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Chiral Metal Complexes.
29*. A Crystallographic Study of the Stereoselective Hydrogenation of 1,2-Dehydroproline Coordinated to Cobalt(III)

EWAN F. BIRSE, PETER A. WILLIAMS**
Department of Chemistry, University College, P.O. Box 78, Cardiff CF1 1XL, U.K.
FREDERICK S. STEPHENS and ROBERT S. VAGG**
School of Chemistry, Macquarie University, N.S.W. 2109, Australia

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Abstract

The crystal structure of the complex Λ-β_2-[Co(*R,R*-picchxn)(pro-*2H*)]Cl·ClO$_4$·H$_2$O (I) (where *R,R*-picchxn is *N,N'*-bis(2-picolyl)-1*R*,2*R*-diaminocyclohexane and pro-*2H* is the 1,2-dehydroprolinate anion) has been determined. The complex crystallises in the orthorhombic space group $P2_12_12_1$, with a = 8.063(5), b = 15.320(9), c = 21.043(11) Å and Z = 4. The structure was refined by full-matrix least-squares methods to R = 0.049 for 2501 non-zero reflexions. The coordinated dehydroproline iminoacid is closely planar, and the structure suggests that the C=N double bond would be equally accessible to a reacting species approaching from either side of the ring.

The crystal structures of the two products obtained after hydrogenation of I, *i.e.* Λ-β_2-[Co(*R,R*-picchxn)(*R*-pro)](ClO$_4$)$_2$ (II) and Λ-β_2-[Co(*R,R*-picchxn)(*S*-pro)](ClO$_4$)$_2$·H$_2$O (III), have also been determined by similar means. Complex II is monoclinic, space group $P2_1$ with a = 9.385(3), b = 15.066(5), c = 10.492(7) Å, β = 110.79°, Z = 2, and was refined to R = 0.029 for 2650 non-zero reflexions. Crystals of III are trigonal, space group $P3_221$ with a = 11.417(2), c = 38.586(7) Å, Z = 6, and was refined to R = 0.039 for 2684 non-zero reflexions.

The molecular geometry of the Co^{III}(*R,R*-picchxn) fragment is essentially the same in each structure. However, upon hydrogenation of I the iminoacid C=N bond increases by 0.22 Å in conjunction with the expected lack of planarity of the aminoacid pyrolidine and chelate rings. Short non-bonded H...H contacts that are produced in the hydrogenation products II and III suggest that III would be the more sterically hindered. Comparisons are made between these structures and those of models computed for Λ-β_1-pro analogues.

Introduction

In the previous paper in this series [1] the stereoselective hydrogenation of coordinated 1,2-dehydroproline in the complex ion Λ-β_2-[Co(*R,R*-picchxn)(pro-*2H*)]$^{2+}$, where *R,R*-picchxn is *N,N'*-bis(2-picolyl)-1*R*,2*R*-diaminocyclohexane and pro-*2H* is the dehydroprolinate anion, was reported. The product ratio demonstrated a pronounced preference for the complex ion containing *R*-prolinate. This preference is in contrast with the results obtained when [Co(*R,R*-picchxn)(pro)]$^{2+}$ species are synthesised from the reaction of Λ-β-[Co(*R,R*-picchxn)Cl$_2$]$^+$ and the free amino acid [2]. Hence we have undertaken the crystal structure determinations of the precursor and the two product complex cations in order to see if there are any prominent structural features that could, at least in part, account for the observed chiral induction.

Experimental

The preparation of the three complexes was reported previously [1].

Structure Analyses

Crystal data, data collection and refinement details are summarised in Table I. The structures were solved by the heavy atom method. Difference maps indicated the approximate positions of most hydrogen atoms, however their coordinates were optimised assuming C–H, N–H 1.0 Å and O–H 0.9 Å and the appropriate geometries of the atoms to which they are bonded. The structures were refined by full-matrix least-squares in which the function minimised was $\Sigma w\Delta^2$. The weights, w, for each reflexion were taken from the counting statistics. Neutral atom scattering factors [3], corrected for anomalous dispersion [3], were used and all calculations were carried out on a FACOM 340S computer with

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*Part 28 is ref. 1.

**Authors to whom correspondence should be addressed.

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TABLE I. Summary of Crystal Data, Data Collection and Structure Refinements

Compound[a]	I	II	III
Colour	red	red	red
Crystal data			
Formula	$C_{23}H_{32}N_5O_7Cl_2Co$	$C_{23}H_{32}N_5O_{10}Cl_2Co$	$C_{23}H_{34}N_5O_{11}Cl_2Co$
M_r	620.4	663.4	686.4
System	orthorhombic	monoclinic	trigonal
Space group	$P2_12_12_1$ (No. 19)	$P2_1$ (No. 4)	$P3_221$ (No. 154)
a (Å)	8.063(5)	9.385(3)	11.417(2)
b	15.320(9)	15.066(5)	
c	21.043(11)	10.492(7)	38.586(7)
β (°)		110.79(4)	
γ			120
U (Å^3)	2599.3	1386.9	4355.4
D_m (by flotation)	1.55	1.59	1.56
Z	4	2	6
D_c (g cm^{-3})	1.585	1.600	1.570
μ-Mo Kα (cm^{-1})	9.48	9.03	8.68
F(000)	1288	692	2136
Data Collection			
Crystal size (mm)	0.6 × 0.6 × 0.4	0.2 × 0.2 × 0.68	0.16 × 0.14 × 0.64
Temperature (°C)	−110	−110	−110
Instrument	Nicolet XRD P3 [9] four-circle diffractometer		
Radiation		Mo Kα	
2θ (min, max)	4.0, 55.0	5.0, 52.0	4.0, 52.0
Absorption corr.		empirical	
Transmission factors (min, max)	0.672, 0.771	0.647, 0.705	0.858, 0.913
Total reflexions	2912	3001	3323
No. $I > 3\sigma(I)$	2501	2650	2684
Refinement			
Anisotropic	all non-hydrogen atoms		
H atoms	parameters included but not refined		
R	0.049	0.029	0.039
$R'([\Sigma w\Delta^2/\Sigma w\lvert F_o\rvert^2]^{1/2})$	0.041	0.023	0.026
$(\Delta/\sigma)_{max}$	0.1	0.1	0.1
Final Δ map (ρ e Å^{-3})	$< \lvert 0.7 \rvert$	$< \lvert 0.3 \rvert$	$< \lvert 0.7 \rvert$

[a] I, Λ-β_2-[Co(*R*,*R*-picchxn)(pro-2*H*)]Cl·ClO_4·H_2O; II, Λ-β_2-[Co(*R*,*R*-picchxn)(*R*-pro)]$(ClO_4)_2$; III, Λ-β_2-[Co(*R*,*R*-picchxn)(*S*-pro)]$(ClO_4)_2$·H_2O.

programmes written by F.S.S. Final atomic coordinates for all non-hydrogen atoms in each structure are given in Tables II–IV.

For the *S*-prolinate complex the systematic absences indicate the space group to be $P3_121$ (No. 151), $P3_121$ (No. 152) or their enantiomorphs. The Patterson map is consistent with the point group 321 and the space group $P3_221$ (No. 154) was chosen. The second perchlorate ion in this structure was found to possess space group imposed 2(C_2) symmetry, necessitating the positioning of the two chlorine atoms each with half occupancy. Difference maps showed further that there is disorder in one of these groups with respect to one of the oxygen atoms, the two positions for this atom, O(3b) and O(3c), being included each with half occupancy.

TABLE II. Final Atomic Coordinates (fractional × 10^4) for Non-hydrogen Atoms for Λ-β_2-[Co(*R*,*R*-picchxn)(pro-2*H*)]-Cl·ClO_4·H_2O[a]

	x	y	z
Co	6276.0(13)	1318.3(7)	2857.6(5)
N(11)	7616(8)	374(4)	3161(3)
N(21)	7490(8)	2274(4)	3221(3)
N(1)	7661(7)	1190(4)	2105(3)
N(2)	5125(8)	2234(4)	2419(3)
N(3)	4775(7)	1308(4)	3577(3)
O(31)	4846(7)	437(3)	2532(2)
O(32)	2844(7)	−473(3)	2880(3)
C(31)	3731(11)	168(5)	2932(4)
C(32)	3698(11)	696(5)	3524(4)

(continued)

TABLE II. *(continued)*

	x	y	z
C(33)	2562(11)	592(6)	4097(4)
C(34)	3284(12)	1308(7)	4541(4)
C(35)	4688(11)	1754(6)	4208(4)
C(11)	7767(11)	78(6)	3772(4)
C(12)	8568(12)	−680(5)	3915(4)
C(13)	9221(10)	−1174(5)	3440(4)
C(14)	9119(9)	−883(5)	2821(4)
C(15)	8335(9)	−114(5)	2703(4)
C(16)	8135(9)	289(5)	2042(4)
C(1)	6702(9)	1547(5)	1561(3)
C(2)	6044(10)	2421(5)	1809(3)
C(3)	4969(10)	2904(6)	1305(4)
C(4)	6036(11)	3051(6)	705(4)
C(5)	6700(11)	2168(6)	464(4)
C(6)	7757(11)	1670(5)	956(4)
C(21)	8975(10)	2238(5)	3526(4)
C(22)	9642(11)	2946(6)	3810(4)
C(23)	8797(12)	3733(6)	3782(3)
C(24)	7309(10)	3788(5)	3458(3)
C(25)	6681(9)	3031(5)	3188(3)
C(26)	5066(9)	3006(5)	2830(4)
Cl(1)	3601(3)	4263(1)	4593(1)
Cl(2)	1347(3)	1751(1)	2271(1)
O(1a)	3467(8)	3838(4)	3982(2)
O(1b)	4081(7)	3608(4)	5053(2)
O(1c)	2017(7)	4656(4)	4754(3)
O(1d)	4794(8)	4956(4)	4567(3)
O(w)	1989(10)	913(6)	840(4)

[a] e.s.d.s given in parentheses.

TABLE III. Final Atomic Coordinates (fractional ×10⁴) for Non-hydrogen Atoms for Λ-β_2-[Co(R,R-picchxn)(R-pro)]$(ClO_4)_2$[a]

	x	y	z
Co	688.4(6)	0	4112.7(5)
N(11)	1705(4)	955(3)	3426(4)
N(21)	1690(4)	−1014(3)	3661(4)
N(1)	2342(4)	257(2)	5818(3)
N(2)	40(4)	−909(3)	5135(4)
N(3)	−1180(4)	−198(2)	2481(3)
O(31)	−438(3)	920(2)	4541(3)
O(32)	−2206(4)	1930(2)	3503(3)
C(31)	−1612(5)	1217(3)	3514(5)
C(32)	−2208(5)	595(3)	2307(5)
C(33)	−2290(7)	998(4)	921(5)
C(34)	−2194(6)	209(4)	90(5)
C(35)	−1115(5)	−429(3)	1094(5)
C(11)	1626(5)	1143(3)	2139(4)
C(12)	2342(6)	1871(3)	1844(5)
C(13)	3180(6)	2428(3)	2881(5)
C(14)	3281(5)	2239(3)	4188(4)
C(15)	2562(5)	1492(3)	4442(4)
C(16)	2722(5)	1219(3)	5855(4)
C(1)	1856(4)	−39(4)	6956(4)

(continued)

TABLE III. *(continued)*

	x	y	z
C(2)	1204(5)	−967(3)	6543(4)
C(3)	568(5)	−1361(3)	7585(4)
C(4)	1857(5)	−1375(4)	9004(5)
C(5)	2535(6)	−453(4)	9413(5)
C(6)	3157(5)	−70(4)	8341(4)
C(21)	2838(5)	−982(3)	3157(4)
C(22)	3372(5)	−1732(3)	2750(5)
C(23)	2741(5)	−2549(3)	2859(5)
C(24)	1605(5)	−2585(3)	3424(4)
C(25)	1111(4)	−1808(3)	3798(4)
C(26)	−107(5)	−1772(3)	4424(4)
Cl(1)	6291(1)	−2273(1)	1030(1)
Cl(2)	6361(1)	−82(1)	5642(1)
O(1a)	7751(3)	−2710(2)	1409(3)
O(1b)	6428(3)	−1534(2)	1955(3)
O(1c)	5834(4)	−1949(3)	−344(3)
O(1d)	5179(4)	−2884(2)	1178(3)
O(2a)	6828(4)	−692(2)	4792(4)
O(2b)	7682(4)	247(2)	6710(3)
O(2c)	5516(4)	642(3)	4832(4)
O(2d)	5399(4)	−568(3)	6219(4)

[a] e.s.d.s given in parentheses.

TABLE IV. Final Atomic Coordinates (fractional ×10⁴) for Non-hydrogen Atoms for Λ-β_2-[Co(R,R-picchxn)(S-pro)]$(ClO_4)_2 \cdot H_2O$[a]

	x	y	z
Co	1782.0(7)	5897.5(7)	1015.0(2)
N(11)	907(4)	3907(4)	984(1)
N(21)	3421(4)	6275(4)	770(1)
N(1)	727(4)	5655(4)	597(1)
N(2)	2506(4)	7844(4)	944(1)
N(3)	2600(4)	5980(4)	1473(1)
O(31)	312(3)	5747(4)	1276(1)
O(32)	−595(4)	5333(4)	1802(1)
C(31)	315(5)	5480(5)	1601(1)
C(32)	1452(5)	5308(5)	1728(1)
C(33)	2010(6)	5939(7)	2085(1)
C(34)	3509(6)	6856(6)	2031(1)
C(35)	3587(6)	7252(5)	1649(1)
C(11)	1284(5)	3080(6)	1135(1)
C(12)	595(6)	1699(6)	1079(1)
C(13)	−528(6)	1146(5)	864(1)
C(14)	−930(6)	1966(6)	714(1)
C(15)	−193(5)	3349(5)	774(1)
C(16)	−551(5)	4328(5)	617(1)
C(1)	509(5)	6838(5)	566(1)
C(2)	1883(6)	8036(6)	616(1)
C(3)	1843(6)	9363(6)	615(1)
C(4)	1247(6)	9468(6)	265(1)
C(5)	−137(6)	8224(7)	208(1)
C(6)	−94(5)	6912(6)	221(1)
C(21)	3704(6)	5353(5)	634(1)

(continued)

TABLE IV. *(continued)*

	x	y	z
C(22)	4962(6)	5726(6)	494(2)
C(23)	5943(7)	7060(7)	498(2)
C(24)	5663(6)	8014(7)	628(2)
C(25)	4381(5)	7592(6)	763(1)
C(26)	4000(5)	8576(5)	911(1)
Cl(1)	3424.6(16)	7762.3(17)	3082.8(3)
Cl(2)	2349.5(19)	0	1667
Cl(3)	7337.0(22)	0	1667
O(1a)	3790(5)	6971(5)	3300(1)
O(1b)	3272(5)	8667(5)	3303(1)
O(1c)	2242(5)	6960(5)	2902(1)
O(1d)	4473(4)	8467(5)	2841(1)
O(2a)	3232(5)	344(6)	1383(1)
O(2b)	2248(7)	1103(6)	1776(1)
O(3a)	6727(4)	161(5)	1367(1)
O(3b)	8527(11)	1568(11)	1697(4)
O(3c)	8000(12)	−658(13)	1616(3)
O(w)	798(5)	2247(5)	2176(1)

[a] e.s.d.s given in parentheses.

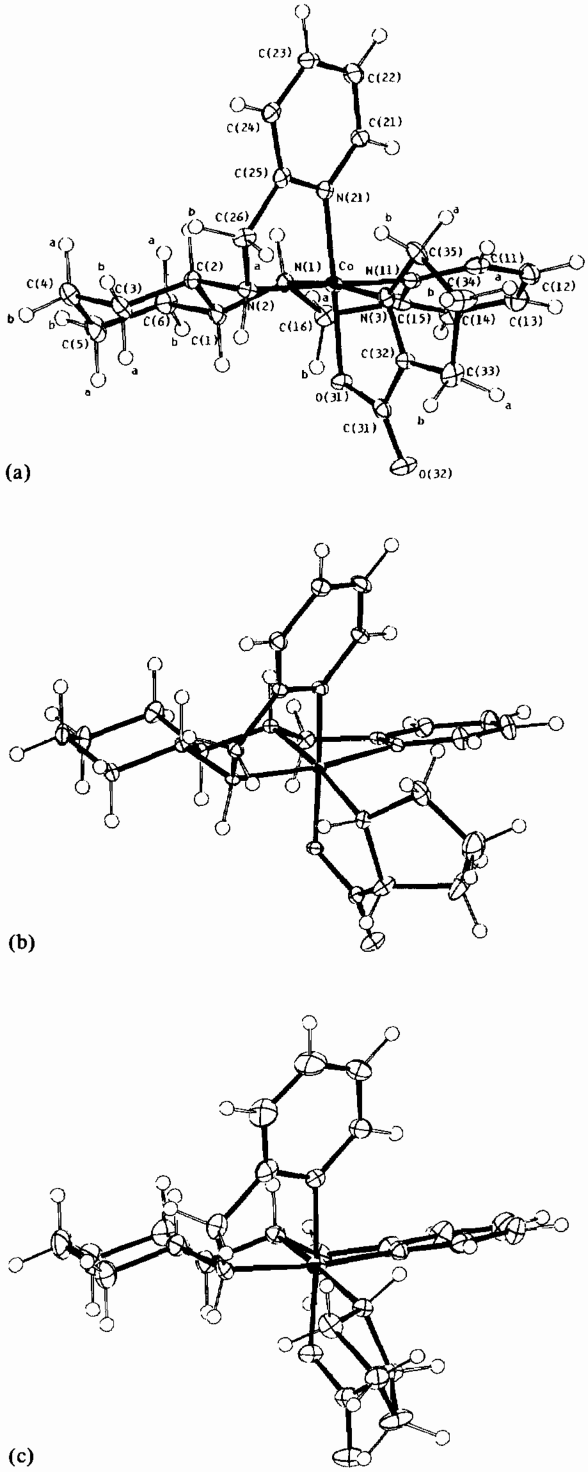

Fig. 1. Perspective drawings of the complex cations with thermal ellipsoids drawn to include 35% probability. The atom labelling scheme common to the three structures is shown. Hydrogen atoms are numbered according to the atoms to which they are attached, and where ambiguity exists the secondary labelling is shown. (a) Λ-β_2-[Co(R,R-picchxn)(pro-$2H$)]$^{2+}$, (b) Λ-β_2-[Co(R,R-picchxn)(R-pro)]$^{2+}$, (c) Λ-β_2-[Co(R,R-picchxn)(S-pro)]$^{2+}$.

Discussion

Table V gives selected bond lengths and angles for the coordination spheres and proline ligands of the cations. Perspective drawings [4] of these cations, together with the atom labelling schemes, are given in Fig. 1. All three cations exhibit Λ-β_2 coordination geometry, confirming the deductions of spectroscopic studies [1]. The molecular geometry of the Co^{III}-(R,R-picchxn) fragment in each structure is in accord with those previously reported [5, 6]. In the three structures the ions are held by hydrogen bonding networks which involve the lattice water molecules where present. The hydrogen bonding proposed, together with any close intermolecular distances, is given in Table VI.

In the dehydroprolinate complex the dehydropyrolidine ring is unexpectedly closely planar, the maximum deviation of a constituent atom from the mean plane being 0.01 Å. However, an inspection of the thermal ellipsoids of the ring carbon atoms reveals that this apparent planarity results from an unresolved positional disorder in the ring. The thermal ellipsoid for C(34) has a pronounced elongation in the direction normal to the plane of the ring (Fig. 1). Analysis of the vibration parameters for this atom shows the principal axis of its ellipsoid to be 6.5° from the normal to the NC_4-plane with a r.m.s. amplitude of vibration of 0.36 Å, a value some 0.14 Å larger than that for any other atom in the ring.

The structures of the R- and S-prolinate complexes show that the change from an iminoacid to an aminoacid is accompanied by the expected increase in both the N(3)–C(32) and the Co–N(3) bond lengths

TABLE V. Selected Bond Parameters in the Three Complex Cations

	pro-*2H*	*R*-pro	*S*-pro
Bond length (A)			
Co–N(11)	1.915(6)	1.997(4)	1.976(4)
Co–N(21)	1.920(6)	1.938(4)	1.942(4)
Co–N(1)	1.949(6)	1.946(3)	1.948(4)
Co–N(2)	1.918(6)	1.965(4)	1.965(4)
Co–N(3)	1.938(6)	1.991(3)	1.978(3)
Co–O(31)	1.903(5)	1.891(3)	1.889(3)
O(31)–C(31)	1.298(9)	1.317(5)	1.292(5)
O(32)–C(31)	1.220(9)	1.207(5)	1.240(5)
C(31)–C(32)	1.486(10)	1.514(6)	1.490(7)
N(3)–C(32)	1.283(9)	1.505(5)	1.508(6)
N(3)–C(35)	1.495(9)	1.519(5)	1.484(6)
C(32)–C(33)	1.522(11)	1.553(7)	1.537(6)
C(33)–C(34)	1.554(12)	1.496(7)	1.509(8)
C(34)–C(35)	1.497(11)	1.517(7)	1.531(6)
Bond angle (°)			
N(11)–Co–N(1)	82.6(2)	82.0(1)	82.3(2)
N(21)–Co–N(2)	83.1(3)	81.7(2)	82.4(2)
N(1)–Co–N(2)	87.7(2)	86.4(1)	85.7(2)
O(31)–Co–N(3)	84.1(2)	85.3(1)	84.6(1)
N(11)–Co–N(2)	170.3(3)	168.4(1)	167.7(1)
N(1)–Co–N(3)	172.8(3)	172.7(1)	171.7(2)
N(21)–Co–O(31)	173.3(3)	174.8(2)	172.9(2)
Co–O(31)–C(31)	114.3(5)	115.5(3)	115.6(3)
O(31)–C(31)–O(32)	127.7(7)	124.0(4)	122.7(5)
O(31)–C(31)–C(32)	112.5(7)	115.3(4)	117.2(4)
O(32)–C(31)–C(32)	120.1(8)	120.7(4)	120.1(3)
Co–N(3)–C(32)	111.1(5)	108.4(2)	106.9(3)
Co–N(3)–C(35)	136.0(5)	122.4(2)	124.4(3)
C(32)–N(3)–C(35)	112.3(6)	107.9(3)	103.9(3)
N(3)–C(32)–C(31)	117.3(8)	111.1(3)	108.0(4)
N(3)–C(32)–C(33)	114.5(7)	103.9(4)	114.8(4)
C(31)–C(32)–C(33)	128.2(7)	114.9(4)	107.3(4)
C(32)–C(33)–C(34)	100.2(7)	104.0(4)	105.1(4)
C(33)–C(34)–C(35)	108.9(7)	105.2(4)	102.6(4)
C(34)–C(35)–N(3)	104.1(7)	106.0(4)	104.4(4)

TABLE VI. Contact Distances[a] (A)

Λ-β_2-[Co(*R*,*R*-picchxn)(pro-*2H*)]Cl·ClO$_4$·H$_2$O			
Proposed hydrogen bonding			
N(1)-H(N1)....Cl(2$^{\mathrm{I}}$)	3.113(6)	O(w)-H(wa)....Cl(2)	3.314(8)
N(2)-H(N2)....Cl(2)	3.150(7)	O(w)-H(wa)....O(1d$^{\mathrm{II}}$)	3.100(11)
Intermolecular distances < 3.3 A			
O(32)...C(24$^{\mathrm{III}}$)	3.038(9)	C(26)...O(1a)	3.026(9)
O(32)...C(14$^{\mathrm{IV}}$)	3.071(9)	C(11)...O(1c$^{\mathrm{V}}$)	3.186(10)
O(32)...C(25$^{\mathrm{III}}$)	3.233(9)	C(21)...O(1b$^{\mathrm{V}}$)	3.261(9)
O(32)...C(26$^{\mathrm{III}}$)	3.240(9)	C(24)...O(1a)	3.288(10)
Λ-β_2-[Co(*R*,*R*-picchxn)(*R*-pro)](ClO$_4$)$_2$			
Proposed hydrogen bonding			
N(3)-H(N3)....O(1b$^{\mathrm{VI}}$)	2.918(4)	N(1)-H(N1)....O(2d)	3.016(5)
N(2)-H(N2)....O(2a$^{\mathrm{VI}}$)	2.925(5)		

(continued)

TABLE VI. *(continued)*

Intermolecular distances <3.3 Å			
C(15)...O(2c)	2.948(5)	C(22)...O(1d)	3.255(6)
C(14)...O(2c)	3.104(6)	O(32)...C(25^{VII})	3.260(5)
O(32)...C(26^{VII})	3.149(5)	C(22)...O(1b)	3.272(5)
O(32)...C(24^{VII})	3.155(5)	C(16)...O(2c)	3.284(5)
C(35)...O(1b^{VI})	3.222(5)	C(33)...O(1d^{IX})	3.286(6)
C(12)...O(1c^{VIII})	3.237(6)		
Λ-β_2{Co(*R*,*R*-picchxn)(*S*-pro)](ClO$_4$)$_2$·H$_2$O			
Proposed hydrogen bonding			
N(1)-H(N1)....O(1b^{X})	2.935(5)	O(w)-H(wb)....O(2b)	3.000(6)
N(2)-H(N2)....O(2a^{XI})	3.055(6)	O(w)-H(wa)....O(3b^{XIII})	2.955(12)
N(3)-H(N3)....O(32^{XII})	3.055(6)	O(w)-H(wa)....O(3c^{XIV})	2.822(11)
Intermolecular Distances <3.3 Å			
C(12)...O(3c^{XIV})	3.121(14)	C(26)...O(1a^{XI})	3.229(6)
C(26)...O(2a^{XI})	3.150(7)	N(21)...O(1a^{XI})	3.235(5)
O(32)...C(11^{XV})	3.160(6)	C(22)...O(1c^{XII})	3.274(9)
C(16)...O(1b^{XI})	3.207(6)		

Roman numeral superscripts refer to the following equivalent positions relative to x, y, z

I	$1+x, y, z$	II	$1-x, y-\frac{1}{2}, \frac{1}{2}-z$	III	$1-x, y-\frac{1}{2}, 1\frac{1}{2}-z$
IV	$x-1, y, z$	V	$\frac{1}{2}+x, \frac{1}{2}-y, 1-z$	VI	$x-1, y, z$
VII	$-x, \frac{1}{2}+y, 1-z$	VIII	$1-x, \frac{1}{2}+y, -z$	IX	$-x, \frac{1}{2}+y, -z$
X	$1-y, 1+x-y, z-\frac{1}{3}$	XI	$x, 1+y, z$	XII	$1+x-y, 1-y, \frac{1}{3}-z$
XIII	$x-1, y, z$	XIV	$x-y-1, -y, \frac{1}{3}-z$	XV	$x-y, 1-y, \frac{1}{3}-z$

[a] e.s.d.s given in parentheses.

(Table V) and both the aminoacid pyrolidine and chelate rings lose planarity. The maximum and average absolute deviations of constituent atoms from their mean planes are 0.22, 0.14 and 0.25, 0.16 Å for the pyrolidine rings and are 0.14, 0.09 and 0.19, 0.12 Å for the chelate rings in the *R* and *S* forms respectively. The Co–N(11) distances also are substantially lengthened by *ca.* 0.07 Å from that of 1.915(6) Å in the pro-*2H* complex cation. These distances are significantly longer than those we have observed in the structures of other Co^{III}(*R*,*R*-picchxn) complexes [5–7] and may reflect the need to accommodate the bulky proline ligands. The hydrogenation process necessarily occurs by *cis* addition to the double bond and as a result there is a folding about the N(3)–C(32) bond by *ca.* 50° away from the coplanar arrangement in the iminoacid. The direction of this fold determines the absolute configurations of N(3) and C(32), which are necessarily the same, in the aminoacid complex so chosen.

Figure 2 shows the dehydroprolinate complex cation projected so as to demonstrate that the N(3)–C(32) double bond is equally accessible to a reactant species approaching from either side. In addition, the diagram suggests that intramolecular contacts involving the atoms N(3) and C(35) with atoms C(11) and C(26) will be of significance upon hydrogenation of the N(3)–C(32) double bond. Table VII lists these

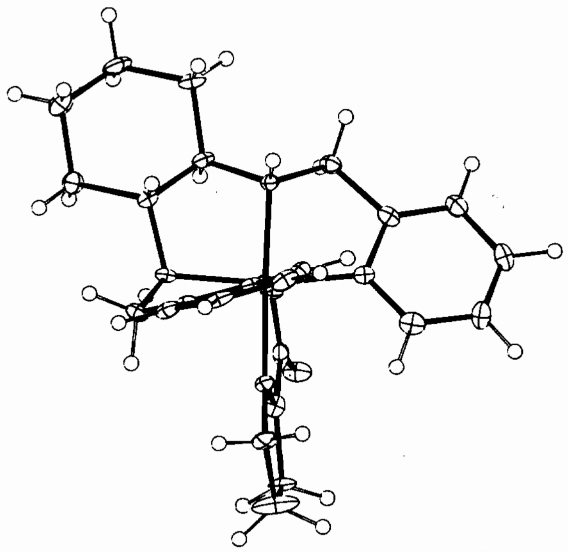

Fig. 2. The Λ-β_2-[Co(*R*,*R*-picchxn)(pro-*2H*)]$^{2+}$ cation viewed so as to show the steric environment on both sides of the plane of the iminoacid.

TABLE VII. Interligand Contacts (Å) Involving the Proline and Picchxn Ligands

	pro-*2H*	*R*-pro	*S*-pro
C(35).....C(11)	3.688(12)	3.381(6)	4.583(6)
H(35a)...H(11)	2.38	2.75	4.75
C(35).....C(26)	3.491(11)	3.854(6)	3.145(6)
H(35b)...H(26a)	2.35	3.15	2.17
H(35b)...H(26b)	3.82	3.95	2.22
N(3)......C(11)	3.089(11)	3.438(6)	3.153(7)
H(N3)....H(11)		3.98	1.97
N(3)......C(26)	3.048(10)	3.056(5)	3.361(6)
H(N3)....H(26a)		1.88	3.64

contact distances for the three structures. In the *R*-prolinate complex ion there is only one close H....H contact (H(N3)...H(26a) at 1.88 Å) whereas in the *S*-prolinate complex there are three such contacts (H(N3)...H(11) 1.97 and H(35b)...H(26a), H(26b) 2.17, 2.22 Å), suggesting that the latter structure is the more sterically hindered.

Although this is consistent with the chiral preference observed [1], it seems unlikely that these steric differences are sufficiently severe as to be the predominent determining factor, especially for the more flexible species in solution. Further, using the structural details of the *S*- and *R*-prolinates to compute molecular models for the corresponding β_1 configurations [8] it is clear that severe steric hindrance would be present in the Λ-β_1-*R*-pro form. In particular, the position of C(35) relative to C(1) and N(2) in that form is such that short H...H contacts are apparent. In this computed structure these contacts are H(35a)...H(1) 1.02 Å and H(35a)...H(N2) 2.57 Å, and any bond rotation within the pyrolidine ring will only serve to lengthen the former and shorten the latter. This situation is sufficient to account for the observed [2] lack of formation of the Λ-β_1-*R*-pro species. Although the Λ-β_2-*R*-pro species can be formed by hydrogenation of the iminoacidate complex, attempts to prepare it from the dichloro precursor also have failed [2]. It is probable that the short H(N3)...H(26a) contact observed here in the crystal structure reflects the interaction which prevents entry of the free aminoacid ligand into the coordination sphere. The model calculated for the Λ-β_1-*S*-pro species shows that the pyrolidine ring can be flexed to eliminate the more prominent steric interactions observed in the β_2 structures. This agrees with the observed preference for β_1 coordination in the synthesis from the dichloro precursor.

Supplementary Material

Lists of hydrogen atomic coordinates, anisotropic thermal parameters, observed and calculated structure factors and bonding parameters for the three structures are available from F.S.S. upon request.

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