}{2}-y, 1-z$. [b] Bifurcated hydrogen bond.

or the hydrated *geminal* diol derivative, formation of which is greatly facilitated by coordination to metal ions [21]. Two isomers Λ-β_2-[Co(R,R-picchxn)(R,S-hpm)]$^{2+}$ are observed in dmso-d_6/D_2O in NMR. No aldehydic proton resonance is found at about δ 10 ppm; rather, two resonances corresponding to the methine, *geminal*, diol protons are observed at δ 5.45 and 5.59 ppm, as singlets with almost equal integrated intensities. Thus there appears to be little chiral discrimination between the two diastereoisomers in solution under these conditions. This interpretation is borne out by the ^{13}C NMR spectrum. No signal attributable to C=O of the aldehyde at δ 180–200 ppm is observed, but two resonances at δ 102.1 and 102.3 ppm, corresponding to the two $CH(OH)_2$ groups, are evident. Confirmation of the above is found in the ^{13}C spectrum of 2-pyridinecarboxaldehyde in dmso-d_6/DCl, in that this species, which is about 50% hydrated in this instance [22], shows both C=O and $CH(OH)_2$ signals at δ 199.5 and 95.8 ppm, respectively. The isolation of one diastereoisomer in the solid state is thus readily explained as being the result of an asymmetric transformation of the second kind.

A comment on the conditions employed for the synthesis of the complexes is warranted. In the reaction mixture containing a large excess of H_2O, a substantial proportion of the pcp remains undissolved, and the pH of the solution is sufficiently low to account for the persistence of a significant amount of Λ-β_1-[Co(R,R-picchxn)(pcp)]$^{3+}$. Prolonged reaction times, however, led to the exclusive formation of Λ-β_2-[Co(R,R-picchxn)(hpm)]$^{2+}$, apart from minor amounts of unidentified decomposition products. Furthermore, in reaction mixtures containing greater amounts of methanol (typically 50% by volume), complete solution of the Schiff base occurs to give a more alkaline starting solution and the pcp ligand is readily hydrolyzed. Under these conditions, for comparable reaction times, negligible amounts of Λ-β_1-[Co(R,R-picchxn)(pcp)]$^{3+}$ are detected in the chromatographic work-up of the reaction mixture.

Supplementary material

Lists of observed and calculated structure factors, atomic coordinates for the hydrogen atoms, anisotropic thermal parameters, proposed hydrogen bond parameters and a comprehensive table of bond lengths and angles are available from the authors on request.

Acknowledgements

We thank the SERC for studentships awarded to M.A.C. and P.D.N., and Macquarie University Research Grants Scheme for financial support. We also thank Professor Ward Robinson of the University of Christchurch, New Zealand, for the Collection of the X-ray data.

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