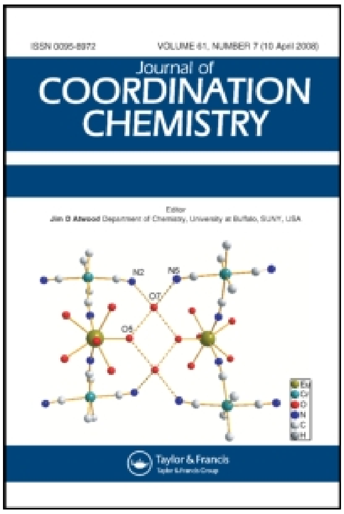

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

CHIRAL METAL COMPLEXES. 48. STEREOSELECTIVITY IN TERNARY CO(III) COMPLEXES OF N,N'-DI (2*S*-PYRROLIDIN-2-YL)-1*R*, 2*R*

Michael A. Cox[a]; Frederick S. Stephens[b]; Robert S. Vagg[b]; Peter A. Williams[a]
[a] Department of Chemistry, University of Western Sydney, Kingswood, Australia [b] School of Chemistry, Macquarie University, Australia

To cite this Article Cox, Michael A. , Stephens, Frederick S. , Vagg, Robert S. and Williams, Peter A.(1997) 'CHIRAL METAL COMPLEXES. 48. STEREOSELECTIVITY IN TERNARY CO(III) COMPLEXES OF N,N'-DI (2*S*-PYRROLIDIN-2-YL)-1*R*, 2*R*', Journal of Coordination Chemistry, 41: 4, 291 — 301

To link to this Article: DOI: 10.1080/00958979708045506

URL: http://dx.doi.org/10.1080/00958979708045506

J. Coord. Chem., 1997, Vol. 41, pp. 291-301
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science Publishers
Printed in Malaysia

CHIRAL METAL COMPLEXES. 48.* STEREOSELECTIVITY IN TERNARY CO(III) COMPLEXES OF *N,N′*-DI (2*S*-PYRROLIDIN-2-YL)-1*R*, 2*R*-DIAMINOCYCLOHEXANE

MICHAEL A. COX[a], FREDERICK S. STEPHENS[b], ROBERT S. VAGG[b], and PETER A. WILLIAMS[a,†]

[a]*Department of Chemistry, University of Western Sydney, Nepean, P.O. Box 10, Kingswood, NSW 2747, Australia;* [b]*School of Chemistry, Macquarie University, NSW 2109, Australia*

(Received 1 August 1996)

The ternary complexes Δ-β_1-, Δ-β_2- *and* Λ-β_2-*[Co(S,R,R,S*-pychxn)(*S*-ala)]$^{2+}$ have been synthesised and characterised using electronic and CD spectroscopy and X-ray diffraction methods (*S,R,R,S*-pychxn = *N,N′*-di(2*S*-pyrrolidin-2-yl)-1*R*, 2*R*-diaminocyclohexane; S-alaH = *S*-alanine). A single-crystal X-ray structural study of the diperchlorate monohydrate salt of the Δ-β_1 diastereoisomer has been undertaken. The complex is orthorhombic, space group $P2_12_12_1$, with a = 9.607(3), b = 11.803(5) c = 23.936(7)Å, Z = 4. The structure was refined by full-matrix least-squares methods to R = 0.061 and R_w = 0.060 for 2648 reflections with $I > 3\sigma(I)$. Both nitrogen atoms of the coordinated pyrrolidyl groups adopt *S* configurations but the two internal nitrogen donors have opposite configurations, with that at the fold of the tetradendate being *R*. It is apparent that *S,R,R,S*-pychxn is not stereospecific in its coordination to octahedral transition metal ions, as has been previously claimed.

Keywords: cobalt(III); tetradentate; aminoacid; stereochemistry; X-ray structure

INTRODUCTION

We have been exploring for some time, stereochemical effects in metal complexes containing chiral tetradentate ligands.[1] In particular, our attention has focussed on Co(III) and Ru(II) complexes of picen-type ligands, especially those of *N,N′*-di(2-picolyl)-1*R*, 2*R*-diaminocyclohexane (*R,R*-picchxn). Complexes of this

---

* Part 47 is Ref. 1

† Authors for correspondence

class of ligand are, however, not particularly robust under basic reaction conditions because of the presence of the aromatic pyridine ring. Due to the need to control the stereochemistry of reactions of such complexes in base, we were prompted to examine complexes of analogous, fully saturated ligands. Accordingly, we have explored the stereospecificity of the ligands *N,N'*-di(2*S*-pyrrolidin-2-yl)-1*R*, 2*R*-diaminocyclohexane (*S,R,R,S*-pychxn) and its diastereoisomer based upon 1*S*, 2*S*-diaminocyclohexane (*S,S,S,S*-pychxn), with respect to ternary Co(III) complexes containing, *inter alia*, aminoacidate ligands. *S,R,R,S*-Pychxn has been previously reported[2] as being remarkably stereospecific in its coordination to Co(III). Here we report a study of ternary Co(III) complexes of *S,R,R,S*-pychxn with *S*-alanine (*S*-alaH) and the single crystal X-ray structure of the D-b_1 diastereoisomer as a structural key to a more extensive study of such complexes with other diaminoacidates.[3]

EXPERIMENTAL

Electronic and CD spectroscopic measurements were carried out using a Perkin Elmer Lamda 5 and a Jobin Yvon CNRS Dichrographe III instrument, respectively. ^{1}H NMR measurements were performed using a Bruker WM 360 spectrometer. Water analyses were obtained using a Stanton Redcroft TG750 thermogravimetric balance. 1*R*,2*R*-Diaminocyclohexane was resolved using Whitney's method[4] and used in the synthesis of *S,R,R,S*-pychxn according to the published procedure.[2] The ligand was not converted to the hydrochloride salt, but was used for subsequent syntheses as the neutral ligand (a pale yellow oil), which was pure, as judged by ^{1}H NMR measurements.

Trans-[Co(S,R,R,S-pychxn)Cl₂]ClO₄. $\frac{1}{2}H_2O$

The hemihydrate was synthesised in a slightly different manner to the reported monohydrate.[2] *S,R,R,S*-Pychxn (9.87 g, 35 mmol) and $CoCl_2.6H_2O$ (6.98 g, 29 mmol) were dissolved in water (150 cm^3). After aeration of the solution for 3 hours, its pH was found to be 8 and aeration was continued overnight. The red-brown reaction mixture was filtered and to it, in an evaporating basin, was added conc. HCl (3.0 cm^3) and conc. $HClO_4$ (6.0 cm^3). A thick brown oil separated out, and which redissolved upon warming on a steam bath. Whilst the volume of the solution was being reduced on the steam bath the oily film which formed was dispersed by stirring. When the solution had been reduced by half, it was removed from the steam bath and allowed to cool to room temperature. The green precipitate which formed was collected at the pump and washed sparingly with water, ethanol and diethyl ether until the filtrate was colourless. The solid was air dried. Yield: 4.43 g (29.4% based on Co). *Anal.* Calc. for $C_{16}H_{33}N_4Cl_3O_{4.5}Co$ (%): C, 37.0; H, 6.4; N, 10.8; H_2O, 1.6. Found: C, 37.3; H, 6.2; N, 10.3; H_2O, 1.0. Spectroscopic data, recorded in conc. HCl: $\varepsilon_{620} = 440$, $\varepsilon_{447} = 1657$ dm^2 mol^{-1} (maxima); $\Delta\varepsilon_{653} = -9.4$, $\Delta\varepsilon_{583} = +4.0$, $\Delta\varepsilon_{464} = +19.8$, $\Delta\varepsilon_{387} = +13.8$ dm^2 mol^{-1} (extrema). Recorded in methanol: $\varepsilon_{624} = 500$, $\varepsilon_{447} = 1547$ dm^2 mol^{-1} (maxima); $\Delta\varepsilon_{642} = -11.8$, $\Delta\varepsilon_{574} = +4.1$, $\Delta\varepsilon_{467} = +27.8$, $\Delta\varepsilon_{393} = +16.8$ dm^2 mol^{-1} (extrema).

Diastereoisomers of **[*Co*(S,R,R,S,-*pychxn*(S-*ala*)]$^{2+}$**

Trans-[Co(*S*,*R*,*R*,*S*-pychxn)Cl_2]ClO_4 · $\frac{1}{2}H_2O$ (0.254 g, 0.49 mmol) and $AgNO_3$ (0.166 g, 0.98 mmol) were dissolved in water (30 cm^3) with gentle heating. After 2 hours at room temperature, the precipitated AgCl was filtered off. Finely ground *S*-alaH (0.095 g, 1.07 mmol) was added to the filtrate with stirring. When all the solid had dissolved the pH of the solution was adjusted to 7.2 by dropwise addition of aqueous 1.0M NaOH. The solution was heated on a steam bath for 35 minutes and then allowed to cool. After standing at room temperature overnight it was applied to a column of CM-Sephadex C-25 exchange resin (30 × 1.5 cm) and washed with water. On eluting the Sephadex column with aqueous 0.2M NaCl, several bands developed. A fast-moving intense purple band (known to be a carbonato species) was followed, in turn, by two purple bands and one red band. The latter were each collected in fractions and their electronic and CD spectra recorded. In a second experiment following the same method, but with the pH of the solution adjusted to 7.0, the same bands were developed but more of the slowest moving isomer was present. The consistency of the CD spectra of the collected fractions showed that each band contained only one ternary species.

Δ-β_2-**[*Co*(S,R,R,S-*pychxn*)(S-*ala*)](*ClO*$_4$)$_2$**

Fractions from the first eluted purple band were combined, saturated aqueous $NaClO_4$ was added and the volume reduced initially using a rotary evaporator, then more slowly by evaporation over silica gel at room temperature. Red-purple crystals precipitated and these were collected at the pump and dried by rolling on filter paper. Yield = 0.064 g (10.6% based on Co). *Anal.* Calc. for $C_{19}H_{38}N_5O_{10}Cl_2Co$ (%): C, 36.4; H, 6.1; N, 11.2. Found: C, 36.2;H, 6.8; N, 9.9. Spectroscopic data (H_2O): $\varepsilon_{497} = 1452$, $\varepsilon_{361} = 1751$ dm^2 mol^{-1} (maxima); $\Delta\varepsilon_{554} = +3.1$, $\Delta\varepsilon_{483} = -14.6$, $\Delta\varepsilon_{356} = +6.6$ dm^2 mol^{-1} (extrema).

Δ-β_1-[*Co*(S,R,R,S-*pychxn*)(S-*ala*)](*ClO*$_4$)$_2$.*H*$_2$*O*

This complex was isolated from the combined fractions of the second eluted purple band mentioned above. Evaporation of solutions containing $NaClO_4$ gave red-purple plates which were collected at the pump and air dried after washing with a minimum amount of water. Yield: 0.099 g (15.4% based on Co). After a week, a second crop, yield = 0.011 g (1.7%), was collected in the same way. Spectroscopic data (H_2O): ε_{517} = 1976, ε_{367} = 1561 dm^2 mol^{-1} (maxima); $\Delta\varepsilon_{552}$ = −6.1, $\Delta\varepsilon_{503}$ = +2.0, $\Delta\varepsilon_{401}$ = −2.5, $\Delta\varepsilon_{357}$ = +2.4 dm^2 mol^{-1} (extrema).

Λ-β_2-[*Co*(S,R,R,S-*pychxn*)(S-*ala*)](*ClO*$_4$)$_2$.*nNaClO*$_4$.*mH*$_2$*O* (*n* = *1*, *m* = *2.5* and *n* = *2*, *m* = *8*)

These salts were isolated from the slowest moving red band to elute from the column as described above. Combined fractions were concentrated at room temperature in the presence of excess aqueous $NaClO_4$ to yield fine, feathery, red-purple needles. These were collected at the pump, washed with a minimum of ice-cold water and air dried. Yield: 0.51 g (64% based on Co). The salt proved to be a *mono* sodium perchlorate adduct containing 2.5 molecules of water of crystallization (n = 1, m = 2.5). *Anal.* Calc. for $C_{19}H_{43}N_5O_{16.5}Cl_3NaCo$ (%): C, 28.7; H, 5.4; N, 8.8; H_2O, 5.7. Found: C, 28.7; H, 5.3; N, 9.1; H_2O, 5.5. Spectroscopic data (H_2O): ε_{500} = 1915, ε_{359} = 2148 dm^2 mol^{-1} (maxima); $\Delta\varepsilon_{503}$ = +25.2, $\Delta\varepsilon_{352}$ = +1.1 dm^2 mol^{-1} (extrema).

On concentrating the filtrate from the above, a second crop of feathery red needles was obtained. Yield: 0.027 g (2.7% based on Co). analysis indicated this product was a *di*-sodium perchlorate adduct containing eight waters of crystallization (n = 2, m = 8). *Anal.* Calc. for $C_{19}H_{54}N_5O_{26}Cl_4Na_2Co$ (%): C, 22.5; H, 5.4; N, 6.9; H_2O, 14.2. Found: C, 22.5; H, 4.7; N, 6.9; H_2O, 14.6. Spectroscopic data for this salt are identical to those of the mono adduct given above.

Crystal and Molecular Structure of Δ-β_1-[*Co*(S,R,R,S-*pychxn*)(S-*ala*)](*ClO*$_4$)$_2$.*H*$_2$*O*

Crystal Data: $C_{19}H_{40}N_5O_{11}Cl_2Co$, M_r = 644.40, orthorhombic, a = 9.607(3), b = 11.803(5), c = 23.936(7) Å, U = 2714.0 Å^3, Z = 4, D_c = 1.577 g cm^{-3}, $F(000)$ = 1288, m(Mo-Kα) = 8.9 cm^{-1}, space group $P2_12_12_1$ (No. 19).

Data for the complex were collected at −135°C on a Nicolet XRD-P3 four-circle diffractometer[5] using Mo*K*α radiation. Accurate cell parameters were obtained from a least-squares fit to diffractometer data. Intensities were measured in the range $5.0 < 2\Theta < 52.0°$ and of the 3028 reflections recorded 2648 had $I > 3\sigma(I)$ and these were used for the structure determination. The intensities were corrected for Lorentz, polarisation and absorption effects, the latter using an empirical method in which T_{max}, T_{min} and μR were 0.578, 0.524 and 0.200, respectively.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares methods. Difference maps revealed disorder in the oxygen atoms of the perchlorate ion involving atom Cl(1). Seven O atom positions were apparent and these define two ClO_4 orientations whose peak heights indicated one common O atom and two sets of three O atoms with approximate occupancies of 0.66 and 0.34. Further difference maps revealed all hydrogen atom positions, which were optimised assuming C,N-H 1.0 Å and O-H 0.9 Å. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms excluding the O atoms with partial occupancy. The weight for each reflection was $w = (1.0 + \sigma^2(F))^{-1}$. Refinement was terminated when the maximum shift in any parameter was < 0.1 σ. The final values for R and $R_w\{=(\Sigma w(F_o\text{-}F_c)^2/\Sigma wF_o^2)^{0.5}\}$ were 0.061 and 0.060, respectively, and with $\eta = 1.15(9)$ confirming the correct configurations of the chiral centres. A final difference map showed no unusual features with all electron density maxima $<|0.9|eÅ^{-3}$. Calculations were carried out on a FACOM M350S computer using programs written by F.S.S. Neutral atom scattering factors, corrected for anomalous dispersion were taken from *International Tables for X-ray Crystallography*.[6]

RESULTS AND DISCUSSION

In terms of the isomers isolated for ternary Co(III) complexes of *S,R,R,S*-pychxn with *S*-alanine the tetradentate can hardly be claimed to be stereospecific in its coordination. Three diasteroisomers have been isolated and characterised. It has proved possible to distinguish β_1 from β_2 isomers by means of characteristic spectroscopic features. These features are not merely confined to the ternary complexes reported here, but are observed for several scores of related Co(III) complexes comprising an aminoacidate ligand and an aliphatic, linear, nitrogenous tetradentate.[7-10] All of the aminoacidate complexes synthesised possess the two usual absorption bands in the visible region of their electronic spectrum. These absorption bands have ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ parentage (*Oh* symmetry) and appear at longer and shorter wavelengths, respectively.[11] In the visible region, for complexes having β_1 geometry, the extinction coefficient of the longer wavelength component (*ca* 500 nm) is invariably greater than that of the shorter wavelength component (*ca* 350 nm). The reverse is true (*i.e.*,

$\varepsilon_{350} > \varepsilon_{500}$) for complexes having the β_2 geometry. No exception is known in the literature for complexes which have been structurally characterised.[12–13] It should of course be noted that all of the alaninato complexes reported here have C_1 symmetry. However, the non-degenerate transitions which comprise the two visible absorption bands are not resolved in the electronic spectrum of any of the isomers.

The complex isolated from the fastest moving band on the column has a complex CD spectrum, with the lowest energy visible transition being positive in sign, but with the $^1A_{1g} \rightarrow {}^1T_{1g}$ envelope being dominated by a strongly negative transition. In this, the CD spectrum is very similar, albeit of opposite sign to those of ternary Λ - β_2 complexes[1,7,14] of aminoacidates and *R*, *R*-picchxn, which have been structurally characterized. Absolute configurations of the next bands eluted from the columns are easily assigned on the basis of CD spectra and confirmed in the case of the Δ-β_1 diastereoisomer by an X-ray structure determination.

Structure of $\Delta\beta_I$-[Co(S,R,R,S-pychxn)(S-ala)]$(ClO_4)_2.H_2O$

Final atomic coordinates for the non-hydrogen atoms are given in Table I and selected bond distances and angles in Table II. No usual geometric features are noted for the complex cation, a view of which is shown in Figure 1. A network of hydrogen bonds links it with the perchlorate groups and the water molecule of crystallization. No significant non-bonded contacts are noted in the lattice (Table III).

TABLE I Final Atomic Coordinates (fractional $\times 10^4$) for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses for Δ-β_I-[Co(*S*,*R*,*R*,*S*-pychxn) (*S*-ala)] $(ClO_4)_2 \cdot H_2O$

	x/a	*y/b*	*z/c*	*B**
Co	1820.5(11)	897.5(9)	975.1(4)	1.2
N(1)	3387(7)	108(5)	1321(2)	1.6
N(2)	1030(7)	–616(5)	831(2)	1.5
N(11)	2866(7)	2313(5)	1185(2)	1.3
N(21)	593(7)	896(7)	1655(3)	2.0
N(3)	2777(6)	912(6)	245(2)	1.2
O(31)	336(6)	1595(5)	581(2)	1.6
O(32)	–344(6)	2182(5)	–255(2)	2.2
C(31)	552(9)	1819(7)	53(3)	1.6
C(32)	2033(9)	1684(7)	–146(3)	1.5
C(33)	2140(9)	1277(8)	–748(3)	2.2
C(11)	2296(9)	3277(7)	1524(3)	2.0
C(12)	3594(9)	3883(7)	1711(3)	1.8
C(13)	4548(9)	2924(7)	1894(3)	1.9
C(14)	4243(9)	1973(7)	1476(3)	1.4
C(15)	4036(8)	810(7)	1751(3)	1.5
C(1)	2942(9)	–1054(7)	1496(3)	1.9

TABLE I *(Continued)*

	x/a	*y/b*	*z/c*	B^*
C(2)	2062(9)	−1501(7)	1021(4)	2.2
C(3)	1418(10)	−2652(8)	1194(4)	2.7
C(4)	2612(12)	−3480(8)	1316(4)	3.5
C(5)	3583(12)	−3030(7)	1768(4)	3.7
C(6)	4165(10)	−1847(7)	1616(4)	2.4
C(21)	−470(9)	1854(8)	1708(4)	2.1
C(22)	−1899(10)	1315(8)	1684(4)	2.7
C(23)	−1665(11)	156(9)	1937(3)	3.2
C(24)	−246 (1)	−204(8)	1692(4)	2.4
C(25)	−363(9)	−661 (7)	1103(3)	2.1
Cl(1)	1874(3)	821(2)	3152(1)	3.0
O(1a)	1666(10)	1747(6)	2780(3)	4.2
O(1b)	3168(15)	237(11)	3068(5)	4.9(3)
O(1c)	1777(14)	1258(10)	3709(5)	4.2(2)
O(1d)	698(19)	90(15)	3072(7)	8.1(4)
O(1e)	1960(29)	−216(20)	2813(9)	4.8(5)
O(1f)	1012 (25)	704(20)	3613(9)	4.3(5)
O(1g)	3413(29)	814(25)	3297(11)	5.7(6)
Cl(2)	3826(3)	4666(2)	4867(1)	2.6
O(2a)	3955(8)	5229(6)	4333(3)	3.8
O(2b)	5117(8)	3982(8)	4919(4)	5.8
O(2c)	2680(9)	3900(8)	4886(3)	5.6
O(2d)	3884(14)	5400(7)	5301(3)	8.5
O(w)	3469(13)	1420(6)	4687(3)	6.3

$^*B_{iso}$ with estimated standard deviations in parentheses or B_{eq}.

TABLE II Bond Lengths and Angles with Estimated Standard Deviations in Parentheses for Δ-β_1-[Co(*S,R,R,S*-pychxn) (*S*-ala)] $(ClO_4)_2 \cdot H_2O$

a) Distances (Å)

Co N(11)	2.013(6)	Co—N(21)	2.009(6)
Co—N(1)	1.953(7)	Co—N(2)	1.971(6)
Co—N(3)	1.974(6)	Co—O(31)	1.898(5)
C(32)—N(3)	1.489(9)	C(31)—O(31)	1.308(9)
C(32)—C(31)	1.510(11)	C(31)—O(32)	1.211(9)
C(32)—C(33)	1.522(10)		
C(1)—C(2)	1.511(11)	C(4)—C(5)	1.523(13)
C(2)—C(3)	1.549(11)	C(5)—C(6)	1.547(12)
C(3)—C(4)	1.535(14)	C(6)—C(1)	1.529(12)
		n = 1	n = 2
	N(n1)—C(n1)	1.502(10)	1.528(11)
	N(n1)—C(n4)	1.548(10)	1.532(12)
	C(n1)—C(n2)	1.505(11)	1.515(13)
	C(n2)—C(n3)	1.520(11)	1.512(13)
	C(n3)—C(n4)	1.531(11)	1.543(13)
	C(n4)—C(n5)	1.534(11)	1.513(12)
	N(n)—C(n5)	1.461(10)	1.489(10)
	N(n)—C(n)	1.496(10)	1.510(10)
	Cl(n)—O(na)	1.423(6)	1.446(6)
	Cl(n)—O(nb)	1.436(14)	1.485(9)
	Cl(n)—O(nc)	1.431(11)	1.425(8)
	Cl(n)—O(nd)	1.434(18)	1.354(8)
	Cl(n)—O(ne)	1.470(23)	

TABLE II (*Continued*)

a) Distances (Å)			
Cl(n)—O(nf)	1.386(22)		
Cl(n)—O(ng)	1.519(28)		
b) Angles (°)			
N(11)—Co—N(1)	84.6(3)	N(21)—Co—N(2)	85.1(3)
N(1)—Co—N(2)	86.5(3)	O(31)—Co—N(3)	84.6(2)
N(2)—Co—N(11)	171.0(3)	N(1)—Co—O(31)	175.0(2)
N(3)—Co—N(21)	171.8(3)		
N(11)—Co—N(21)	95.2(3)	N(21)—Co—O(31)	87.8(2)
N(11)—Co—N(3)	88.9(3)	N(1)—Co—N(3)	91.1(2)
N(11)—Co—O(31)	98.0(2)	N(2)—Co—N(3)	91.9(3)
N(21)—Co—N(1)	96.2(3)	N(2)—Co—O(31)	90.9(2)
Co—N(3)—C(32)	109.8(4)	Co—O(31)—C(31)	116.7(5)
N(3)—C(32)—C(31)	108.6(6)	O(31)—C(31)—O(32)	123.2(7)
N(3)—C(32)—C(33)	111.8(6)	O(31)—C(31)—C(32)	115.6(7)
C(31)—C(32)—C(33)	113.3(7)	O(32)—C(31)—C(32)	121.0(7)
		n = 1	n = 2
Co—N(n1) —C(n1)		125.6(5)	117.3(5)
Co—N(n1) —C(n4)		108.9(4)	110.9(5)
C(n1)—N(n1)—C(n4)		105.4(6)	105.7(6)
N(n1)—C(n1)—C(n2)		102.6(6)	107.0(7)
C(n1)—C(n2)—C(n3)		103.4(6)	103.3(8)
C(n2)—C(n3)—C(n4)		104.1(6)	103.2(8)
C(n3)—C(n4)—N(n1)		105.5(6)	104.7(7)
C(n3)—C(n4)—C(n5)		113.6(6)	112.7(7)
N(n1)—C(n4)—C(n5)		108.3(6)	106.7(6)
N(n)—C(n5)—C(n4)		105.1(6)	109.1(7)
Co—N(n)—C(n)		109.6(5)	108.7(5)
Co—N(n)—C(n5)		110.9(5)	107.3(5)
C(n)—N(n)—C(n5)		116.4(6)	115.7(6)
N(1)—C(1)—C(2)	105.6(6)	N(2)—C(2)—C(1)	110.6(6)
N(1)—C(1)—C(6)	113.2(7)	N(2)—C(2)—C(3)	115.2(7)
C(2)—C(1)—C(6)	110.9(7)	C(1)—C(2)—C(3)	109.2(7)
C(1)—C(6)—C(5)	108.6(8)	C(2)—C(3)—C(4)	108.1(7)
C(6)—C(5)—C(4)	111.7(7)	C(3)—C(4)—C(5)	111.8(9)
O(1a)—Cl(1)—O(1b)	113.7(6)	O(1a)—Cl(1)—O(1e)	107.6(9)
O(1a)—Cl(1)—O(1c)	107.2(5)	O(1a)—Cl(1)—O(1f)	119.4(10)
O(1a)—Cl(1)—O(1d)	105.6(8)	O(1a)—Cl(1)—O(1g)	106.5(11)
O(1b)—Cl(1)—O(1c)	111.0(7)	O(1e)—Cl(1)—O(1f)	112.9(14)
O(1b)—Cl(1)—O(1d)	112.0(8)	O(1e)—Cl(1)—O(1g)	98.8(15)
O(1c)—Cl(1)—O(1d)	106.8(9)	O(1f)—Cl(1)—O(1g)	113.5(14)
O(2a)—Cl(2)—O(2b)	104.6(5)	O(2b)—Cl(2)—O(2c)	107.3(5)
O(2a)—C1(2)—O(2c)	112.7(5)	O(2b)—Cl(2)—O(2d)	104.4(7)
O(2a)—Cl(2)—O(2d)	112.4(5)	O(2c)—Cl(2)—O(2d)	114.4(6)

TABLE III Intermolecular Contacts (Å) with Estimated Standard Deviations in Parentheses for Δ-β_I-[*Co(S,R,R,S*-pychxn) (*S*-ala)]$(ClO_4)_2 \cdot H_2O$

*a) Proposed hydrogen bonding**			
N(11)....O(32^{I})	2.875(8)	N(3)H(a) ....O(32^{I})	2.885(9)
N(21)....O(1a)	3.054(9)	N(3)H(b) ....O($2b^{\mathrm{II}}$)	3.072(11)
N(1)....O($2a^{\mathrm{II}}$)	2.999(10)	O(w)H(a) ....O(1c)	2.857(15)
N(2)....O(w^{III})	2.939(9)	O(w)H(b) ....O(2c)	3.062(12)

TABLE III (*Continued*)

b) Contacts <3.4 Å*

O(32)....C(32^{IV})	3.00(1)	0(2) ....C(w^{III})	3.34(1)
C(3)....O($1f^{V}$)	3.07(3)	C(21) ....O(1a)	3.29(1)
O(32)....C(14^{IV})	3.11(1)	N(3) ....O(w^{III})	3.29(1)
C(5)....O($1g^{II}$)	3.20(3)	C(25) ....O($2C^{V}$)	3.29(1)

*Roman numeral superscripts refer to the following equivalent positions relative to x, y, z: I $\frac{1}{2}+x$, $\frac{1}{2}-y$, $-z$; II $1-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$; III $\frac{1}{2}-x$, $-y$, $z-\frac{1}{2}$; IV $x-\frac{1}{2}$, $\frac{1}{2}-y$, $-z$; V $-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$.

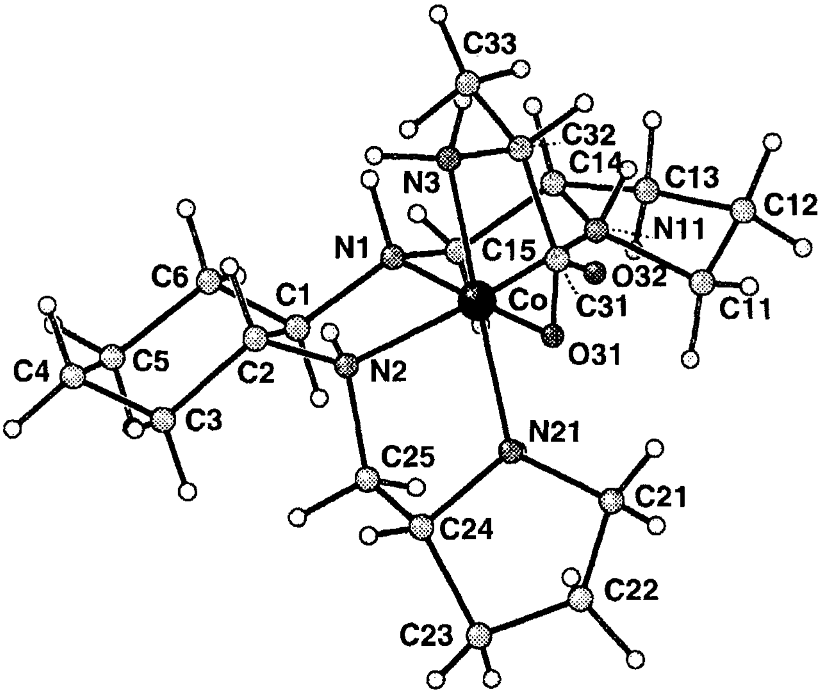

FIGURE 1 Perspective view of the complex cation Δ-β_1-[Co(*S*,*R*,*R*,*S*)-pychxn)(*S*-ala)]$^{2+}$ showing the atom labelling scheme.

The cobalt atom absolute configuration is Δ as described and the *S*-alaninato ligand is coordinated to give the β_1 isomer. Other stereochemical centres in the molecule refer to the four coordinated secondary nitrogen atoms of the tetradentate. Both pyrrolidyl nitrogens have absolute configuration *S*, as does the nitrogen atom N(2) in the fold of the tetradentate. The other internal nitrogen atom N(1) has absolute configuration *R*. There is no obvious reason for the adoption of this particular stereochemistry in this diastereoisomer. It contrasts with the known α isomers in which the geometries of the internal donor atoms of the tetradentate are fixed, and also with the known Λ-β isomers of *S*,*R*,*R*,*S*-pychxn. In the latter, molecular models reveal that the four donor N atoms are constrained to adopt the *S* configuration, in agreement with the proposal of Kitagawa *et al.*[15] for analogous Ni(II) species.

Both Λ-β_1 and Λ-β_2 diastereoisomers have been isolated and identified. On the other hand, only the β_2 complex of absolute configuration Δ was able to be obtained. Again, no obvious reasons exist for the absence of the β_1 disastereoisomer. Nevertheless, while the choice between β_1 and β_2 forms may be subtle in nature, it is clearly established that the S,R,R,S-pychxn ligand is not enantiospecific in its coordination in that b isomers of both Δ and Λ configuration can be isolated in ternary complexes. Moreover, neither does the ligand specifically adopt a *cis* configuration, as evidenced by the fact that the dichloro precursor complex was isolated in the trans form. We note in passing that the CD spectra of the trans complex that we have isolated, obtained in methanol, is similar to that reported previously.[2] However, the spectrum of the dichloro complex in methanol differs significantly from that obtained in conc. HCl. In any event, Jun and Liu[2] isolated both *trans* and Λ–β forms of the dichloro complex, again demonstrating the stereochemical flexibility of this tetradentate ligand.

Acknowledgments

The authors wish to thank the Australian Research Council for financial support, and the Science & Engineering Research Council (U.K.) for a scholarship to M.A.C.

References

[1] P. Leverett, J. Petherick, P.A. Williams and R.S. Vagg, *J. Coord. Chem.*, **37**, 195 and refs. therein (1996).

[2] M.-J. Jun and C.F. Liu, *Inorg. Chim. Acta*, **15**, 111 (1975).

[3] M.A. Cox, R.S. Vagg and P.A. Williams, unpublished results.

[4] T.A. Whitney, *J. Org. Chem.*, **45**, 4214 (1980).

[5] G.M. Sheldrick, *SHELXTL User Manual*, Revision 3, (Nicolet XRD Corporation, Cupertino, CA, 1981).

[6] *International Tables for X-ray Crystallography*, Vol 4, (Kynoch Press, Birmingham, UK, 1974), pp. 72–78 and 149.

[7] T.J. Goodwin, R.S. Vagg and P.A. Williams, *J. Proc. Roy. Soc. New South Wales*, **117**, 1 (1984).

[8] C.Y. Lin and B.E. Douglas, *Inorg. Chim. Acta*, **4**, 3 (1970).

[9] R.C. Job and T.C. Bruice, *J. Am. Chem. Soc.*, **96**, 809 (1974).

[10] M. Yamaguchi, S. Yamamatsu, T. Furusawa, S. Yano, M. Saburi and S. Yoshikawa, *Inorg. Chem.*, **19**, 2010 (1980).

[11] B. Bosnich, *Proc. Roy. Soc., Ser. A.*, **297**, 88 (1967).

[12] M. Yamaguchi, S. Yano, M. Saburi and S. Yoshikawa, *Inorg. Chem.*, **19**, 2016 (1980).

[13] M. Yashiro, M. Ajoika, S. Yano, K. Toriumi, T. Ito and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **59**, 2255 (1986).

[14] M.A. Cox, T.J. Goodwin, P. Jones, P.A. Williams, F.S. Stephens and R.S. Vagg, *Inorg. Chim. Acta*, **127**, 49 (1987).
[15] S. Kitagawa, T. Murakami and M. Hatamo, *Inorg. Chem.*, **14**, 2347 (1975).

SUPPLEMENTARY MATERIAL

Full lists of observed and calculated structure factors, bond lengths and angles, H atom positions and anisotropic thermal parameters are available from the authors upon request.