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Chiral Metal Complexes.
13.* The Crystal and Molecular Structures of Four Diastereoisomeric Forms of β_1-{S-Alaninato[2,5-diaza-3-methyl-1,6-di(2-pyridyl)hexane]cobalt(III)} Perchlorate in One Single Crystal

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A crystalline form of β_1-$[Co(\pm picpn)(S\text{-}ala)]ClO_4$ *has been shown by X-ray analysis to contain four diastereoisomeric cations in a single crystal. The crystals are monoclinic, space group* $P2_1$, *with* $a = 17.204(4)$, $b = 9.037(2)$, $c = 17.631(3)$ Å, $\beta = 116.85(2)^\circ$ *and* $Z = 4$. *The structure was refined by block-matrix least-squares methods to* R *of 0.040 for 2313 non-zero reflexions.*

The compound crystallizes as a quasi-racemic mixture, with the Λ *and* Δ *cationic species in the asymmetric unit each representing two different diastereoisomers present in an abundance ratio of 0.62:0.38. Differences between the molecular structures of cations of like hand are derived from the alternative positions allowed for the methyl group of picpn when coordinated in* β*-topology. A pseudo n-glide operation exists between the chiral pairs. The perchlorate groups, which are involved in hydrogen-bonding to amine protons of the cations, are disordered.*

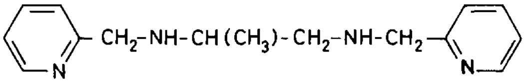
The four cationic diastereoisomers observed in the crystal, together with their respective abundances, are Δ-β_1-S,S-endo-$[Co(S\text{-}picpn)(S\text{-}ala)]^{2+}$ *(62%),* Δ-β_1-S,S-exo-$[Co(S\text{-}picpn)(S\text{-}ala)]^{2+}$ *(38%),* Λ-β_1-R,R-endo-$[Co(R\text{-}picpn)(S\text{-}ala)]^{2+}$ *(62%) and* Λ-β_1-R,R-exo-$[Co(R\text{-}picpn)(S\text{-}ala)]^{2+}$ *(38%). The S-alanine conformation is different in the two* Λ *forms, whereas in the* Δ *forms the S-alanine atomic positions are crystallographically equivalent. The observed preference for* endo *arrangements in the isomers is consistent with previously reported molecular strain energy calculations.*

Small angular distortions in the octahedral coordination spheres are consistent with the multidentate behaviour of the ligand. The average Co–O, Co–N(amine) and Co–N(pyridine) bond lengths are 1.89(1), 1.94(3) and 1.93(1) Å *respectively. There are no unfavourable intramolecular contacts evident involving the S-alanine groups of the cations.*

Introduction

It has been shown [1] that several discriminatory factors can give rise to various isomer distributions in ternary complexes of the kind Δ,Λ-$[Ru(diimine)_2(aa)]^{n+}$ where *aa* is an optically active α-amino acid. Similar results are found for Co(III) analogues. The most significant steric interactions in such complexes, between the diimine ligands and the amino acidate bidentates, would be essentially preserved in related complexes of linear tetradentates based on 2,5-diaza-1,6-di(2-pyridyl)hexane, picen. One attractive advantage concerning the choice of these ligands to study chiral discriminations is that they may be obtained optically active when appropriately substituted, and complexes derived from them may display unusual behavior.

In this connection, we recently reported [2, 3] a number of novel inversions which occur during the reactions of Λ-α-$[Co(R\text{-}picpn)Cl_2]^+$, where picpn is the ligand shown in (*1*), with simple symmetrical mono- and bidentates. In view of the results of our earlier work we decided to explore the nature of the complexes formed between Co(III) complexes of picpn and optically active α-amino acids. Many diastereoisomers are possible in this system, but few



(*1*)

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*Part 12 is T. J. Goodwin, P. A. Williams, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 88,* 165 (1984).

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in fact are observed to form. Four isomers of general formula β-[Co(picpn)(*S*-ala)]$^{2+}$, where *S*-ala is the *S*-alaninate anion, have been found to co-crystallize. We report here the determination of their crystal and molecular structures.

Experimental

Δ,Λ-β_1-exo,endo-*[Co(*R,*S-picpn)(S-alanine)](ClO$_4$)$_2$*

To an aqueous suspension of Δ,Λ-α-[Co(*R,S*-picpn)Cl$_2$]ClO$_4$ [3] (1.0 g, 1.43 mmol, in 20 cm^3 water) was added *S*-alanine (0.13 g, 1.43 mmol) and 1.0 mol dm^3 aqueous NaOH (1.4 cm^3), dropwise. The mixture was heated on a steam bath for 0.5 hr during which time all the solids dissolved and a deep-orange coloured solution was obtained. This was cooled to room temperature and diluted five-fold with water. The whole of the reaction mixture was then applied to a CM Sephadex® C-25 cation exchange column (30 X 2 cm) in the Na$^+$ cycle, and after the column had been thoroughly flushed with water, 1% (w/w) aqueous sodium perchlorate was employed to elute the mixture of cationic species. Two orange bands developed, and these were collected in fractions. Measurements of optical density (Beckman DK 2A ratio recording spectrometer) and circular dichroism (Jobin–Yvon CNRS Dichrograph III) indicated that the latter half of the faster moving orange band had approximately constant composition. These fractions were combined and evaporated to dryness at 40° *in vacuo*. The residue was dissolved in the minimum of water at 40° and allowed to cool to room temperature, then the solution evaporated over silica gel at room temperature. Over two weeks prisms of the title compound up to 3 mm long crystallized. These were collected at the pump, washed with a few drops of ice-cold water and air-dried. Proton NMR spectra (Bruker WM-360) of D$_2$O or d$_6$-DMSO solutions of single crystals of the compound showed that four diastereoisomers were present [4], and in approximately constant ratio for all crystals studied. The complex crystallizes as orange rectangular prisms with [010] elongation.

Crystal Data

$C_{18}H_{26}N_5Cl_2O_{10}Co$, M_r = 602.3, Monoclinic, a = 17.204(4), b = 9.037(2), c = 17.631(3) Å, β = 116.85(2)°, U = 2445.6(17) Å^3, Z = 4, D_c = 1.636 Mg m^{-3}, $F(000)$ = 1240, μ(Mo-K$_\alpha$) = 0.985 mm^{-1}. Systematic absences: 0*k*0 when k $\neq 2n$, space group $P2_1$ (No. 4) or $P2_1/m$ (No. 11).

Initially, unit cell parameters were determined from single crystal oscillation and Weissenberg photographs using Cu-K_α radiation. Accurate cell parameters were obtained from a least-squares fit to diffractometer data. Intensities were collected on an Enraf-Nonius CAD4 diffractometer using monochromated Mo-K_α radiation by Dr M. B. Hursthouse at Queen Mary College, London. Of the 4591 reflexions recorded 2313 have $I > 3\sigma(I)$ and these were used for the structure analysis. For the *h*0*l* zone with $h + l$ odd only 24 reflexions gave significant counts, which is consistent with the precursory photographic investigation. Intensities were corrected for Lorentz, polarization and absorption effects.

Structure Determination

Only the space group $P2_1$ would allow retention of the amino acid asymmetry, and hence it was adopted in the analysis. This, with Z = 4, requires that the asymmetric unit contains two molecular formula units. The structure was solved for the Co and Cl atoms using a Patterson synthesis. The positions of most of the non-hydrogen atoms were then determined by Fourier methods. This indicated that, consistent with the NMR analysis, the asymmetric unit did not contain only two discrete isomers but rather that an alternative form of lower occupancy was present for each. In particular, difference syntheses indicated that the methyl groups of the picpn ligands were located, with varying occupancies, bonded to either of the carbon atoms of each central ethyl link. Alternative configurations for the amino acid molecules and disordering of the perchlorate groups were indicated also. For the majority of atoms in the structure, however, no distinction could be made between equivalent atoms in isomeric pairs.

Further evidence for the presence of more than the two major isomers was provided by the failure of isotropic refinement to reach convergence when only those isomers were included. Atoms with partial occupancies were included and the refinement process recommenced with four isomers thus defined. Initially an isomeric ratio of 2:1 was used which was consistent both with the indicated electron densities and with the NMR spectra. The population parameters for these atoms were varied during the refinement process so as to give thermal parameters which were comparable with all other atoms in the structure. In the final stages of isotropic refinement these population parameters for the cations were allowed to refine, although this led to no significant change in their values. An isomeric ratio of 0.62: 0.38 was indicated using this method, which was highly consistent throughout the structure, and this was maintained during anisotropic refinement.

Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The closely located amino acid carbonyl atoms C(A11) and C(A11') could be distinguished in difference maps, but were too close to allow individual refinement. In the later cycles of refinement the thermal parameters for these two atoms were averaged and their positional parameters were held constant.

TABLE I. Final Atomic Coordinates (fractional, ×10^4) with Estimated Standard Deviations in Parentheses.

Atom	Occupancy[a]		*x*		*y*		*z*	
	n = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 1	*n* = 2
Co(*n*)			1089(1)	6093(1)	−965	768(2)	−915(1)	4091(1)
O(A*n*1)			560(4)	5587(5)	−2532(7)	2414(8)	−614(4)	4360(4)
O(A*n*2)	0.62		−622(10)	4416(4)	−3316(26)	3106(9)	−486(14)	4493(4)
O(A*n*2′)		0.38	−668(33)		−3072(64)		−596(33)	
N(A*n*)			88(5)	5071(5)	168(10)	−308(9)	−993(5)	3963(5)
N(*n*1)			506(6)	5524(4)	−1176(13)	1146(9)	−2130(6)	2877(4)
N(*n*2)			1604(5)	6640(5)	722(13)	−852(8)	−1176(6)	3828(5)
N(*n*3)			1825(6)	6775(4)	−296(15)	315(9)	276(6)	5276(4)
N(*n*4)			2066(5)	7073(5)	−2210(12)	2060(8)	−723(5)	4293(5)
C(*n*11)			581(6)	5621(8)	−2(13)	−47(14)	−2578(7)	2465(8)
C(*n*12)			231(8)	5190(8)	−102(16)	26(16)	−3447(8)	1530(7)
C(*n*13)			−122(9)	4759(8)	−1442(19)	1199(19)	−3828(8)	1150(6)
C(*n*14)			−198(8)	4709(7)	−2560(15)	2468(18)	−3395(8)	1597(7)
C(*n*15)			153(7)	5098(7)	−2394(16)	2390(12)	−2518(7)	2479(7)
C(*n*41)			2622(9)	7628(6)	−2411(19)	2272(10)	101(8)	5127(6)
C(*n*42)			3354(8)	8366(7)	−3185(16)	3154(16)	361(8)	5359(7)
C(*n*43)			3540(6)	8539(10)	−3892(17)	3853(18)	−230(7)	4782(10)
C(*n*44)			2995(7)	7918(9)	−3753(15)	3645(18)	−1042(8)	3904(7)
C(*n*45)			2232(7)	7257(7)	−2930(12)	2710(16)	−1319(6)	3755(7)
C(*n*1)			1085(8)	6063(6)	1202(13)	−1420(12)	−2016(9)	2925(6)
C(*n*2)			1917(9)	6811(7)	1657(15)	−2082(13)	−448(10)	4478(7)
C(*n*3)			2390(9)	7285(6)	985(19)	−1039(14)	356(9)	5282(7)
C(*n*4)			2295(7)	7388(7)	−1746(15)	1512(15)	694(6)	5726(6)
C(M*n*2)	0.62	0.62	2195(11)	7385(11)	3238(28)	−3240(20)	−668(13)	4493(12)
C(M*n*3)	0.38	0.38	2720(25)	7746(15)	1765(61)	−1712(38)	1161(24)	6234(22)
C(A*n*1)	0.62		−215[b]	4780(9)	−2334[b]	2190(15)	−699[b]	4237(6)
C(A*n*1′)	0.38		−128[b]		−2265[b]		−558[b]	
C(A*n*2)	0.62		−661(16)	4390(6)	−890(46)	756(14)	−1051(16)	3862(7)
C(A*n*2′)	0.38		−347(30)		−620(81)		−725(29)	
C(A*n*3)	0.62		−1384(15)	3655(9)	−900(28)	265(17)	−1798(14)	3845(11)
C(A*n*3′)	0.38		−1337(15)		−321(30)		−928(15)	
Cl(*n*1)			−1243(3)	3710(2)	−588(5)	585(5)	3644(2)	8608(2)
Cl(*n*2)			895(2)	5909(3)	−1280(4)	1192(4)	2064(2)	7072(2)
O(*n*11)	0.60	0.50	−1629(13)	3583(13)	−90(24)	36(22)	4106(14)	9282(9)
O(*n*12)	0.67	0.35	−783(10)	4428(20)	378(17)	−386(34)	4306(9)	9313(16)
O(*n*13)	0.67	0.60	−686(15)	3899(20)	−851(33)	1947(24)	3373(14)	8902(14)
O(*n*14)	0.40	0.65	−1620(20)	3071(16)	10(38)	189(49)	2899(13)	8124(17)
O(*n*15)	0.50	0.50	−2170(10)	4051(15)	−35(26)	320(29)	3162(14)	8001(12)
O(*n*16)	0.67	0.30	−1470(11)	2834(31)	−1869(24)	816(92)	3974(10)	7798(20)
O(*n*17)	0.50	0.30	−563(26)	3846(35)	−1486(49)	−854(39)	3832(22)	8286(26)
O(*n*18)		0.35		4468(21)		790(68)		8864(24)
O(*n*19)		0.40		3250(34)		2001(42)		8379(35)
O(*n*21)			971(7)	5933(5)	−2707(11)	2550(10)	2416(5)	7502(4)
O(*n*22)	0.50	0.65	−41(9)	4964(12)	−906(21)	766(23)	1542(10)	6736(13)
O(*n*23)	0.50	0.35	1416(11)	6450(63)	−252(21)	−169(108)	2787(10)	7494(61)
O(*n*24)	0.50	0.65	1062(22)	6393(16)	−1734(37)	1185(24)	1385(20)	6687(13)
O(*n*25)	0.50	0.35	1744(14)	6730(24)	−756(33)	828(67)	2116(15)	7377(26)
O(*n*26)	0.50	0.35	552(17)	5185(16)	−430(20)	1077(39)	2404(14)	6323(16)
O(*n*27)	0.50	0.65	604(15)	6114(14)	−1429(25)	5(29)	1170(16)	7584(17)

[a] Atoms with no value given have full (1.00) occupancy. [b] The positions of these atoms were held during the last cycles of refinement; hence no e.s.d.'s are given.

The least-squares calculations minimized the function $\Sigma w \Delta^2$, with the weight given to each reflexion being obtained from counter statistics.

After isotropic refinement a difference synthesis was used to locate the hydrogen atoms. Their positions then were optimised assuming C–H and N–H to

TABLE II. Hydrogen Atomic Coordinates (Fractional × 10^3).

	x		y		z	
	$n = 1$	$n = 2$	$n = 1$	$n = 2$	$n = 1$	$n = 2$
H(*n*12)	34	532	65	−82	−375	125
H(*n*13)	−55	445	−150	130	−452	48
H(*n*14)	−53	447	−357	340	−368	132
H(*n*15)	−2	500	−334	314	−223	277
H(*n*42)	372	881	−348	324	97	598
H(*n*43)	409	910	−449	433	−11	498
H(*n*44)	302	811	−442	411	−145	349
H(*n*45)	192	690	−272	253	−192	314
H(C*n*11)	145	634	177	−182	−225	261
H(C*n*12)	67	557	202	−208	−198	288
H(C*n*21)	137	625	211	−235	−48	451
H(C*n*22)^{b}	216	720	270	−289	−54	445
H(C*n*31)	290	791	58	−77	37	536
H(C*n*32)^{a}	265	757	140	−172	94	581
H(C*n*41)	282	779	−137	124	127	629
H(C*n*42)	194	692	−238	227	84	580
H(M*n*21)^{a}	226	758	408	−391	−28	496
H(M*n*22)^{a}	181	721	324	−363	−122	391
H(M*n*23)^{a}	260	800	308	−288	−84	460
H(M*n*31)^{b}	330	819	174	−231	150	621
H(M*n*32)^{b}	242	730	262	−239	112	620
H(M*n*33)^{b}	248	813	94	−118	148	675
H(N*n*2)	220	723	28	−56	−111	389
H(N*n*3)	144	642	−11	6	58	558
H(A*n*2)	-74^{a}	401	-56^{a}	103	-54^{a}	313
H(A*n*2′)^{b}	−22		−30		−5	
H(A*n*31)	-141^{a}	330	-132^{a}	84	-222^{a}	367
H(A*n*32)	-162^{a}	386	11^{a}	10	-192^{a}	449
H(A*n*33)	-184^{a}	350	-125^{a}	−81	-162^{a}	364
H(A*n*31′)^{b}	−148		−77		−143	
H(A*n*32′)^{b}	−152		67		−111	
H(A*n*33′)^{b}	−143		−63		−43	
H(NA*n*1)	-15^{a}	523	83^{a}	−99	-150^{a}	447
H(NA*n*2)	31^{a}	486	90^{a}	−97	-46^{a}	344
H(NA*n*1′)^{b}	−22		56		−157	
H(NA*n*2′)^{b}	34		103		−58	

[a] Occupancy = 0.62. [b] Occupancy = 0.38.

be 1.0 Å; they were assigned $B = 5.0$ Å^2 and their parameters were held during further refinement.

Due to the large number of varying parameters (811) block matrices were used during anisotropic refinement. The thirteen matrices used contained (1) the overall scale and thermal parameters, and the parameters for (2) and (3) the two Co atoms and their coordinated amino acids, (4) and (5) the two picpn ligands, (6)–(9) the four pyridine rings and (10)–(13) the four perchlorate groups.

The refinement process was terminated when the change in the minimization function was <0.5%, the maximum parameter shift being <0.3σ. A final difference map showed no residual electron density greater than $|0.2|$ e Å^{-3}. The final value for R based on all 2313 reflexions was 0.040 and R' $[=(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}]$ was 0.028.

All calculations were carried out on a UNIVAC 1106 computer using programmes written by F.S.S. Neutral atom scattering factors were taken from 'International Tables for X-Ray Crystallography' [5], with corrections being applied for anomalous dispersion. Final atomic parameters are given in Tables I and II. Lists of observed and calculated structure factors (14 pages) and anisotropic thermal parameters have been deposited with the Editor.

Description of Structure

The complex cation is seen to co-crystallize in four distinct diastereoisomeric forms, each with *cis*-β_1 topology [6], in a quasi-racemic mixture. The Λ and Δ cationic species in the asymmetric unit each represent two different diastereoisomers present in an abundance ratio of 0.62:0.38. A close *n*-glide

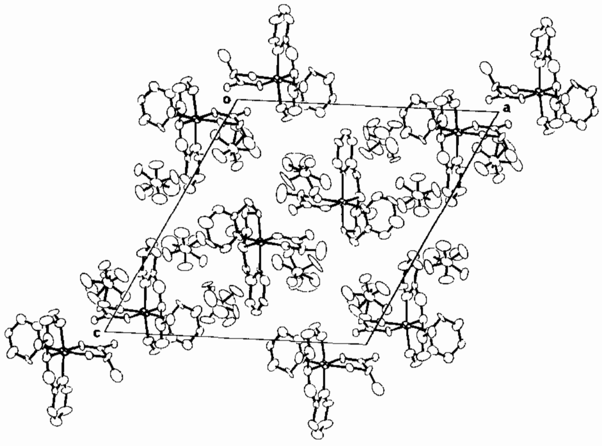
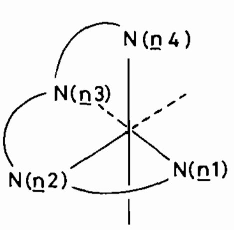


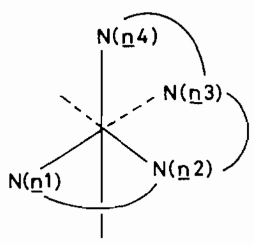
Fig. 1. The packing of the molecular ions in the crystal. Only the two Δ and Λ cations of higher occupancy (62%) are shown. The disordering of the O atoms of the perchlorate groups is demonstrated.

relationship exists between these chiral pairs, evident in both Tables I and II and in Fig. 1, which is consistent with the few weak *h*0*l* observed reflexions when $h + l \neq 2n$.

The molecular structures of the four cations are shown in Figs. 2, 3 together with the atomic labelling scheme [7]. In these β-isomers the labelling is such that the nitrogen atoms N(*n*1), N(*n*2) and N(*n*3) of the tetradentate all lie meridionally in both Δ and Λ diastereoisomers, as represented in (*2*) and (*3*). As a consequence of this choice of numbering, the methyl group of picpn may then be bonded to either C(*n*2) or C(*n*3), as indicated in Fig. 2, and the presence or absence of H(C*n*22) and H(C*n*32) is thus dictated.

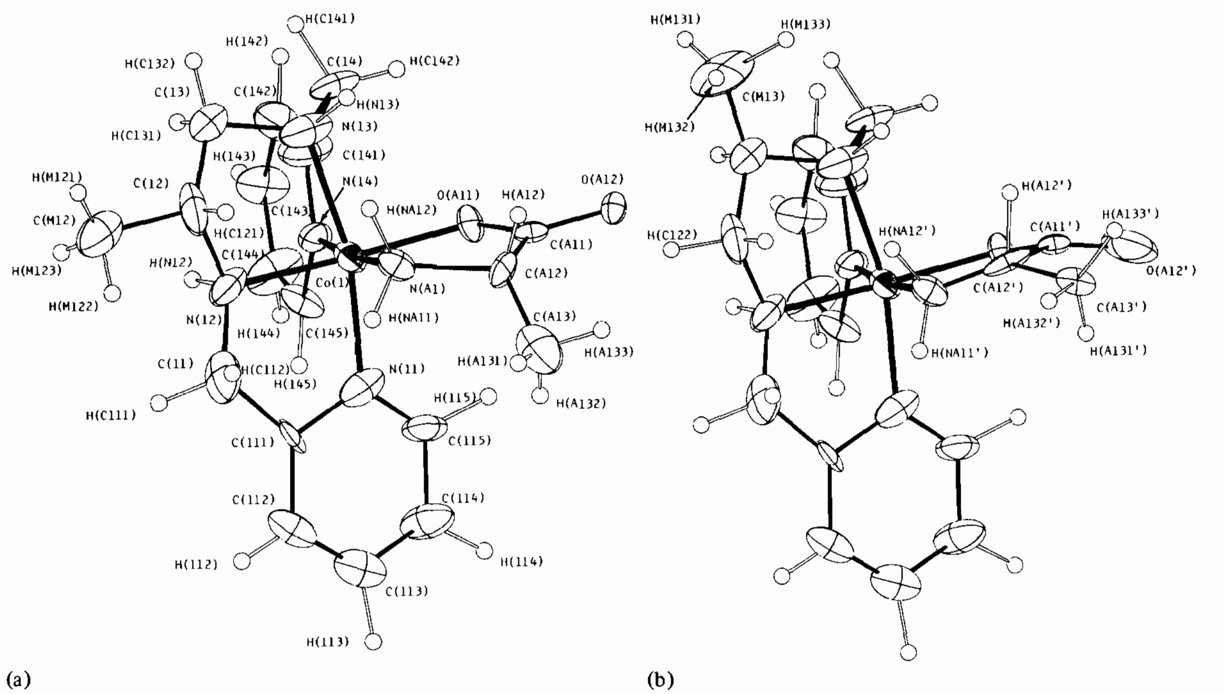


(*2*)



(*3*)

We adopt here the usual nomenclature for the absolute configuration at tetrahedral and octahedral centres, as well as that to distinguish β_1 and β_2 geometrical isomers in these ternary amino acidate complexes containing the CoN_5O chromophore. The absolute configurations of the nitrogen atoms N(*n*2) and N(*n*3) are given without regard to the methyl group of picpn. This convention has generally been adopted in the past, and thus the configurations are



(a) (b)

Fig. 2. Perspective drawings of the two Λ cationic forms in the crystal, with thermal ellipsoids scaled to include 35% probability. Hydrogen atoms have been included with $B = 1.0$ Å^2. (a) The Λ-β_1-*R*,*R*-*endo*-[Co(*R*-picpn)(*S*-ala)]$^+$ ion present in 62% occupancy. (b) The Λ-β_1-*R*,*R*-*exo*-[Co(*R*-picpn)(*S*-ala)]$^+$ ion present in 38% occupancy. Labelled atoms demonstrate the unique differences between this and the *endo* isomer shown in (a).

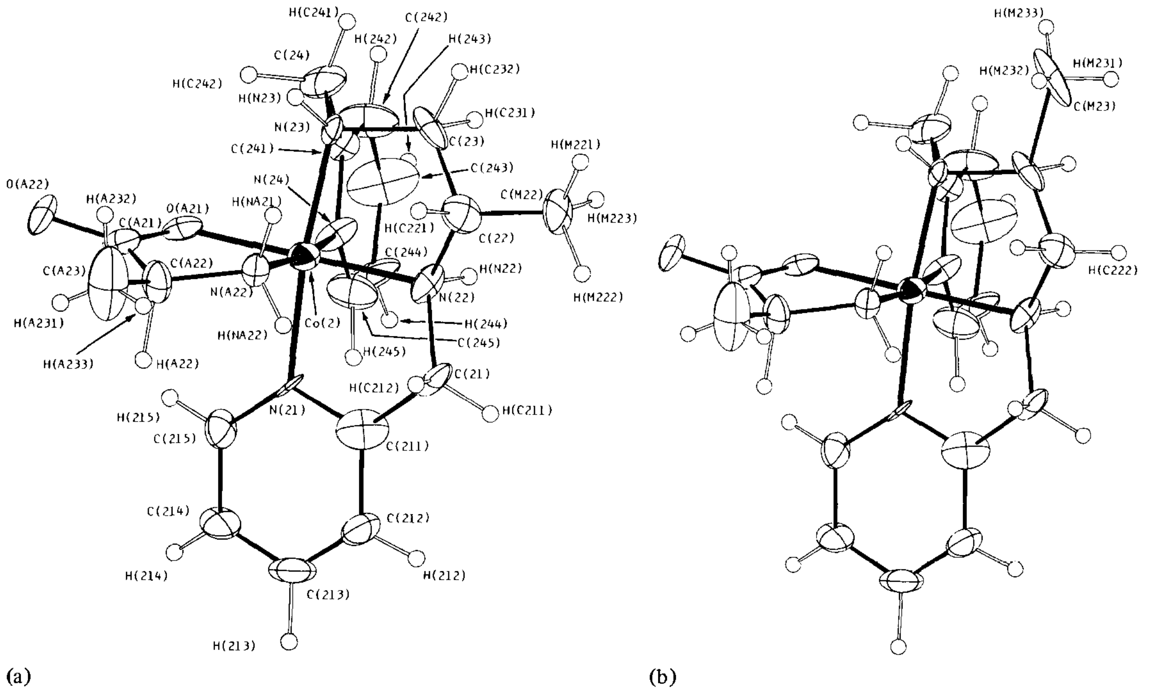
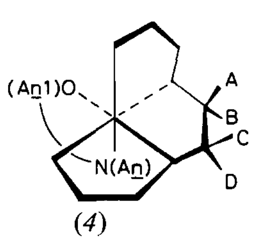


Fig. 3. Perspective drawings of the two Δ cationic forms in the crystal, with thermal ellipsoids scaled to include 35% probability. Hydrogen atoms are included with $B = 1.0$ Å^2. (a) The Δ-β_1-*S,S-endo*-[Co(*S*-picpn)(*S*-ala)]$^+$ ion present in 62% occupancy. (b) The Δ-β_1-*S,S-exo*-[Co(*S*-picpn)(*S*-ala)]$^+$ ion present in 38% occupancy. Labelled atoms demonstrate the unique differences between this and the *endo* isomer shown in (a).

the same as they would be in analogous complexes of picen.

As has been pointed out by other workers [8], and is obvious from Figs. 2 and 3 with the isomers represented in (*2*) and (*3*), the disposition of the methyl group in the central chelate ring gives rise to another kind of geometrical isomerism in the β-topology. Four possible diastereomers arise for the Λ-β_1 arrangement shown in (*4*) when the chiralities of the amino acid and N(*n*2) are specified. Conveniently in this case, the positions shown as A and C in (*4*) lie *endo* and those shown as B and D lie *exo* with respect to the folded tetradentate. This arrangement, together with the assignment of absolute configuration to either C(*n*2) or C(*n*3), serves to uniquely specify any of the 64 possible diastereoisomers in the β-[Co(*R,S*-picpn)(*R,S*-aminoacidate)]$^{n+}$ system.



(*4*)

In this analysis no distinction could be made between many of the corresponding atoms in cations of like hand, and thus these atoms have been treated as crystallographically equivalent with full occupancy. None-the-less it should be remembered that this superimposition of atom pairs, including the Co atoms, does exist throughout the crystal and that each relevant parameter reported would thus represent a weighted average. An analysis of vibration for all atoms shows no obvious anomalies resulting from this positional averaging. The r.m.s. displacement values defining the principal axes of the thermal ellipsoids for atoms in the complex cations give full occupancy range from 0.05 to 0.51 Å. The corresponding minima and maxima for uniquely positioned atoms with fractional occupancies are 0.05 and 0.63 Å respectively.

The four perchlorate ions in the asymmetric unit show a high degree of disorder (Fig. 1), and there is no obvious correlation between the suggested occupancies of these oxygen atoms and the determined cation ratio. The Cl–O bond lengths range from 1.10(3) to 1.57(3) Å with the average being 1.39 Å. Oxygen atoms O(121) and O(221) are the only perchlorate O's with full occupancy, and it would seem that these are involved in H-bonding with the NH_2 groups of the amino acids (Table III). Other weak H-bonds involving perchlorate O atoms and amine protons of the complex cations are suggested by the N···O distances.

TABLE III. Possible Hydrogen Bonds (Å). Donor-acceptor Distances are given with e.s.d.'s in Parentheses.

N(12). . . .O(211)	at $x, y, z-1$	3.19(2)
N(13). . . .O(124)	at x, y, z	3.09(4)
N(13). . . .O(A12)	at $\bar{x}, ½+y, \bar{z}$	2.88(2)
N(22). . . .O(111)	at $x+1, y, z$	2.87(2)
N(23). . . .O(224)	at x, y, z	2.95(2)
N(23). . . .O(A22)	at $1-x, y-½, 1-z$	3.02(1)
N(A1) . . .O(A12)	at $\bar{x}, ½+y, \bar{z}$	2.71(2)
N(A1) . . .O(A12′)	at $\bar{x}, ½+y, \bar{z}$	2.97(6)
N(A1) . . .O(121)	at $\bar{x}, ½+y, \bar{z}$	3.03(1)
N(A2) . . .O(221)	at $1-x, y-½, 1-z$	3.06(1)
N(A2) . . .O(A22)	at $1-x, y-½, 1-z$	2.84(1)

The two shortest intermolecular contacts in the crystal are 2.81(3) Å between O(116) and C(M22) at $x-1, y, z$, and 2.82(3) Å between C(A11′) and O(127). These distances, which are less than those calculated from van der Waal's radii [9], involve only atoms which are present in partial occupancy, and therefore may not represent true interatomic contacts in the real lattice. In fact, this indicated packing difficulty may be a major contributor to the disorder observed. The minor structural differences between pairs of cations of like hand would seem to be well accommodated by the crystal lattice, with unfavourable contacts being avoided through perchlorate disordering.

The bond parameters in the molecular cations are closely comparable (Table IV) with only minor differences between the coordination spheres of the two hands being apparent. The average Co–O, Co–N$_{\text{amine}}$ and Co$_{\text{pyridyl}}$ bond lengths are 1.89(1), 1.94(3) and 1.93(1) Å respectively. Angular distortions in the metal coordination spheres are consistent with the multidentate behaviour of the ligand, and approximate those calculated from the minimization of strain energy in Co(*S*-picpn) models [10].

The pyridyl rings in these cations demonstrate the expected planarity (Table V, planes 1–4) with the Co atoms displaced from these planes to varying degrees. The pyridine rings defined by N(14) and N(24) are approximately perpendicular to their respective meridional N$_3$ planes (planes 5 and 6) with each of the other pyridine rings demonstrating a significant rotation out of these meridional planes (Table V (c)).

The two different configurations adopted by the *S*-alanine molecule in the Λ-diastereoisomers may be seen as the result of crystal packing effects arising from co-crystallization of the four isomeric forms. The fact that the observed occupancy ratio of these two configurations is identical with that of the *endo*/*exo* forms of *R*-picpn demonstrates that this disorder is not random but rather that only the

TABLE IV. Bond Lengths (Å) and Angles (°) in the Complexes.

	$n=1$	$n=2$
Co(*n*)–O(A*n*1)	1.884(6)	1.889(7)
Co(*n*)–N(A*n*)	1.954(8)	1.930(8)
Co(*n*)–N(*n*1)	1.921(9)	1.939(7)
Co(*n*)–N(*n*2)	1.921(10)	1.907(8)
Co(*n*)–N(*n*3)	1.994(9)	1.922(7)
Co(*n*)–N(*n*4)	1.921(9)	1.948(7)
N(*n*1)–C(*n*11)	1.362(13)	1.352(13)
C(*n*11)–C(*n*12)	1.373(14)	1.472(14)
C(*n*12)–C(*n*13)	1.385(17)	1.294(16)
C(*n*13)–C(*n*14)	1.308(17)	1.416(18)
C(*n*14)–C(*n*15)	1.392(15)	1.390(14)
C(*n*15)–N(*n*1)	1.294(14)	1.353(12)
C(*n*11)–C(*n*1)	1.463(17)	1.489(16)
C(*n*1)–N(*n*2)	1.409(14)	1.534(11)
N(*n*2)–C(*n*2)	1.423(15)	1.527(12)
C(*n*2)–C(M*n*2)	1.608(25)	1.430(19)
C(*n*2)–C(*n*3)	1.414(17)	1.588(15)
C(*n*3)–C(M*n*3)	1.450(34)	1.616(33)
C(*n*3)–N(*n*3)	1.476(16)	1.502(12)
N(*n*3)–C(*n*4)	1.541(15)	1.468(13)
C(*n*4)–C(*n*41)	1.517(17)	1.466(11)
C(*n*41)–C(*n*42)	1.328(16)	1.396(13)
C(*n*42)–C(*n*43)	1.378(15)	1.339(16)
C(*n*43)–C(*n*44)	1.317(14)	1.443(16)
C(*n*44)–C(*n*45)	1.392(13)	1.344(15)
C(*n*45)–N(*n*4)	1.371(11)	1.272(13)
N(*n*4)–C(*n*41)	1.342(13)	1.356(10)
O(A*n*1)–C(A*n*1)	1.284(5)	1.322(13)
C(A*n*1)–O(A*n*2)	1.288(22)	1.238(12)
C(A*n*1)–C(A*n*2)	1.499(40)	1.472(16)
C(A*n*2)–C(A*n*3)	1.343(27)	1.328(14)
C(A*n*2)–N(A*n*)	1.570(33)	1.464(12)
O(A*n*1)–C(A*n*1′)	1.254(5)	
C(A*n*1′)–O(A*n*2′)	1.159(53)	
C(A*n*1′)–C(A*n*2′)	1.530(73)	
C(A*n*2′)–C(A*n*3′)	1.598(60)	
C(A*n*2′)–N(A*n*)	1.268(69)	
O(A*n*1)–Co(*n*)–N(A*n*)	83.8(3)	85.9(3)
O(A*n*1)–Co(*n*)–N(*n*1)	99.5(4)	94.5(3)
O(A*n*1)–Co(*n*)–N(*n*2)	176.0(3)	177.9(3)
O(A*n*1)–Co(*n*)–N(*n*3)	95.2(4)	91.1(3)
O(A*n*1)–Co(*n*)–N(*n*4)	90.3(3)	86.6(3)
N(A*n*)–Co(*n*)–N(*n*1)	88.5(4)	88.9(3)
N(A*n*)–Co(*n*)–N(*n*2)	93.1(4)	96.3(3)
N(A*n*)–Co(*n*)–N(*n*3)	92.0(4)	95.5(3)
N(A*n*)–Co(*n*)–N(*n*4)	172.8(4)	172.2(3)
N(*n*1)–Co(*n*)–N(*n*2)	82.9(4)	85.7(3)
N(*n*1)–Co(*n*)–N(*n*3)	165.4(5)	173.1(3)
N(*n*1)–Co(*n*)–N(*n*4)	96.5(4)	93.5(3)
N(*n*2)–Co(*n*)–N(*n*3)	82.5(5)	88.6(3)
N(*n*2)–Co(*n*)–N(*n*4)	92.6(4)	91.3(3)
N(*n*3)–Co(*n*)–N(*n*4)	84.4(4)	82.8(3)
Co(*n*)–N(*n*1)–C(*n*11)	115.5(8)	109.2(7)
Co(*n*)–N(*n*1)–C(*n*15)	123.9(10)	127.2(7)
C(*n*11)–N(*n*1)–C(*n*15)	120.0(10)	123.5(8)

(continued overleaf)

TABLE IV. *(continued)*

	n = 1	*n* = 2
N(*n*1)–C(*n*11)–C(*n*12)	119.2(12)	116.4(11)
N(*n*2)–C(*n*2)–C(*n*3)	117.4(14)	94.9(8)
N(*n*2)–C(*n*2)–C(M*n*2)	110.1(12)	116.5(11)
C(*n*3)–C(*n*2)–C(M*n*2)	121.6(15)	110.3(10)
C(*n*2)–C(*n*3)–C(M*n*3)	124.4(28)	121.1(16)
C(*n*2)–C(*n*3)–N(*n*3)	100.7(11)	114.5(8)
N(*n*3)–C(*n*3)–C(M*n*3)	115.2(22)	109.0(15)
C(*n*3)–N(*n*3)–Co(*n*)	114.6(9)	104.4(6)
C(*n*3)–N(*n*3)–C(*n*4)	116.2(10)	108.8(8)
Co(*n*)–N(*n*3)–C(*n*4)	101.1(7)	111.5(6)
N(*n*3)–C(*n*4)–C(*n*41)	106.6(10)	108.9(8)
C(*n*4)–C(*n*41)–N(*n*4)	112.8(12)	115.2(8)
C(*n*4)–C(*n*41)–C(*n*42)	124.0(12)	124.9(9)
C(*n*41)–N(*n*4)–Co(*n*)	114.2(9)	114.2(6)
C(*n*41)–N(*n*4)–C(*n*45)	118.1(10)	117.0(9)
C(*n*45)–N(*n*4)–Co(*n*)	127.7(7)	128.8(9)
N(*n*4)–C(*n*41)–C(*n*42)	123.1(12)	119.9(9)
C(*n*41)–C(*n*42)–C(*n*43)	119.4(12)	122.1(11)
C(*n*42)–C(*n*43)–C(*n*44)	118.9(11)	116.3(12)
C(*n*43)–C(*n*44)–C(*n*45)	121.9(11)	116.2(11)
C(*n*44)–C(*n*45)–N(*n*4)	118.4(10)	128.2(11)
C(*n*11)–C(*n*12)–C(*n*13)	118.3(12)	119.8(12)
C(*n*12)–C(*n*13)–C(*n*14)	121.9(13)	122.8(10)
C(*n*13)–C(*n*14)–C(*n*15)	117.3(13)	117.5(12)
C(*n*14)–C(*n*15)–N(*n*1)	122.9(13)	120.0(11)
N(*n*1)–C(*n*11)–C(*n*1)	111.7(10)	121.8(10)
C(*n*1)–C(*n*11)–C(*n*12)	129.1(12)	121.5(12)
C(*n*11)–C(*n*1)–N(*n*2)	112.5(10)	102.6(8)
C(*n*1)–N(*n*2)–Co(*n*)	110.8(7)	110.5(6)
C(*n*2)–N(*n*2)–Co(*n*)	106.5(7)	109.0(6)
C(*n*1)–N(*n*2)–C(*n*2)	124.6(12)	110.5(8)
O(A*n*1)–C(A*n*1)–O(A*n*2)	122.9(9)	120.3(13)
O(A*n*2)–C(A*n*1)–C(A*n*2)	118.7(12)	116.2(11)
O(A*n*2)–C(A*n*1)–C(A*n*2)	118.4(14)	123.3(12)
C(A*n*1)–C(A*n*2)–N(A*n*)	104.6(17)	110.2(9)
C(A*n*1)–C(A*n*2)–C(A*n*3)	118.3(27)	122.7(12)
N(A*n*)–C(A*n*2)–C(A*n*3)	116.0(24)	119.0(12)
O(A*n*1)–C(A*n*1)–O(A*n*2′)	129.4(27)	
O(A*n*1)–C(A*n*1′)–C(A*n*2′)	109.3(24)	
O(A*n*2′)–C(A*n*1′)–C(A*n*2′)	118.6(33)	
C(A*n*1′)–C(A*n*2′)–N(A*n*)	118.8(48)	
C(A*n*1′)–C(A*n*2′)–C(A*n*3′)	110.6(4)	
N(A*n*)–C(A*n*2′)–C(A*n*3′)	124.8(14)	
Co(*n*)–O(A*n*1)–C(A*n*1)	118.1(4)	114.0(8)
Co(*n*)–N(A*n*)–C(A*n*2)	110.9(16)	108.7(7)
Co(*n*)–O(A*n*1)–C(A*n*1′)	118.1(4)	
Co(*n*)–N(A*n*)–C(A*n*2′)	109.2(31)	108.7(6)

two discrete Λ forms are present in the crystal. This same ratio is maintained in the Δ diastereoisomers containing S-picpn, which would tend to maximize the symmetry of the crystal packing.

There are no unfavourable intramolecular contacts evident involving the S-alanine groups of the cations. In particular no such interaction with the pyridyl rings is observed as is apparent in like complexes containing coordinated diimines [11]. The adoption of β_1 topologies avoids such an interaction which would be possible, however, if either a β_2 or α topology were to be adopted.

Discussion

It has previously been found [2, 3] that Λ-α-[Co(R-picpn)Cl$_2$]$^+$ reacts with oxalate and nitrite ions in aqueous solution to yield Δ-α-[Co(R-picpn)Ox)]$^+$ and Δ-β-[Co(R-picpn)(NO$_2$)$_2$]$^+$, respectively. These results confirm that optically active picpn does not coordinate entirely stereospecifically, as was first thought [12]. Bosnich [12] originally pointed out that R-picpn is least strained in the Λ-α complex as was subsequently found in the least soluble diastereoisomer of [Co(R-picpn)Cl$_2$]ClO$_4$. The reason for this is related to the requirement for the methyl group of the central chelate ring to lie in an equatorial position. For the Λ-α complex of R-picpn this conformation leads to the pyridyl groups being attached to the axial position of the coordinated diamine nitrogen atoms. Considerably greater strain is introduced in the Δ-α arrangement, in which the methylene bridges to the pyridyl rings are attached equatorially with respect to the above nitrogen atoms. Notwithstanding these considerations it has proved possible to prepare Δ-α-[Cr(R-picpn)Cl$_2$]$^+$ or its mirror image [13], and an analogous complex of N,N'-bis(2-picolyl)-*trans*-1,2-diaminocyclohexane [14]. Evidently such steric strain can be accommodated in certain instances.

The isolation of four diastereoisomers here, two for each hand of picpn, illustrates again the flexibility of the tetradentate, and highlights the fact that extensive changes in the coordination sphere may accompany the reactions of Co(III) complexes of this and related ligands. Of the four isomers described above, both the β diastereomers containing R-picpn adopt the Λ absolute configuration and were both derived from Λ-α-[Co(R-picpn)Cl$_2$]$^+$. The converse is true when the ligand has the S configuration. It is possible that this preferential adoption of Δ or Λ hands in the β isomers of [Co(picpn)(S-ala)]$^{2+}$ reflects differences is stability between these and other possible configurations.

Brubaker and Euler [10] carried out a series of strain energy minimization calculations and concluded that Co(III) complexes of S-picpn with Δ-β topology are more stable than their Λ-β analogues. Interestingly, although little difference was found for the total strain energies for *exo* and *endo* arrangements for the same absolute configurations, it was shown that the *endo* form was slightly favoured. These results parallel the isomeric distribution found in the structural analysis reported above and it is then evident that the ratios of diastereomers present may indeed be due to differences of stability. How-

TABLE V. Least-squares Planes Data.

(a) Least-squares planes and their equations given by $lX' + mY' + nZ' - p = 0$ where X', Y' and Z' are orthogonal coordinates (Å) derived with respect to the orthogonal axes *a'*, *b*, *c*

Plane No.	Atoms Defining Plane	*l*	*m*	*n*	*p*
1	N(111), C(111)–C(115)	0.8874	–0.3299	–0.3221	2.3842
2	N(141), C(141)–C(145)	0.4974	0.8098	–0.3111	0.8347
3	N(211), C(211)–C(215)	0.8389	0.3757	–0.3937	7.2140
4	N(241), C(241)–C(245)	0.5337	–0.7880	–0.3068	3.6921
5	N(11), N(12), N(13)	0.7483	–0.5763	–0.3285	2.5567
6	N(21), N(22), N(23)	0.7550	0.5766	–0.3122	6.7546
7	N(A1), C(A11), O(A11), Co(1)	–0.4608	–0.2276	–0.8578	1.4935
8	N(A1), C(A11'), O(A11), Co(1)	–0.5218	–0.2585	–0.8131	1.3621
9	N(A2), C(A21), O(A21), Co(2)	0.4155	–0.2285	0.8804	5.9505
10	O(A11), O(A12), C(A12)	–0.3823	–0.3813	–0.8417	1.8216
11	O(A11), O(A12'), C(A12')	–0.4427	–0.0941	–0.8917	1.1886
12	O(A21), O(A22), C(A22)	0.3738	–0.4296	0.8220	5.0190

(b) Deviations (Å) of relevant atoms from least-squares planes defined above.

Plane No.	
1	N(111) –0.008, C(111) 0.017, C(112) –0.024, C(113) 0.023, C(114) –0.013, C(115) 0.006, Co(1) 0.18, C(11) 0.15
2	N(141) 0.021, C(141) –0.019, C(142) 0.008, C(143), C(144) 0.001, C(145) –0.012, Co(1) 0.05, C(14) –0.19
3	N(211) –0.019, C(211) 0.017, C(212) 0.004, C(213) –0.022, C(214) 0.020, C(215) 0.001, Co(2) –0.08, C(21) –0.06
4	N(241) –0.001, C(241) –0.016, C(242) 0.011, C(243) 0.008, C(244) –0.024, C(245) 0.022, Co(2) –0.01, C(24) –0.05
7	N(A1) –0.031, C(A11) 0.053, O(A11) –0.067, Co(1) 0.044, O(A12) –0.05, C(A12) 0.31
8	N(A1) 0.007, C(A11') –0.012, O(A11) 0.015, Co(1) –0.010, O(A12') 0.32, C(A12') –0.12
9	N(A2) 0.030, C(A21) –0.048, O(A21) 0.060, Co(2) –0.042, O(22) 0.18, C(A22) –0.31
10	Co(1) –0.06, C(A11) 0.006
11	Co(1) 0.35, C(A11') –0.12
12	Co(2) 0.22, C(A21) –0.04

(c) Angles (°) between planes

2–5	89.6	1–5	16.3
4–6	87.5	3–6	13.4
7–8	4.7		

ever, it should be noted that the second fraction eluted from the column (see Experimental sections) has proved [4] to be a Δ-β isomer of *R*-picpn, and therefore other isomers are also accessible in this system.

That this is the case is illustrated by a recent crystallographic structure determination of a related Co(III) complex of *N,N'*-di-8-quinolyl-*R*-1,2-diaminopropane, *R*-dqpn, and acetylacetone, acacH [15]. Both Δ- and Λ-β-[Co(*R*-dqpn$_{-H}$)(acac)]$^+$ complex ions are present in the compound, in two crystallographically independent sites, and with an approximate centre of symmetry. Suzuki *et al.*, [15] remarked that the structure is disordered in that the methyl group was attached to both carbon atoms of the aliphatic chelate ring. Of course this is not really a disordering *per se*, but rather one more example of both *exo* and *endo* isomers occupying the same crystallographic site. Indeed, the ^{1}H NMR spectra of the complex in d_6-acetone and 12 mol/dm^3 DCl in D_2O, can only be interpreted on the basis that there are more than two isomers present because of the multiplicity of resonances corresponding to particular protons.

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