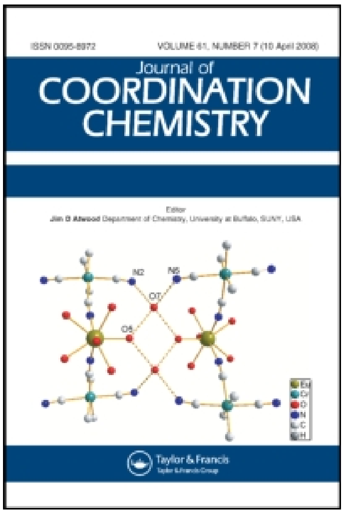

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Crystal and Molecular Structures of Three Salts of Λ-β_1-[Co(*R*,*R*-Picchxn)(*R*-Phe)]$^{2+}$ (Picchxn=*N*,*N*^{1}-DI(2-Picolyl)-1,2-Diaminocyclohexane; Phe = Phenylalaninato(1-))

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To cite this Article Emseis, Paul , Hibbs, David E. , Leverett, Peter and Williams, Peter A.(2003) 'Crystal and Molecular Structures of Three Salts of Λ-β_1-[Co(*R*,*R*-Picchxn)(*R*-Phe)]$^{2+}$ (Picchxn=*N*,*N*^{1}-DI(2-Picolyl)-1,2-Diaminocyclohexane; Phe = Phenylalaninato(1-))', Journal of Coordination Chemistry, 56: 5, 389 — 395
To link to this Article: DOI: 10.1080/0095897031000092395
URL: http://dx.doi.org/10.1080/0095897031000092395

J. Coord. Chem., 2003, Vol. 56, No. 5, pp. 389–395

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CRYSTAL AND MOLECULAR STRUCTURES OF THREE SALTS OF Λ-β_1-[Co(R,R-PICCHXN)(R-PHE)]$^{2+}$ (PICCHXN = N,N^1-DI(2-PICOLYL)-1,2-DIAMINO-CYCLOHEXANE; PHE = PHENYLALANINATO(1−))

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(Received 30 October 2002; In final form 3 December 2002)

Single-crystal X-ray structures of Λ-β_1-[Co(R,R-picchxn)(R-phe)]Br$_2$, Λ-β_1-[Co(R,R-picchxn)(R-phe)]Br$_2\cdot$3H$_2$O and Λ-β_1-[Co(R,R-picchxn)(R-phe)]I$_2$ are reported. In each structure there are three formula units in the asymmetric unit. Considerable disorder attends the anions and water molecules of crystallisation. In every case the conformer adopted by the coordinated aminoacidate is such that the phenylalaninato side chain is extended in order to minimize non-bonded steric interactions with the Co(tetradentate)fragment. Such an arrangement is in accord with the fact that this kind of diastereoisomer does not participate in any strong intramolecular π–π or NH–π interaction.

Keywords: Cobalt; Tetradentate; Phenylalanine; Diastereoisomers; Crystal structures

INTRODUCTION

As part of a study of intramolecular π–π and NH–π interactions in ternary coordination complexes of Co(III), R^*,R^*-picchxn (picchxn = N,N^1-di(2-picolyl)-1,2-diaminocyclohexane) and aromatic amino acids we have systematically explored the structures of the various isomers possible in these systems [1]. This is because each possesses a unique combination of the above interactions and examination of these permits an evaluation of the energetics of separate π–π or NH–π contributions to various conformers in specific isomers. In β complexes, the unsymmetrical bidentate aminoacidate ligand may coordinate in two ways, β_1 or β_2, as shown in **1** and **2**, for the Λ-complex of R,R-picchxn.

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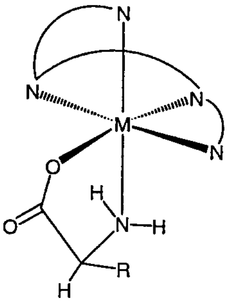
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897031000092395



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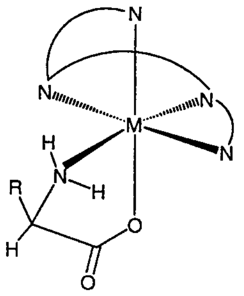

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For reasons that are not apparent, β_2 complexes of aromatic of *S*-aminoacidates are formed in only very small amounts employing the synthetic methods we have developed. Both β_1 and β_2 species are isolated in the case of *R*-aminoacidates. Of these, β_2-*R*-aa (aa = aminoacidate) complexes display intramolecular π–π interactions involving the aromatic substituents of the aminoacidate and a pyridyl group of the tetradentate, as revealed by single crystal X-ray studies [1]. These persist in solution and the rotamer giving rise to it predominates, as revealed by analysis of rotamer populations and nOe experiments in the ^{1}H NMR.

Topological constraints prevent such interactions for Λ-β_1-[Co(*R*,*R*-picchxn)(*R*-aa)]$^{2+}$, except for the possibility of a weak NH–π contact in one conformer. In line with this constraint, rotamer populations in dmso and aqueous solutions are distributed approximately equally at ambient temperatures [2]. Thus it is expected that in the solid state the side arm of the aminoacidates would most likely adopt the conformer with minimised non-bonded steric interactions. This is borne out in single-crystal X-ray studies of Λ-β_1-[Co(*R*,*R*-picchxn)(*R*-phe)]Br$_2$, **3** (phe = phenylalaninato), the analogous trihydrate **4** and the corresponding anhydrous diiodide salt **5**, details of which are presented below.

EXPERIMENTAL

Syntheses

Λ-β-[Co(*R*,*R*-picchxn)Cl$_2$]ClO$_4$.0.5H$_2$O was synthesised as previously described [3].

Λ-β_1-[Co(*R*,*R*-picchxn)(*R*-phe)]$^{2+}$ salts

R-Phenylalanine (0.78 g, 4.72 mmol) was added to a stirred solution of Λ-β-[Co(*R*,*R*-picchxn)Cl$_2$]ClO$_4\cdot$0.5H$_2$O (0.50 g, 0.94 mmol) in water (30 cm^3) at 60°C. When dissolution was complete, aqueous NaOH (1.0 cm^3, 1.0 M) was added dropwise to the crimson solution, which was then allowed to cool to room temperature with stirring. Upon stirring overnight at room temperature, fluffy, pink-orange needles of a mixture of isomers crystallised. The solid was dissolved in water and the orange solution applied to a column of CM-Sephadex® C-25 cation exchange resin in the Na$^+$ cycle (35 × 2 cm). The absorbed material was washed with water (50 cm^3) then eluted with 0.3 M aqueous

NaCl. Two orange bands separated cleanly on the column, with traces of a yellow-brown decomposition product as a very faint band in between these two orange bands. The slower moving broad orange band contained the majority of complex. The two orange bands were collected in fractions ($26 \times 11\,\mathrm{cm}^3$). Measurement of the electronic spectra of these confirmed the presence of two resolved isomers, one in each band.

Fractions from the slower moving band were combined and the solvent removed *in vacuo* at 40°C. The dull orange residue was desalted by dissolution in a minimum of absolute ethanol, followed by gravity filtration of residual NaCl. The filtrate was evaporated to dryness, and the residue taken up in water (*ca* $25\,\mathrm{cm}^3$). Solid CF_3SO_3K (*ca* 0.2 g) was added to the orange solution, which was desiccated over silica gel. The anhydrous triflate salt crystallised as orange, flattened-needles during one week at room temperature. These were collected at the pump, washed sparingly with ice-cold water and air-dried. Yield: 0.16 g. *Anal.* Calc. for $C_{29}H_{37}N_5O_{9.5}F_6S_2Co$ (%): C, 41.24; H, 4.42; N, 8.29. Found: C, 41.16; H, 4.51; N, 8.21. Electronic spectrum: λ_{max}/nm (H_2O) 345 (ε/dm^3 mol^{-1} cm^{-1} 231), 484 (193). CD spectrum: λ/nm, extrema (H_2O) 354.4 ($\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1} −0.20), 388.8 (+0.18), 502.1 (+2.73).

Λ-β_1-[Co(*R*,*R*-picchxn)(*R*-phe)](Br)$_2$, 3, and Λ-β_1-[Co(*R*,*R*-picchxn)(*R*-phe)](Br)$_2$ · 3H_2O, 4

The bromides were obtained from water by metathesis with NaBr. Two kinds of crystal were found and subsequent single-crystal structure analyses revealed that they were the anhydrous salt and the trihydrate. The latter is efflorescent, and should be stored in contact with the mother liquor or under silicone oil.

Λ-β_1-[Co(*R*,*R*-picchxn)(*R*-phe)](*I*)$_2$, 5

The anhydrous iodide was obtained from water by metathesis with NaI. *Anal.* Calc. for $C_{27}H_{38}N_5O_4I_2Co$ (%): C, 40.07; H, 4.73; N, 8.65. Found: C, 40.27; H, 4.27; N, 8.49.

Crystal Structure Determinations

Single-crystal, high-resolution, low-temperature data were collected on a Bruker SMART 1000 CCD diffractometer using MoKα radiation ($\lambda = 0.71073$ Å). Data were collected at 150(2) K with ω-scan increments of 0.3°. Reflections were integrated with the program SAINT [4] and merged with the program SADABS [4]. Details concerning crystal data and refinement parameters are given in Table I. Intensities were corrected for Lorentz and polarisation effects but absorption corrections were not applied. Structures were solved by Patterson and difference Fourier techniques using SHELXS-86 [5] and SHELXL-97 [6] and refined by full-matrix least-squares methods in which function $\Sigma w(F_o^2 - F_c^2)^2$ was minimised. Weights for each reflection in the final cycles of refinements are given by $w = 1/[\sigma^2(F_o^2) + (nP)^2]$ where $P = [2F_c^2 + \mathrm{Max}(F_o^2, 0)]/3$, as defined by SHELX-97. Weighting schemes gave uniform analyses of variance in terms of F_c^2.

The crystals of **3**, **4** and **5** were found to be merohedrally twinned, with attempts to solve and refine the structures being frustrated by the fact that the anions were

TABLE I Crystal data and structure refinement for **3**, **4** and **5**

Crystal data	**3**	**4**	**5**
Empirical formula	$C_{27}H_{34}Br_2CoN_5O_2$	$C_{27}H_{40}Br_2CoN_5O_5$	$C_{27}H_{34}CoI_2N_5O_2$
Formula weight	679.39	733.41	773.35
Crystal size (mm)	0.34 × 0.30 × 0.25	0.35 × 0.25 × 0.15	0.40 × 0.30 × 0.30
Crystal system	Trigonal	Trigonal	Trigonal
Space group	$P3_2$	$P3_2$	$P3_2$
a (Å)	19.869(4)	19.696(3)	19.8791(14)
b (Å)	19.869(4)	19.696(3)	19.8791(14)
c (Å)	20.456(4)	20.445(5)	20.772(3)
V (Å^3)	6994(3)	6869(2)	7108.9(12)
Z	9	9	9
D_{calc} (Mg m^{-3})	1.452	1.596	1.626
F(000)	3096	3231	3420
T (K)	150(2)	150(2)	150(2)
Index ranges	$-20 \leq h \leq 22$	$-26 \leq h \leq 13$	$-26 \leq h \leq 13$
	$-21 \leq k \leq 22$	$0 \leq k \leq 26$	$0 \leq k \leq 26$
	$-22 \leq l \leq 22$	$-27 \leq l \leq 27$	$-27 \leq l \leq 27$
Reflections collected	31711	21085	20955
Independent reflections	13298 ($R_{\text{int}} = 0.1291$)	21055 ($R_{\text{int}} = 0.0000$)	20930 ($R_{\text{int}} = 0.0000$)
Observed data [$I > 2\sigma(I)$]	10736	16417	14428
Data/restraints/parameters	13298/1/1083	21055/1/1046	20930/0/487
Weighting scheme (w)[a]	$n = 0.1393$	$n = 0.1300$	$n = 0.1697$
Goodness-of-fit on F^2	1.007	0.885	1.005
Final R indices (obs. data)	$R_1 = 0.080$	$R_1 = 0.066$	$R_1 = 0.102$
	$R_w = 0.202$	$R_w = 0.168$	$R_w = 0.246$
R indices (all data)[b]	$R_1 = 0.094$	$R_1 = 0.082$	$R_1 = 0.135$
	$R_w = 0.211$	$R_w = 0.177$	$R_w = 0.268$
Extinction coefficient	0.0017(3)		
Largest diff. max/min (e Å^{-3})	1.757/− 0.709	2.253/− 0.747	4.059/− 1.398

[a] $w = 1/[\sigma^2(F_o^2) + (nP)^2]$ where $P = [2F_c^2 + \text{Max}(F_o^2, 0)]/3$; [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = \{[\Sigma w(F_o^2 - F_o^2)^2/\Sigma w(F_o^2)^2]^{1/2}\}$.

considerably affected by disorder in all cases. Refinement of the data produced a regular structural array, but with the disordered anions, rationalised by a sensible structural model accounting for disordered anion occupancies. After anisotropic refinement of the structures of **3** and **4** excluding hydrogen atoms, all hydrogen atoms were positioned using the appropriate geometry and relevant C–H and N–H bond lengths; the accuracy of these positions was confirmed by a subsequent difference Fourier synthesis. Refinement was continued with hydrogen atoms riding on the atoms to which they are bonded, with fixed isotropic thermal parameters, and with anisotropic temperature factors for all other atoms. Refinement was terminated when the minimisation factor changed by < 0.1% and a final difference map showed no significant residual electron density. The iodide salt, **5**, was refined isotropically due to complications arising from the extensive disorder of the iodide counterions. Treatment of the hydrogen atoms was carried out in a similar fashion to that for **3** and **4**, except with the hydrogen atoms riding on the atoms to which they are bonded, with fixed isotropic thermal parameters for all atoms.

RESULTS AND DISCUSSION

As noted above, there are three formula units in the asymmetric unit of each of the structures **3**, **4** and **5**. However, in every case the conformer giving rise to the extended

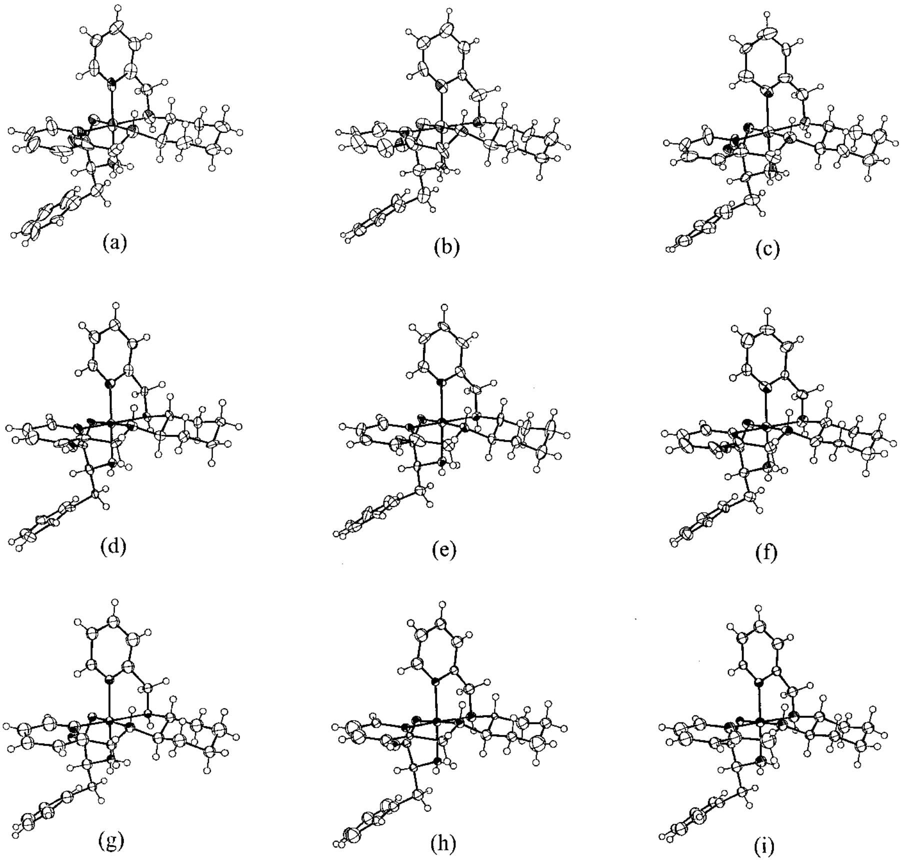

FIGURE 1 Perspective views of the crystallographically-independent cation Λ-β_1-[Co(*R*,*R*-picchxn)(*R*-aa)]$^{2+}$ in **3** (a–c), **4** (d–f) and **5** (g–i).

side chain of the aminoacidate is observed (we have explored a number of related salts, as here, in order to assess the relative effects of crystal packing on the nature of the particular conformer observed in the solid state [1,2]). This is illustrated in Fig. 1, which shows the nine discrete cations found in the three structures. Figure 2 shows a perspective view of one of the cations in **4**, together with the atom numbering scheme. In no structure was any unusual dimensional parameter observed. Table II lists final atomic coordinates for the non-hydrogen atoms of the cation shown in Fig. 2.

The Λ-β_1 topology is clearly established and no intramolecular contact (in this case involving the phenyl ring and an amino N*H* atom of phe) is observed. Thus it is apparent that the potential interaction is weak and outweighed *in these cases* by a combination of crystal packing effects and the tendency to minimize non-bonded contacts. This is not the situation in related congeners containing tyrosine, *O*-methyltyrosine and tryptophane [1,2]. This may be because the interaction is weak, but may also be influenced by packing effects in that the complexes examined contain other counteranions. In any event, analysis of rotamer populations in solution shows that in these Λ-β_1 complexes containing aromatic *R*-aminoacidates, the conformer

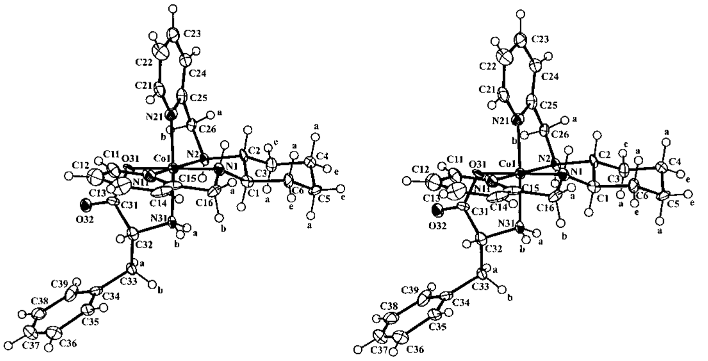

FIGURE 2 A stereoscopic view of one of the crystallographically-independent cations, Λ-β_1-[Co(*R*,*R*-picchxn)(*R*-aa)]$^{2+}$ in **4**, together with the atom numbering scheme. Coordinates for non-hydrogen atoms for this cations are listed in Table II.

TABLE II Final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the non-hydrogen atoms with estimated standard deviations in parentheses for the Co(1) cation of the complex Λ-β_1-[Co(*R*,*R*-picchxn)(*R*-phe)]$Br_2 \cdot 3H_2O$. *U*(*eq*) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	y/b	z/c	U_{eq}
Co(1)	6385(1)	12525(1)	10071(1)	17(1)
O(31)	6206(4)	12756(4)	10932(3)	21(1)
N(1)	6567(5)	12274(5)	9200(3)	23(2)
N(2)	5480(4)	12553(4)	9704(3)	15(1)
N(11)	7325(5)	12499(5)	10276(4)	27(2)
N(21)	6905(5)	13629(5)	9878(4)	23(2)
N(31)	5766(5)	11438(5)	10350(3)	20(2)
O(32)	5763(5)	12216(4)	11915(3)	32(2)
C(1)	5808(5)	11882(6)	8902(4)	20(2)
C(2)	5461(6)	12422(6)	8989(4)	19(2)
C(3)	4658(6)	12090(6)	8685(5)	28(2)
C(4)	4689(7)	11945(6)	7967(4)	28(2)
C(5)	5027(6)	11354(5)	7873(5)	31(2)
C(6)	5808(6)	11698(6)	8164(4)	28(2)
C(11)	7763(6)	12782(6)	10792(5)	26(2)
C(12)	8406(7)	12734(8)	10948(7)	47(3)
C(13)	8653(7)	12430(8)	10444(7)	44(3)
C(14)	8224(6)	12123(6)	9847(7)	38(3)
C(15)	7568(6)	12188(5)	9812(6)	28(2)
C(16)	7006(5)	11866(5)	9225(4)	22(2)
C(21)	7703(6)	14172(7)	9841(4)	27(2)
C(22)	7994(7)	14922(7)	9678(6)	37(2)
C(23)	7484(6)	15222(6)	9547(5)	29(2)
C(24)	6678(6)	14674(6)	9567(5)	27(2)
C(25)	6431(6)	13956(6)	9765(4)	24(2)
C(26)	5579(5)	13333(6)	9851(4)	19(2)
C(31)	5923(6)	12162(5)	11357(5)	23(2)
C(32)	5790(6)	11402(6)	11084(4)	22(2)
C(33)	5101(5)	10680(5)	11357(4)	19(2)
C(34)	5267(6)	10417(5)	12003(4)	22(2)
C(35)	5757(6)	10109(6)	12046(5)	27(2)
C(36)	5871(8)	9818(7)	12668(6)	41(3)
C(37)	5533(9)	9922(7)	13202(6)	51(3)
C(38)	5062(7)	10236(6)	13169(5)	36(2)
C(39)	4893(6)	10476(7)	12576(5)	33(2)

that gives rise to the NH–π interaction is not present in excess. In cases involving related topologies when favourable intramolecular NH–π and π–π contacts are feasible, these serve to markedly skew the distribution of rotamers in solution. Further structural studies of related species will be communicated in due course.

Acknowledgments

PE wishes to thank DEST for the award of a postgraduate studentship.

Supplementary Data

Full lists of crystallographic data are available from the authors upon request.

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