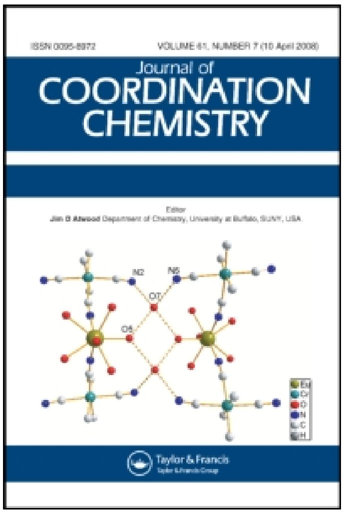

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CHIRAL METAL COMPLEXES. 49. STRUCTURAL STUDIES OF TERNARY Co(III) COMPLEXES OF *N,N'*-DI (2*S*-PYRROLIDIN-2-YL)-1*S*, 2*S*-DIAMINOCYCLOHEXANE AND α-AMINOACIDS

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CHIRAL METAL COMPLEXES. 49*. STRUCTURAL STUDIES OF TERNARY Co(III) COMPLEXES OF *N,N'*-DI (2*S*-PYRROLIDIN-2-YL)-1*S*, 2*S*-DIAMINOCYCLOHEXANE AND α-AMINOACIDS

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Ternary complexes of the type Δ-$\beta_{1,2}$-[Co(*S,S,S,S,*-pychxn)(aa)]$^{2+}$ where S,S,S,S-pychxn is *N,N'*-di(2*S*-pyrrolidin-2-yl)-1*S*,2*S*-diaminocyclohexane and aa is an aminoacidate (glyH = glycine, alaH = alanine) have been synthesized and structurally characterized. Δ-β_1-[Co(*S,S,S,S*-pychxn)-(gly)]$(ClO_4)_2.2H_2O$ is orthorhombic, space group $P2_12_12_1$, with a = 10.133(2), b = 14.418(2), c = 19.646(5) Å and Z = 4. The structure was refined to R = 0.065 and R_w = 0.072 for 2224 reflections with I >3σ(*I*). Δ-β_2-[Co(*S,S,S,S*-pychxn) (*R*-ala)]$(ClO_4)_2.2H_2O$ is orthorhombic, space group $P2_12_12_1$, with a = 10.933(4), b = 13.667(2), c = 18.853(3) Å, and Z = 4. This structure was refined to R = 0.040 and R_w = 0.033 for 2221 reflections with $I > 3\sigma$(I). Both complex structures are analogous in that the coordination of the tetradentate is identical with both nitrogen atoms of coordinated pyrrolidyl groups adopting *S* absolute configurations; the two internal nitrogen atoms have opposite configurations with that at the fold of the tetradentate being *R*. While S,S,S,S-pychxn is not absolutely stereospecific with respect to its coordination with Co(III) it is markedly more so than its congener *S,R,R,S*,-pychxn. The structural study benchmarks stereochemistries adopted by this class of compound with respect to further studies.

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

INTRODUCTION

We have recently reported[1] studies of ternary complexes of *N,N'*-di(2S-pyrrolidin-2-yl)-1*R*, 2*R*-diaminocyclohexane (*S,R,R,S*-pychxn) and *S*-alanine (*S*-alaH) with

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Co(III). It had been reported[2] that the tetradentate *S,R,R,S*-pychxn was quite stereospecific with respect to its complexes with Co(III),[2] but it is now apparent that it can achieve a diverse range of stereochemstries with that ion. Kitagawa *et al.*[3] prepared *S,R,R,S*-pychxn and its diastereoisomer based upon 1*S*, 2*S*-diaminocyclohexane, *S,S,S,S*-pychxn, and studied the formation of their complexes with Ni(II). In setting out a number of stereochemical constraints which applied to the ligands (and other related species), they concluded that the stereochemstries of subsequent ternary complexes formed with diamines and aminoacidates remained unclear.

Here we provide structural benchmarks for an extensive study of such ternary complexes involving Co(III). In particular, we report the crystal and molecular structures of the complex salts Δ-β_1-[Co(*S,S,S,S*-pychxn)(gly)]$(ClO_4)_2.2H_2O$ (glyH = glycine) and Δ-β_2-[Co(*S,S,S,S*-pychxn)(*R*-ala)]$(ClO_4)_2.2H_2O$ (*R*-alaH = *R*-alanine). We further comment on the nature of the stereoselectivity that exists in this class of complexes.

EXPERIMENTAL

Electronic and CD spectroscopic measurements were carried out using a Perkin Elmer Lamda 5 and a Jobin Yvon CNRS Dichrographe III, respectively. Water analyses were obtained using a Stanton Redcroft TG750 thermogravimetric balance. 1*S*, 2*S*-Diaminocyclohexane was resolved using Whitney's method,[4] but by substituting *S,S*-tartaric acid, and used to synthesise *S,S,S,S*,-pychxn using a published procedure.[2] The free ligand was not converted to the hydrochloride salt prior to use in subsequent syntheses.

Δ-[*Co(*S,S,S,S*-pychxn)Cl*$_2$]. $\frac{1}{2}$*CoCl*$_4$

S,S,S,S-Pychxn (13.8 g, 49 mmol) and $CoCl_2.6H_2O$ (11.9 g, 50 mmol) were dissolved in water (200 cm^3) and reacted following the method employed previously for the *S,R,R,S*,-ligand.[1] The purple precipitate obtained was filtered off and triturated on the frit with methanol and then diethylether. The purple solid was air dried. Yield = 4.85 g (19% based on Co). The electronic spectrum indicated the presence of $[CoCl_4]^{2-}$ in this *cis*-complex. *Anal.* Calc. for $C_{16}H_{32}N_4Cl_4Co_{1.5}$ (%): C, 37.6; H, 6.3; N, 11.0. Found: C, 37.4; H, 6.5; N, 11.0. Spectroscopic data, recorded in conc. HCl: ε_{511} = 1587 dm^2 mol^{-1} (maximum); at longer wavelengths the electronic spectrum of the $[CoCl_4]^{2-}$ ion is predominant; $\Delta\varepsilon_{657} = -10.5$, $\Delta\varepsilon_{591} = +33.3$, $\Delta\varepsilon_{510} = -65.5$, $\Delta\varepsilon_{383} = +8.3$ dm^2 mol^{-1} (extrema).

Addition of diethylether (200 cm^3) to the combined methanolic washings caused the precipitation of green crystals of *trans*-[Co(*S,S,S,S*-pychxn)Cl$_2$] ClO$_4$.2CH$_3$OH overnight. These were collected at the pump, washed sparingly with ice cold water, diethylether and air dried. Yield = 1.19 g (4.1% based on Co). *Anal.* Calc. for C$_{18}$H$_{40}$N$_4$Cl$_3$O$_6$Co (%): C, 37.7; H, 7.0; N, 9.8. Found: C, 37.8; H, 6.7; N, 9.4. Spectroscopic data, recorded in conc. HCl: $\varepsilon_{635} = 709$, $\varepsilon_{450} = 1784$ dm^2 mol^{-1} (maxima); $\Delta\varepsilon_{678} = +5.0$, $\Delta\varepsilon_{607} = -12.9$, $\Delta\varepsilon_{453} = +9.0$, $\Delta\varepsilon_{397} = -6.1$ dm^2 mol^{-1} (extrema).

***Trans*-[*Co*(S,S,S,S-*pychxn*)*Cl*$_2$]*ClO*$_4$**

Cis-[Co(*S,S,S,S*-pychxn)Cl$_2$]. $\frac{1}{2}$CoCl$_4$ was converted to the anhydrous perchlorate salt of the *trans* isomer in the following way. The *cis* isomer (2.85 g) was dissolved in conc. HCl (35 cm^3) and conc. HClO$_4$ (0.5 cm^3) added. The green solution was reduced to 10 cm^3 on a stream bath and allowed to cool. The green solid was collected at the pump and tritrated with small quantities of H$_2$O until the filtrate changed colour from brown to pale green. The green solid was washed with diethylether and air dried. Yield = 2.14 g (85%). *Anal.* Calc. for C$_{16}$H$_{32}$N$_4$Cl$_3$O$_4$CO(%): C, 37.7; H, 6.3; N, 11.0. Found: C, 37.8; H, 6.4; N, 10.8. The complex was confirmed to be anhydrous by thermogravimetric analysis.

Trans*-[*Co*(S,S,S,S-*pychxn*)*Cl*$_2$]*Cl

To a cooled solution of *S,S,S,S*-pychxn (4.50 g, 16 mmol) in water (25 cm^3), containing conc. HCl (4.2 cm^3, 49 mmol), was added a suspension of Na$_3$[Co(CO$_3$)$_3$].3H$_2$O[5] (5.87 g, 18 mmol) in H$_2$O (30 cm^3). The mixture was heated on a steam bath for 10 minutes to yield a deep red-purple solution. This was transferred to an evaporating basin and conc. HCl (4.7 cm^3) added. The solution was heated further on a water bath until a precipitate started to form. After cooling, the turquoise-green solid product was filtered off, washed with water, then methanol, and air dried. The solid is insoluble in these solvents. Yield = 3.36 g (41% based on pychxn). *Anal.* Calc. for C$_{16}$H$_{32}$N$_4$Cl$_3$Co (%): C, 43.1; H, 7.2; N, 12.6. Found: C, 43.2; H, 7.3; N, 12.5.

Δ-β_1-[*Co*(S,S,S,S-*pychxn*)(*gly*)](*ClO*$_4$)$_2$.*2H*$_2$*O*

Trans-[Co(*S,S,S,S*-pychxn)Cl$_2$]ClO$_4$.2CH$_3$OH (0.86 g, 1.5 mmol) and AgNO$_3$ (0.51 g, 3.0 mmol) were mixed together in water (50 cm^3) and heated on a steam bath for 1.5 hours. AgCl(s) was filtered off and glycine (glyH, 0.56 g, 7.5 mmol) and aqueous 1.0M NaOH (1.5 cm^3) were added. The reaction mixture was heated on a steam bath for 3 hours and cooled to room temperature. The red solution was filtered, diluted to 250 cm^3 with water and applied to a CM-Sephadex C-25 cation exchange column (40 × 1.5 cm). After washing with water, the column was eluted with aqueous 0.1M $NaClO_4$. Two bands developed, a fast moving, faint purple one (known to be a carbonato species) and an intense deep red band. The deep red band was collected in fractions and the title complex isolated in the usual manner from those fractions at the tail of the band which had constant ΔA/A values. Yield = 0.177 g (18%). Spectroscopic data (H_2O): ε_{516} = 2341, ε_{362} = 1566 dm^2mol^{-1} (maxima); $\Delta\varepsilon_{538}$ = -15.4, $\Delta\varepsilon_{484}$ = +6.6, $\Delta\varepsilon_{399}$ = –6.2 dm^2 mol^{-1} (extrema). The formula of this compound was confirmed by the X-ray analysis reported herein.

Δ-β_2-[*Co*(S,S,S,S-*pychxn*)(*gly*)](*ClO*$_4$)$_2$.2*H*$_2$*O*

The above experiment was repeated using five times the quantities of reactants and the reaction mixture applied to a cation exchange column (100 × 1.5 cm). On elution with aqueous 0.1M $NaClO_4$ two bands developed, an intense, deep red band followed by a faint purple one; these were collected in fractions. Electronic and CD spectroscopic measurements indicated that the deep red band consisted of only *one* isomer. The band was split into four successive fractions to facilitate easier handling during the isolation of the compound. The named isomer precipitated as very fine, pink-red, acicular crystals, from all fractions. Yield (overall) = 1.24 g (25%). *Anal.* Calc. for $C_{18}H_{40}N_5O_{12}Cl_2Co$ (%): C, 33.3; H, 6.2; N, 10.8. Found: C, 33.5; H, 5.9; N, 10.7. Spectroscopic data (H_2O): ε_{495} = 1573, ε_{360} = 1836 dm^2 mol^{-1} (maxima); $\Delta\varepsilon_{509}$ = -20.8, $\Delta\varepsilon_{356}$ = +3.6 dm^2 mol^{-1} (extrema). The fractions containing the faint purple band were treated in a similar manner and precipitated a fine microcrystalline powder. Yield = 0.012g. The solid was characterised as the Δ–β_1 isomer by comparison of its electronic and CD spectra with the previously isolated Δ–β_1 complex.

Δ-β_2-[*Co*(S,S,S,S-*pychxn*)(R-*ala*)](*ClO*$_4$)$_2$. 2*H*$_2$*O*

Trans-[Co(*S,S,S,S*-pychxn)Cl_2]Cl (0.448 g, 1.0 mmol) and $AgNO_3$ (0.512 g, 3.0 mmol) were mixed together in water (75 cm^3) and heated on a steam bath for 1.5 hours. AgCl was filtered off and *R*-alaH (0.445 g, 5.0 mmol) added to the cherry-red filtrate. When it had dissolved, 1.0 M aqueous NaOH (1.0 cm^3) was added with stirring. The solution was heated on a steam bath for 25 hours and then cooled to room temperature. The red solution was diluted three-fold with water and applied to a CM-Sephedex C-25 cation exchange column (40 × 1.5cm). After washing with water, the column was eluted with aqueous 0.1 M $NaClO_4$

solution. During elution, two bands developed, a faint, fast moving, purple one (carbonato species) and an intense, deep red band. The latter was collected in fractions and the electronic and CD spectrum of each fraction recorded. A plot of ΔA/A showed negligible differences throughout the band which was split into three for isolation. Fractions in each group were combined and the volume reduced on a rotary evaporator. The solutions were then concentrated over silica gel at room temperature when deep-red, equant prisms were formed. These were collected at the pump, washed sparingly with water, then diethylether, and air dried. The nature of the complex was established by X-ray diffraction methods (*vide infra*). Spectroscopic data (H_2O): ε_{494} = 1442, ε_{361} = 1675 dm^2 mol^{-1} (maxima); $\Delta\varepsilon_{513}$ = –22.1, $\Delta\varepsilon_{455}$ = +4.3, $\Delta\varepsilon_{385}$ = –2.3, $\Delta\varepsilon_{351}$ = -2.3 dm^2 mol^{-1} (extrema).

Crystal and Molecular Structure of Δ-β_1-[*Co(*S,S,S,S-*pychxn)(gly)*]*$(ClO_4)_2.2H_2O$*

Crystal Data: $C_{18}H_{40}N_5O_{11}Cl_2Co$; M_r = 648.38; orthorhombic, a = 10.133(2), b = 14.418(2), c = 19.646(5) Å; U = 2870.2 Å^3; Z = 4; D_c = 1.500 g cm^{-3}; $F(000)$ = 1360; μ(Mo-Kα) = 8.7 cm^{-1}; space group $P2_12_12_1$ (No. 19).

Data for the complex were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using MoKα radiation. Accurate cell parameters were obtained from a least-squares fit to diffractometer data. The data collection was performed with a and c interchanged and the re-indexing took the form l, k, $-h$ to maintain correct chirality. Intensities were measured in the range $3.0 < 2\Theta < 50.0°$ and of the 2648 reflections recorded 2224 had $I > 3\sigma(I)$ and these were used for the structure analysis. The intensities were corrected for Lorentz, polarisation and absorption effects, the latter using an empirical method. Minimum, maximum and average transmission factors were 0.940, 0.999 and 0.963, respectively.

The structure was solved by the heavy atom method and refined by full-matrix least-squares methods. Difference maps indicated disorder in one pyrrolidine ring and two positions are indicated for atom C(22); for one perchlorate ion two chlorine and six oxygen sites are apparent; the lattice water molecules are distributed over three sites. For atom C(22) and the chlorine atoms Cl(2) and Cl(3) the electron densities at the alternative positions in each case indicated approximate occupancies of $\frac{1}{2}$ and $\frac{2}{3}$. The site occupancies of these atoms were adjusted during the refinement process such that the thermal parameters for each atom pair remained consistant. The O atoms of the disordered perchlorate ion were assigned their appropriate occupancies. Occupancies for the lattice water molecules were adjusted such that their thermal parameters remained approximately equal. Positions for hydrogen atoms for the cation were calculated assuming C,N-H to be 1.0 Å and the appropriate geometry of the atom to which each is bonded. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms other than those involved in the disorder and all perchlorate O atoms. The weight applied to each reflection was unity. Refinement was terminated when the shift in any parameter was $<0.1\sigma$. The final values for R and $R_w\{ = (\Sigma w(F_o-F_c)^2/\Sigma wF_o^2)^{0.5}\}$ were 0.065 and 0.072, respectively, and with $\eta = 1.14(12)$ confirming the correct absolute configurations of the chiral centres. A final difference map showed no unusual features with density maxima $< |0.9|$ e Å^{-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]

Crystal and Molecular Structure of Δ-β_2-*[Co(S,S,S,S-pychxn)(R-ala)](ClO$_4$)$_2$·2H$_2$O*

Crystal Data: $C_{19}H_{42}N_5O_{12}Cl_2Co$; $M_r = 662.4$; orthorhombic, $a = 10.933(4)$, $b = 13.667(2)$, $c = 18.853(3)$ Å; $U = 2817.0$ Å^3; $Z = 4$; $D_c = 1.562$ g cm^{-3}; $F(000) = 1392$; μ(Mo-Kα) = 9.93 cm^{-1}; space group $P2_12_12_1$ (No. 19).

Data for the complex were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using Mo$K\alpha$ radiation. Accurate cell parameters were obtained from a least-squares fit to diffractometer data. Intensities were measured in the range $3.0 < 2\theta < 46.0°$ and of the 2221 reflections recorded 1310 had $I > 3\sigma(I)$ and these were used for the structure analysis. The intensities were corrected for Lorentz, polarisation and absorption effects, the latter using an empirical method. Minimum and maximum transmission factors were 0.998 and 0.948, respectively.

The structure was solved by the heavy atom method and refined by full-matrix least-squares methods. Difference maps yielded positions for all hydrogen atoms and these were optimised assuming C,N-H to be 1.0 Å and O-H 0.9 Å. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms with the weight for each reflection taken from counting statistics. Refinement was terminated when the shift in any parameter was $< 0.1\sigma$. The final values for R and $R_w\{ =(\Sigma w(F_o-F_c)^2/\Sigma wF_o^2)^{0.5}\}$ were 0.040 and 0.033, respectively, and with $\eta = 0.79(12)$ confirming the correct absolute configurations of the chiral centres. A final difference map showed no unusual features with density maxima $<|0.4|$ e Å^{-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

Reaction of the dichloro complex with glycine gave two ternary complexes, which could be completely separated by chromatographic methods. CD measurements showed that both had absolute configuration Δ. For β isomers, the source of the isomerism is of the β_1/β_2 kind. We may exclude the possibility of the presence of α isomers with *pseudo* C_2 symmetry on the basis of ^1H and ^{13}C nmr measurements which give very different chemical shifts for resonances of related pairs of atoms in the tetradentate.[7] The major isomer is assigned as the Δ-β_2 isomer because of a distinguishing spectroscopic feature observed for many Co(III) complexes containing an aminoacidate ligand and an aliphatic linear, nitrogeneous tetradentate.[1,8–11] All the aminoacidate complexes synthesised possess two absorption bands in the visible region of the electronic spectrum. These absorption bands have $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ parentage (O_h symmetry) and appear at longer and shorter wavelengths, respectively.[12] 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 also been structurally characterised.[13–14]

The difference between the two glycinate products is confirmed by their crystallographic properties. Crystals from the major β_2 band are tetragonal, with a = 15.41, c = 48.73 Å, Z = 16, possible space groups $I4$, $I4_1$, $I422$ or $I4_122$. The minor β_1 isomer, whose structure has been separately determined, is orthorhombic as well as conforming to the abovementioned spectroscopic criterion.

Structure of Δ-β_1-*[Co(S,S,S,S-pychxn)(gly)](ClO$_4$)$_2$.2H$_2$O*

A perspective view of the cation is shown in Figure 1. Final fractional coordinates for the non-hydrogen atoms and bondlengths and angles are listed in Tables I and II respectively. The X-ray structural analysis establishes the geometry of the complex cation unambiguously. Aside from statistical considerations, the internal inherent chiral labels in the tetradentate serve to completely distinguish the geometry from its mirror image. Absolute configurations of the four coordinated nitrogen atoms are *S,S,R,S,* in turn, the *R*-nitrogen being that donor at the fold of the tetradentate. This situation is analogous to that found[1] for Δ-β_2-[Co(*S,R,R,S*-pychxn)(*S*-ala)]$^{2+}$. Kitagawa *et al.*[3] had not considered this overall stereochemistry in their study of related Ni(II) complexes.

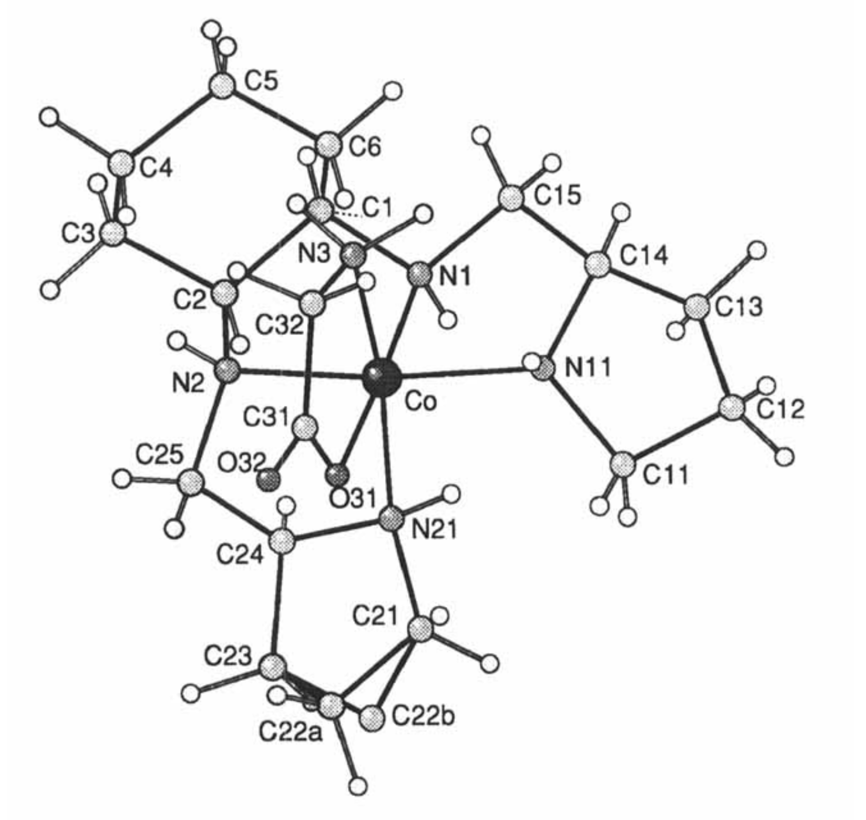

FIGURE 1 Perspective view of the Δ-β_1-[Co(*S,S,S,S*-pychxn)(gly)]$^{2+}$ cation showing the atom labelling system.

TABLE I Final Atomic Coordinates (fractional ×10^4) for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses for Δ-β_1-[Co(*S,S,S,S*-pychxn)(gly)]$(ClO_4)_2 \cdot 2H_2O$

	Occ.	*x/a*	*y/b*	*z/c*	*B**
Co		4559.2(13)	5544.9(9)	2142.3(7)	2.0
N(1)		4082(8)	6775(6)	1838(4)	2.2
N(2)		6039(8)	5634(7)	1494(5)	2.8
N(11)		2982(8)	5665(6)	2747(4)	2.4
N(21)		5897(8)	5957(6)	2828(5)	2.3
N(3)		3397(10)	4938(7)	1463(5)	2.8
O(31)		5009(7)	4303(5)	2397(4)	2.9
O(32)		4782(9)	2828(5)	2133(5)	4.0

TABLE I (*Continued*)

	Occ.	*x/a*	*y/b*	*z/c*	*B**
C(31)		4509(12)	3650(8)	2054(6)	3.0
C(32)		3532(13)	3917(8)	1502(8)	4.1
C(11)		3115(12)	5825(10)	3505(6)	4.2
C(12)		1916(14)	6370(11)	3692(7)	4.8
C(13)		1819(16)	7027(10)	3090(7)	5.2
C(14)		2033(11)	6405(9)	2496(6)	3.2
C(15)		2593(10)	6889(8)	1852(6)	3.2
C(1)		4595(12)	6934(7)	1147(5)	2.6
C(2)		6010(10)	6570(8)	1142(6)	2.7
C(3)		6564(14)	6547(10)	421(6)	4.4
C(4)		6532(15)	7541(12)	140(8)	5.8
C(5)		5157(13)	7969(10)	191(6)	4.4
C(6)		4615(13)	7945(8)	892(6)	3.4
C(21)		6169(12)	5354(9)	3441(6)	3.9
C(22a)	0.62	7473(23)	5010(17)	3426(11)	4.1(4)
C(22b)	0.38	7635(32)	5689(26)	3658(16)	3.8(7)
C(23)		8272(13)	5842(11)	3030(7)	5.4
C(24)		7246(11)	6096(8)	2496(7)	3.3
C(25)		7283(10)	5516(9)	1867(6)	3.2
O(w1)	0.78	3403(14)	5195(10)	16(7)	6.7(3)
O(w2)	0.59	550(20)	4820(13)	1640(10)	6.5(4)
O(w3)	0.63	6413(18)	3986(12)	586(9)	6.5(4)
Cl(1)		827(4)	3466(3)	3269(2)	4.7
O(1a)		632(13)	2503(9)	3333(6)	8.0(3)
O(1b)		444(17)	3925(10)	3864(7)	10.0(4)
O(1c)		2115(17)	3623(11)	3075(8)	11.1(5)
O(1d)		1(20)	3766(12)	2757(9)	13.4(6)
Cl(2)	0.62	246(8)	3290(5)	217(4)	6.3(2)
Cl(3)	0.38	164(11)	4390(9)	621(6)	6.4(2)
O(23a)		982(19)	4185(14)	78(9)	13.0(5)
O(23b)		−670(25)	3588(17)	683(12)	17.3(8)
O(2c)	0.62	−220(24)	2788(16)	−340(12)	9.6(6)
O(2d)	0.62	1023(44)	2737(30)	548(22)	19.5(15)
O(3c)	0.38	500(29)	5092(17)	1180(13)	5.3(5)
O(3d)	0.38	−970(40)	4651(29)	227(20)	10.5(11)

*B_{iso} with estimated standard deviation in parentheses or B_{eq}.

TABLE II Bond Lengths and Angles Involving Non-hydrogen Atoms with Estimated Standard Deviations in Parentheses for Δ-β_1-[Co(*S,S,S,S*-pychxn)(gly)]$(ClO_4)_2 \cdot 2H_2O$

a) Distances (Å)			
Co—N(1)	1.934(8)	Co—N(11)	2.000(8)
Co—N(2)	1.972(8)	Co—N(21)	2.001(8)
Co—N(3)	1.983(10)	Co—O(31)	1.915(7)
N(3)—C(32)	1.480(14)	C(31)—O(31))	1.263(12)
C(31)—C(32)	1.518(17)	(C31)—O(32)	1.227(13)
N(11)—C(11)	1.512(14)	N(21)—C(21)	1.510(14)
N(11)—C(14)	1.519(14)	N(21)—C(24)	1.528(13)
C(12)—C(13)	1.519(18)	C(21)—C(22b)	1.619(35)
C(11)—C(12)	1.493(17)	C(21)—C(22a)	1.412(25)
C(13)—C(14)	1.488(17)	C(23)—C(22a)	1.644(27)
C(14)—C(15)	1.553(16)	C(23)—C(22b)	1.409(33)

TABLE II (*Continued*)

a) Distances (Å)

N(1)—C(15)	1.517(13)	C(23)—C(24)	1.522(16)
N(1)—C(1)	1.471(12)	C(24)—C(25)	1.492(16)
C(1)—C(2)	1.528(15)	N(2)—C(25)	1.469(13)
C(2)—C(3)	1.524(15)	N(2)—C(2)	1.517(14)
C(3)—C(4)	1.536(21)	Cl(1)—O(1a)	1.407(13)
C(4)—C(5)	1.528(19)	Cl(1)—O(1b)	1.399(15)
C(5)—C(6)	1.483(16)	Cl(1)—O(1c)	1.378(17)
C(6)—C(1)	1.541(14)	Cl(1)—O(1d)	1.377(19)
Cl(2)—O(23a)	1.514(19)	Cl(3)—O(23a)	1.383(19)
Cl(2)—O(23b)	1.372(23)	Cl(3)—O(23b)	1.437(25)
Cl(2)—O(2c)	1.394(23)	Cl(3)—O(3c)	1.532(26)
Cl(2)—O(2d)	1.296(45)	Cl(3)—O(3d)	1.434(40)

b) Angles (°)

N(11)—Co—N(1)	84.5(3)	N(11)—Co—N(21)	96.6(3)
N(21)—Co—N(2)	84.3(3)	N(11)—Co—N(3)	87.9(4)
N(1)—Co—N(2)	86.0(4)	N(11)—Co—O(31)	96.6(3)
N(3)—Co—O(31)	84.5(3)	N(21)—Co—N(1)	96.1(3)
N(11)—Co—N(2)	170.5(4)	N(21)—Co—O(31)	86.6(3)
N(1)—Co—O(31)	177.0(4)	N(1)—Co—N(3)	92.7(4)
N(21)—Co—N(3)	170.4(4)	N(2)—Co—N(3)	92.6(4)
Co—N(3)—C(32)	110.4(8)	N(2)—Co—O(31)	92.8(3)
Co—O(31)—C(31)	117.5(7)	Co—N(21)—C(21)	119.3(7)
N(3)—C(32)—C(31)	110.4(11)	Co—N(21)—C(24)	110.9(7)
O(31)—C(31)—O(32)	124.2(12)	C(21)—N(21)—C(24)	104.7(8)
O(31)—C(31)—C(32)	117.0(10)	N(21)—C(21)—C(22a)	110.9(13)
O(32)—C(31)—C(32)	118.8(11)	N(21)—C(21)—C(22b)	101.9(15)
Co—N(11)—C(11)	121.8(7)	C(21)—C(22a)—C(23)	102.3(16)
Co—N(11)—C(14)	111.9(6)	C(21)—C(22b)—C(23)	103.7(21)
C(11)—N(11)—C(14)	105.6(9)	C(22a)—C(23)—C(24)	99.6(12)
N(11)—C(11)—C(12)	104.5(10)	C(22b)—C(23)—C(24)	109.2(17)
C(11)—C(12)—C(13)	100.8(11)	C(23)—C(24)—N(21)	106.5(10)
C(12)—C(13)—C(14)	103.1(11)	C(23)—C(24)—C(25)	114.7(10)
C(13)—C(14)—N(11)	105.1(10)	N(21)—C(24)—C(25)	107.6(9)
C(13)—C(14)—C(15)	114.9(10)	C(24)—C(25)—N(2)	109.0(9)
N(11)—C(14)—C(15)	110.4(8)	Co—N(2)—C(25)	108.8(6)
C(14)—C(15)—N(1)	109.2(9)	Co—N(2)—C(2)	109.7(6)
Co—N(1)—C(15)	110.0(7)	C(25)—N(2)—C(2)	110.3(9)
Co—N(1)—C(1)	109.9(6)	N(2)—C(2)—C(1)	108.7(8)
C(15)—N(1)—C(1)	110.6(9)	N(2)—C(2)—C(3)	113.4(10)
N(1)—C(1)—C(2)	106.5(9)	C(1)—C(2)—C(3)	111.0(9)
N(1)—C(1)—C(6)	116.9(8)	C(2)—C(3)—C(4)	107.8(12)
C(6)—C(1)—C(2)	108.1(7)	C(3)—C(4)—C(5)	111.9(12)
C(1)—C(6)—C(5)	109.2(10)	C(4)—C(5)—C(6)	112.9(11)
O(1a)—Cl(1)—O(1b)	110.7(8)	O(23a)—Cl(2)—O(23b)	100.7(13)
O(1a)—Cl(1)—O(1c)	108.7(9)	O(23a)—Cl(2)—O(2c)	117.9(13)
O(1a)—Cl(1)—O(1d)	106.8(10)	O(23a)—Cl(2)—O(2d)	108.4(20)
O(1b)—Cl(1)—O(1c)	114.5(10)	O(23b)—Cl(2)—O(2c)	117.2(15)
O(1b)—Cl(1)—O(1d)	107.0(10)	O(23b)—Cl(2)—O(2d)	105.6(21)
O(1c)—Cl(1)—O(1d)	108.9(11)	O(2c)—Cl(2)—O(2d)	106.3(21)
O(23a)—Cl(3)—O(23b)	104.2(15)	O(23b)—Cl(3)—O(3c)	127.0(16)
O(23a)—Cl(3)—O(3c)	124.1(16)	O(23b)—Cl(3)—O(3d)	77.6(19)
O(23a)—Cl(3)—O(3d)	96.9(18)	O(3c)—Cl(3)—O(3d)	113.1(21)

No unusual geometric features are observed for the complex, nor are there any apparent reasons for the adoption of the particular β_1 geometry. It seems that either β_1 or β_2 forms can be accommodated without steric strain in this class of complex. No significant intramolecular non-bonded contacts <3.3 Å are found in the complex cation (Table III). The perchlorate ions, water molecules of crystallization and the cation are linked in the crystal lattice by a three-dimensional hydrogen bonding network (Table III).

TABLE III Contact Distances (Å) with Estimated Standard Deviations in Parentheses for Δ-β_1-[Co(*S,S,S,S*-pychxn)(gly)]$(ClO_4)_2 \cdot 2H_2O$

a) Proposed hydrogen bonding*			
N(1) H (N1)....O(32^{I})	2.78 (1)	O(w1)....O(1b^{II})	2.84(2)
N(2) H (N2)....O(w3)	2.99 (2)	O(w1)....O(23a)	2.86(2)
N(11) H (N11)....O(1c)	3.14 (2)	O(w2)....O(1d)	2.73(3)
N(21) H (N21)....O(32^{I})	2.79 (1)	O(w2)....O(23b)	2.87(3)
N(3) H (N3a)....O(w1)	2.87 (2)	O(w2)....O(3d)	3.18(4)
N(3) H (N3b)....O(w2)	2.91(2)	O(w3)....O(23b^{III})	3.02(3)
N(3) H (N3b)....O(3d)	3.00 (3)	O(w3)....O(2c^{IV})	3.08(3)
		O(w3)....O(3d^{III})	2.91(4)
b) Intermolecular distances <3.3 Å*			
C(31) ....O(1c)	3.15 (2)	C(11)....O(23a^{V})	3.22(2)
C(14) ....O(w2)	3.21 (2)		

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

Structure of Δ-β_2-*[Co(S,S,S,S-pychxn)(R-ala)]*$(ClO_4)_2.2H_2O$

A perspective view of the cation is shown in Figure 2 and atomic coordinates for non-hydrogen atoms and bond lengths and angles are given in Tables IV and V, respectively. Many features of the glycinato complex are preserved in the *R*-alaninato case, except that the latter exists in the β_2 isomer form. The absolute configurations of the four nitrogen atoms of the tetradentate are the same as in the glycine complex and no significant intramolecular contacts <3.3 Å are noted for the complex cation (Table VI). Again, no obvious structural reason can be discerned for the slection of the β_2 isomer than a possible β_1 isomer. It is noteworthy that no β_1 species was detected during the synthesis and work up of the complex. Table VI also lists data for the hydrogen bonding network which links the complex cation, the perchlorate anions and the water molecules in the crystal.

TABLE IV Final Atomic Coordinates (fractional $\times 10^4$) for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses for Δ-β_2-[Co(*S,S,S,S*-pychxn)(*R*-ala)]$(ClO_4)_2 \cdot 2H_2O$

	x/a	*y/b*	*z/c*	B_{eq}
Co	509.6(14)	409.2(9)	506.9(8)	2.0
N(1)	–738(7)	–630(5)	461(5)	2.0

TABLE IV (*Continued*)

	x/a	*y/b*	*z/c*	B_{eq}
N(2)	281(8)	328(6)	1538(4)	2.4
N(11)	476(8)	379(6)	−565(4)	2.6
N(21)	1882(7)	−526(6)	662(5)	2.4
N(3)	1519(7)	1610(5)	544(5)	2.3
O(31)	−799(6)	1327(5)	446(4)	2.3
O(32)	−1298(7)	2901(5)	402(4)	3.5
C(31)	−511(12)	2231(8)	397(5)	2.3
C(32)	813(9)	2457(7)	287(6)	2.7
C(33)	1270(11)	3415(8)	616(8)	4.8
C(11)	1552(12)	274(10)	−1040(6)	4.3
C(12)	1611(16)	−797(10)	−1248(7)	6.1
C(13)	443(14)	−1271(8)	−1005(6)	4.5
C(14)	−371(11)	−394(9)	−808(5)	3.2
C(15)	−1344(10)	−571(8)	−249(6)	3.0
C(1)	−1553(10)	−458(8)	1077(6)	2.7
C(2)	−746(9)	−375(8)	1715(5)	2.3
C(3)	−1464(12)	−70(9)	2379(6)	4.2
C(4)	−2456(12)	−856(9)	2495(6)	4.2
C(5)	−3303(12)	−1000(9)	1853(7)	4.3
C(6)	−2532(12)	−1238(9)	1211(7)	4.1
C(21)	3181(9)	−305(9)	439(6)	3.5
C(22)	3919(10)	−1036(10)	868(7)	4.3
C(23)	3357(11)	−1019(10)	1590(7)	4.6
C(24)	1989(10)	−785(9)	1449(7)	3.4
C(25)	1435(12)	34(8)	1874(6)	3.4
Cl(1)	−657(4)	1686(2)	4049(2)	4.4
Cl(2)	4735(4)	2031(2)	1696(2)	4.4
O(1a)	−568(11)	778(5)	4371(6)	7.5
O(1b)	−820(15)	2392(6)	4563(5)	11.0
O(1c)	−1682(9)	1715(7)	3585(5)	6.8
O(1d)	339(11)	1881(11)	3627(7)	12.6
O(2a)	4589(14)	2908(7)	1359(6)	10.9
O(2b)	5438(11)	2116(12)	2293(5)	13.2
O(2c)	5220(13)	1353(7)	1223(5)	9.8
O(2d)	3596(12)	1737(9)	1945(7)	11.1
O(wl)	224(9)	2213(6)	2139(4)	6.6
O(w2)	−2016(10)	2863(11)	1881(6)	11.8

TABLE V Bond Lengths and Angles with Estimated Standard Deviations in Parentheses for Δ-β_2-[Co(*S,S,S,S*-pychxn)(*R*-ala)]$(ClO_4)_2 \cdot 2H_2O$

a) Distances (Å)			
Co—N(11)	2.022(8)	Co—N(21)	1.992(8)
Co—N(1)	1.971(7)	Co—N(2)	1.963(8)
Co—N(3)	1.979(8)	Co—O(31)	1.907(6)
O(31)—C(31)	1.278(11)	O(32)—C(31)	1.257(11)
N(3)—C(32)	1.474(12)	C(31)—C(32)	1.494(16)
C(32)—C(33)	1.533(14)		
C(1)—C(2)	1.496(13)	C(6)—C(1)	1.532(15)
C(2)—C(3)	1.536(14)	C(6)—C(5)	1.510(17)
C(3)—C(4)	1.541(16)	C(5)—C(4)	1.537(16)

TABLE V (*Continued*)

a) Distances (Å)

	n=1	n=2
N(n)—C(n5)	1.495(13)	1.468(14)
N(n)—C(n)	1.483(13)	1.514(12)
N(n1)—C(n1)	1.485(14)	1.511(13)
N(n1)—C(n4)	1.478(13)	1.529(14)
C(n1)—C(n2)	1.517(17)	1.517(15)
C(n2)—C(n3)	1.503(20)	1.494(16)
C(n3)—C(n4)	1.539(16)	1.552(16)
C(n4)—C(n5)	1.518(15)	1.503(15)
Cl(n)—O(na)	1.384(8)	1.366(9)
Cl(n)—O(nb)	1.379(9)	1.369(10)
Cl(n)—O(nc)	1.422(10)	1.390(10)
Cl(n)—O(nd)	1.374(11)	1.390(11)

b) Angles (°)

N(11)—Co—N(1)	85.9(4)	N(11)—Co—N(3)	93.6(4)
N(1)—Co—N(2)	85.1(4)	N(11)—Co—O(31)	86.5(3)
N(2)—Co—N(21)	85.1(3)	N(1)—Co—N(21)	93.8(3)
N(3)—Co—O(31)	82.8(3)	N(1)—Co—O(31)	87.2(3)
N(11)—Co—N(2)	170.5(3)	N(2)—Co—N(3)	94.8(4)
N(1)—Co—N(3)	170.1(3)	N(2)—Co—O(31)	90.1(4)
N(21)—Co—O(31)	174.9(4)	N(21)—Co—N(3)	96.1(3)
N(11)—Co—N(21)	98.5(4)		
Co—O(31)—C(31)	117.1(7)	Co—N(3) —C(32)	110.4(6)
O(31)—C(31)—O(32)	122.3(11)	N(3)—C(32)—C(31)	107.4(8)
O(31)—C(31)—C(32)	116.7(10)	N(3)—C(32)—C(33)	111.6(8)
O(32)—C(31)—C(32)	120.9(10)	C(31)—C(32)—C(33)	115.9(10)
N(1)—C(1)—C(2)	106.7(9)	N(2)—C(2)—C(1)	108.0(8)
N(1)—C(1)—C(6)	116.0(10)	N(2)—C(2)—C(3)	112.8(9)
C(2)—C(1)—C(6)	109.5(10)	C(1)—C(2)—C(3)	112.0(9)
C(1)—C(6)—C(5)	111.8(11)	C(2)—C(3)—C(4)	106.6(10)
C(6)—C(5)—C(4)	108.8(10)	C(3)—C(4)—C(5)	113.7(10)

	n=1	n=2
Co—N(n)—C(n)	105.5(6)	110.4(6)
Co—N(n)—C(n5)	107.9(6)	109.5(7)
C(n)—N(n)—C(n5)	115.2(8)	111.6(8)
Co—N(n1)—C(n1)	126.1(7)	122.6(7)
Co—N(n1)—C(n4)	109.6(6)	110.4(7)
C(n1)—N(n1)—C(n4)	103.9(8)	104.1(8)
N(n)—C(n5)—C(n4)	108.6(9)	108.6(9)
N(n1)—C(n1)—C(n2)	106.4(11)	102.7(9)
C(n1)—C(n2)—C(n3)	107.5(12)	104.8(10)
C(n2)—C(n3)—C(n4)	103.2(10)	104.1(10)
C(n3)—C(n4)—N(n1)	105.6(9)	106.7(10)
C(n5)—C(n4)—N(n1)	109.8(9)	108.3(9)
C(n3)—C(n4)—C(n5)	116.7(11)	116.7(11)
O(na)—Cl(n)—O(nb)	109.1(6)	112.0(8)
O(na)—Cl(n)—O(nc)	110.5(7)	109.4(6)
O(na)—Cl(n)—O(nd)	111.9(9)	107.8(9)
O(nb)—Cl(n)—O(nc)	108.1(8)	111.7(8)
O(nb)—Cl(n)—O(nd)	111.9(9)	104.4(7)
O(nc)—Cl(n)—O(nd)	105.3(6)	111.4(8)

TABLE VI Contact Distances (Å) with Estimated Standard Deviations in Parentheses for Δ-β_2-[Co *(S,S,S,S*-pychxn)(*R*-ala)]$(ClO_4)_2 \cdot 2H_2O$

a) Proposed hydrogen bonding*			
N(11) H(n11)....O $(2a^{I})$	2.94(1)	O(w1) H(w1a)....O(w2)	2.65(1)
N(21) H(N21)....O $(1b^{II})$	3.10(1)	O(w1) H(w1b)....O(1d)	2.84(1)
N(1) H(N1)....O $(1b^{II})$	3.20(1)	O(w2) H(w2a)....O$(2b^{IV})$	3.06(2)
N(2) H(N2)....O (w1)	2.81(1)	O(w2) H(w2b)....O(32)	2.90(1)
N(3) H(N3b)....O (32^{III})	3.05(1)		
b) Intermolecular distances <3.35 Å*			
C(25).....O(w1)	3.30(1)	C(11).....O$(2a^{I})$	3.34(2)
C(13).....O$(1b^{II})$	3.30(1)	C(32).....O$(2c^{I})$	3.34(1)
C(33).....O$(1a^{V})$	3.32(1)	C(3)....O(1a)	3.34(1)
C(25).....O(2d)	3.32(2)		

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

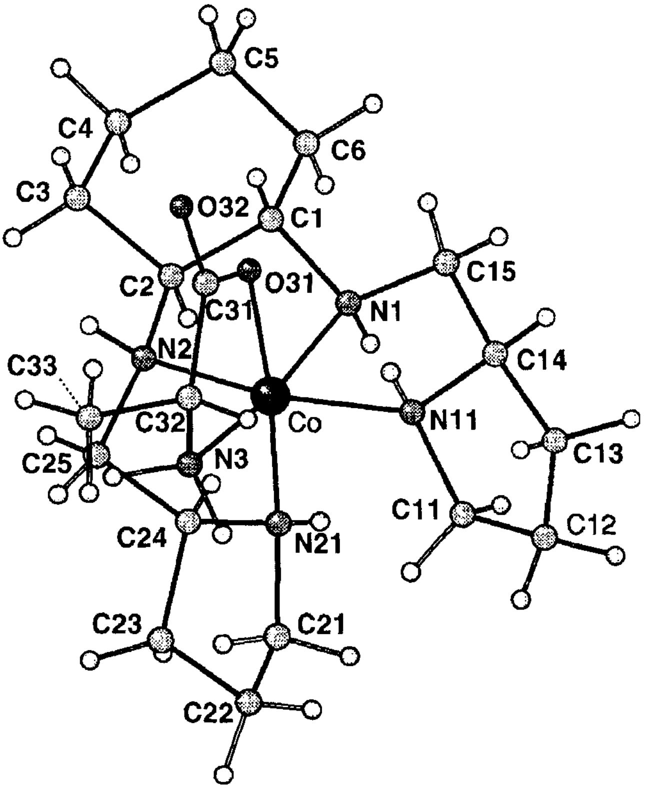

FIGURE 2 Perspective view of the Δ-β_2- $[Co(S,S,S,S\text{-pychxn})(R\text{-ala})]^{2+}$ cation, showing the atom labelling system.

Isomerism in the Complexes

Kitagawa *et al.* [3] suggested that *S,S,S,S*-pychxn formed a ternary complex with Ni(II) and 1,2-diaminoethane of absolute configuration L. However, they did not rule out the possibility of α or β isomerism, nor was the assignment of the CD spectra obtained entirely unambiguous. Here we find only Δ-β isomers for ternary Co(III) complexes of the same tetradentate and amino acids. With this in mind it may be that this ligand is as stereochemically flexible as its S,R,R,S-congener.[1] Related to this is the fact that both *cis* and *trans* isomers of the dichloro complex precursers were able to be easily obtained. The CD spectrum of the *cis* precursor indicates that it too has absolute configuration Δ. [15–16] Thus it appears that the *S,S,S,S*-pychxn is quite stereospecific in its coordination to Co(III), with respect to formation of β species. Selectivities involving β_2 *versus* β_1 geometries with aminoacidates is more problematic. Both complexes are formed with glycine, but only the former was obtained with *R*-alanine (and with other chiral aminoacidates).[7] The reasons for this remain unclear.

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SUPPLEMENTARY MATERIAL

Full lists of H atom positions, aniosotropic thermal parameters and observed and calculated structure factors are available from the authors on request.

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