The Λ-β_2-[Co(2(*S*),10(*S*)-Me$_2$-2,3,2-tet)(*R*- and *S*-ala)]$^{2+}$ complexes have less strained structures. The strain energies of the two isomers are about 4.6 kcal/mol and show only a slight difference. On the other hand, the *SS*-pyht complexes were found to have large strain energies owing to the pyrrolidine rings. Angle deformations and torsinal strains within the pyrrolidine rings are considerably large. Further, the H(11)···H(28) (2.01 Å, 1.1 kcal/mol), H(21)···O(1) (2.34 or 2.37 Å, 0.5 kcal/mol), and H(12)···H(29) (2.24 Å, 0.3 kcal/mol) interactions are derived from the methylene protons of the pyrrolidine rings. The significantly large repulsive contact between the methylene proton of the apical pyrrolidine ring and NH proton of N(3) atom (H(11)···H(28)) appears to cause a large angular distorsion: N(1)–Co–N(3), 98.6° (1.1 kcal/mol) in the *S*-ala complex and 98.5° (1.1 kcal/mol) in the *R*-ala complex. The Co–N(1)–C(1) and Co–N(4)–C(13) angles are expanded: *S*-ala complex, 124.1 (1.9) and 119.0° (0.8 kcal/mol), and *R*-ala complex, 123.9 (1.8) and 119.3° (0.9 kcal/mol), respectively. With respect to the bond length the Co–N(1) bonds are extended: 2.00 Å (0.36 kcal/mol) in both cations.

Final minimized strain energies indicate that the (*S*)-alaninato complex with *SS*-pyht is 0.75 kcal/mol less stable than the (*R*)-alaninato complex. Major contributions to the energy difference come from the torsional strain and angle deformations. Though the difference between the final nonbonded interaction terms is relatively small, initial calculations showed significantly large nonbonded interactions in *S*-ala complex: H(22)···H(31), between the C–H proton of alaninate and the methylene proton of the in-plane pyrrolidine ring, and H(23)···H(25), between the proton of the amino group of alaninate and that of the apical amino group of *SS*-pyht. Twisting about N(5)–C(14) reduces those close contacts, while the (*S*)-alaninate ring adopts a strained, near-planar, conformation: ϕ(N(5)–C(14)), ϕ(C(14)–C(15)), and ϕ(C(15)–O(1)) = 4.8 (1.5), 10.0 (0.4), and 10.5° (0.2 kcal/mol) respectively, in the *S*-ala complex; 23.9 (1.0), 20.7 (0.3), and 6.5° (0.1 kcal/mol), respectively, in the *R*-ala complex.

The strain energy minimization calculations are in good agreement with the relative stability and energy difference for the diastereomers of Λ-β_2-[Co(ala)(*SS*-pyht)]$^{2+}$. These results suggest that the destabilization of the Λ-β_2-[Co(*S*-ala)(*SS*-pyht)]$^{2+}$ ion was due mostly to intramolecular strain energy. However, it fails to predict the energy difference observed between the *R*-ala and *S*-ala complexes with 2(*S*),10(*S*)-Me$_2$-2,3,2-tet, though the difference was relatively small (Λ-*S*/Λ-*R* = 66/34, $\Delta G = -0.41$ kcal/mol). In these calculations electrostatic or dipole interactions have been neglected. Hydrogen bonding and solvation energy are also not taken into consideration. It is possible that these effects play a significant role to make a difference between the diastereomers, though it is difficult to evaluate these terms.[16a,23]

From the viewpoint of asymmetric transformation, N-substitution of the tetraamine, as the pyrrolidine ring of *SS*-pyht, results in an improvement in the stereoselectivity described above. On the other hand, it accelerates some unfavorable side reactions. It seems rather hard to overcome these two conflicting demands for (N$_4$), selectivity and stability, but attempts directed at reducing the decomposition of complex are now in progress. With respect to amino acidate moieties, α-substituted amino acids appear to have a significant effect on the selectivity. In subsequent papers the results of epimerization of other amino acidato complexes will be reported.

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Registry No. **1**, 60872-59-5; **2**, 60801-67-4; **3**, 73396-02-8; **4**, 59202-14-1; **5**$_R$, 73493-96-6; **5**$_S$, 73453-08-4; **6**$_R$, 73493-94-4; **6**$_S$, 73453-06-2; **7**$_R$, 68531-65-7; **7**$_S$, 68567-19-1; **8**$_R$, 73465-04-0; **8**$_S$, 64387-64-0; **9**$_R$, 73465-02-8; **9**$_S$, 73396-00-6; **10**$_R$, 73493-92-2; **10**$_S$, 73453-04-0; **11**$_R$, 73493-90-0; **11**$_S$, 73453-02-8; **12**$_R$, 73493-88-6; **12**$_S$, 73453-00-6; **13**$_R$, 64439-79-8; **13**$_S$, 64387-62-8; 3(*S*),9(*S*)-Me$_2$-2,3,2-tet, 73384-41-5; 2(*S*),8(*S*)-3,7-diaza-2,8-dimethyl-1,9-dibromononane dihydrobromide, 73384-42-6; L-alaninol, 2749-11-3; 1,3-diaminopropane, 109-76-2; sodium tris(carbonato)cobaltate(III), 23311-39-9.

Supplementary Material Available: Final minimized Cartesian atomic coordinates and listings of internal coordinates with their individual strain energies (44 pages). Ordering information is given on any current masthead page.

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Crystal Structure of (+)$_{589}$-β_2-((*R*)-Alaninato)(1,7-bis(2(*S*)-pyrrolidyl)-2,6-diazaheptane)cobalt(III) Perchlorate Dihydrate

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The crystal structure of (+)$_{589}$-β_2-((*R*)-alaninato)(1,7-bis(2(*S*)-pyrrolidyl)-2,6-diazaheptane)cobalt(III) perchlorate dihydrate, (+)$_{589}$-β_2-[Co(*R*-ala)(*SS*-pyht)](ClO$_4$)$_2$·2H$_2$O, has been determined from three-dimensional X-ray data collected by the diffractometer method. The compound forms tetragonal crystals with $a = 9.951$ (3) Å, $c = 52.537$ (25) Å, and $Z = 8$, in space group $P4_12_12$. The structure has been solved by the heavy-atom method and refined by least-squares method with anisotropic temperature factors to give an R value of 0.056 for 1933 observed reflections. The absolute configuration of the complex cation is Λ; the configuration of the alaninato is β_2. The five-membered chelate rings of the tetraamine both have the δ-gauche conformation, and the six-membered chelate ring has a distorted chair conformation. The configuration at the asymmetric centers of the tetraamine are *R* for the inner nitrogen atoms and *S* for the terminal ones.

Introduction

In recent years, the crystal structures of several cobalt(III) complexes containing an α-amino acid and a tetraamine have been determined by X-ray analysis: for example, *cis*-α-, *cis*-β_1-, and *cis*-β_2-[Co(gly)(trien)]$^{2+}$ and Λ-β_2- and Δ-β_2-[Co(*S*-pro)(trien)]$^{2+}$.[1-3] In those studies the tetraamine was tri-

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ethylenetetramine (2,2,2-tet). The crystal structure of an (α-amino acidato)cobalt(III) complex containing a 2,3,2-type tetraamine (2,3,2-tet) has, however, not been reported.

On the other hand, several crystal structures of cobalt(III) complexes containing 2,3,2-tet derivatives have been determined.[4-7] Freeman recently reported the crystal structures of *trans*-[$CoCl_2$(*SS*-pyht)]ClO_4 and Λ-β-[(Co(ox)(*SS*-pyht)]ClO_4,[7] where *SS*-pyht is one of the 2,3,2-type tetraamines, 1,7-bis(2(*S*)-pyrrolidyl)-2,6-diazaheptane. The quadridentate ligand *SS*-pyht in cis form was considered to coordinate stereoselectively in Λ-β configuration and was expected to have a possibility of stereoselectivity upon other ligands coordinated in the remaining two positions of the complex.[8]

Sargeson and co-workers showed[9] that hydroxide ion catalyzed epimerization of the α-amino acidate moiety in cobalt complexes Λ- (or Δ-) [Co(*R*- or *S*-aa)(en)$_2$]$^{2+}$ occurs in basic aqueous solution. It may be considered as an example of "first-order asymmetric transformation"[10] of racemic α-amino acid. Previously, we have studied the epimerization in Λ-β_2-[Co(*R*- or *S*-aa)(N$_4$)]$^{2+}$, where (N$_4$) indicates four nitrogen atoms of chiral tetraamine (trien or 2,3,2-tet derivative), and in the most favorable case, Λ-β_2-[Co(ala)(*SS*-pyht)]$^{2+}$ showed the isomer ratio Λ-*S*/Λ-*R* = 18/82.[11] In this paper the result of an X-ray diffraction study to determine the crystal structure of $(+)_{589}$-β_2-[Co(*R*-ala)(*SS*-pyht)]$(ClO_4)_2 \cdot 2H_2O$, which is the predominant isomer at equilibrium of the epimerization, is reported.

Experimental Section

$(+)_{589}$-β_2-[Co(*R*-ala)(*SS*-pyht)]$(ClO_4)_2 \cdot 2H_2O$ was prepared by the method described elsewhere.[11b]

The specimens are orange-red tetragonal-pyramidal crystals in which the base is parallel to *a* and *b* axes. Weissenberg photographs taken with Cu Kα radiation showed tetragonal symmetry with systematic absence of (h00) when $h \neq 2n$ and (00l) when $l \neq 4n$. It indicated that the space group of the crystal was one of the enantiomorphic pair $P4_12_12$ and $P4_32_12$. Unit cell parameters were obtained from a least-squares refinement of 12 reflections centered on a Rigakudenki four-circle automatic diffractometer using Mo Kα radiation (λ 0.7107 Å). The measured crystal density (D_m = 1.572 g/cm^3, flotation in $CHCl_3/CCl_4$) requires eight formula units per cell (D_x = 1.589 g/cm^3 for Z = 8).

Crystal data for $CoC_{16}H_{38}N_5O_{12}Cl_2$: mol wt 622.3; tetragonal; a = 9.951 (3), c = 52.537 (25) Å; V = 5202.3 Å^3; D_m = 1.572 g/cm^3; Z = 8; D_x = 1.589 g/cm^3; μ(Mo Kα) = 9.55 cm^{-1}; space group $P4_12_12$ ($D_4{}^4$, No. 92).

The crystal used in the data collection was a well-formed tetragonal pyramid with the approximate dimensions of 0.5 × 0.5 × 0.3 mm. The crystal was mounted with the *a* axis approximately parallel to the instrument axis. The intensity data were collected by the ω–2θ scan technique using Mo Kα radiation monochromated by a LiF crystal on a Rigakudenki four-circle automatic diffractometer. The takeoff angle was 3°. As a general check on the electronic and crystal stability, the intensities of four standard reflections (5,0,12), (0,0,32), (−4,4,20), and (0,6,1) were monitored every 50 reflections during the data collection. The net counts of these reflections did not alter noticeably over the period of data collection. A total of about 5000 intensities were measured up to $2\theta = 60°$. Those reflections which were nonequivalent as a result of anomalous dispersion were treated as independent reflections. The reflections of which the intensities were less than 3 times their standard deviations were regarded as "unobserved" and were not included in subsequent calculations. Thus, 1933 independent reflections were collected. The intensities were corrected for Lorentz and polarization effects. An absorption correction (μ = 9.55 cm^{-1}), using the program INCOR, was applied to the data. The intensities were reduced to a set of structure factors *F*.

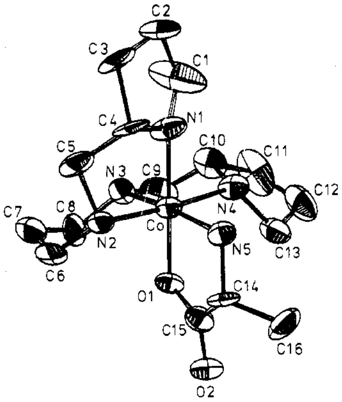

Figure 1. A perspective drawing of the complex cation Λ-β_2-[Co-(*R*-ala)(*SS*-pyht)]$^{2+}$ and the numbering scheme for the atoms. Ellipsoids enclose 50% probability.

Structure Solution and Refinement

A three-dimensional Patterson function revealed the position of the cobalt atom. The remaining nonhydrogen atoms were located by the application of the Fourier method. At this stage, the absolute configuration of the whole complex ion was determined by the known absolute configuration of the asymmetric carbon atoms of the tetraamine and alaninato ligands as internal reference asymmetric centers. And it also revealed that the space group of the crystal was $P4_12_12$. Full-matrix least-squares refinement using both positional and isotropic temperature factors (except hydrogen atoms) reduced the R_1 value to 0.100 and R_2 to 0.127, where $R_1 = \sum \| F_o| - |F_c\| / \sum |F_o|$ and R_2 (the weighted *R* factor) = $(\sum w(|F_o| - |F_c|)^2 / \sum w F_o{}^2)^{1/2}$. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where w = 1.0. Up to this stage one water molecule was included in calculation. A difference Fourier synthesis was then calculated which revealed a position of other water molecule with a height of about one-half that of an oxygen atom. The occupancy factor for this atom was refined and converged at 0.54 (4). Then, the weight 0.5 was used for it. This water molecule was assumed to be disordered, but an effort to locate the other disordered position failed. Several cycles of refinement including second water molecule reduced the *R* value to 0.095.

Next, refinement with 36 all nonhydrogen atoms included (with anisotropic temperature factors) gave R_1 = 0.068 and R_2 = 0.080. At this point, idealized positional coordinates of the hydrogen atoms, other than those of the water molecules, were included in the scattering model (regular tetrahedral geometry, d(C–H) = 0.95 Å, d(N–H) = 0.87 Å).[12] Isotropic thermal parameters for these hydrogens were fixed at values assigned by $B_H = (1.0 + B)$ Å^2 (B is the isotropic thermal parameter of bonded atom).[13] In subsequent several cycles the parameters of the hydrogen atoms were not permitted to vary but were recalculated at every cycle. Least-squares refinement, assigning

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Table I. Final Atomic Parameters

(a) Final Positional Parameters ($\times 10^4$) and Their Estimated Standard Deviations (in Parentheses)

atom	x	y	z	atom	x	y	z
Co	3752.7 (15)	−1054.1 (15)	745.3 (2)	C(9)	4556 (15)	−3202 (14)	422 (2)
Cl(1)	−932.7 (56)	3355.9 (62)	236.6 (6)	C(10)	5816 (14)	−2467 (14)	468 (2)
Cl(2)	−647.7 (41)	−1391.0 (43)	1413.1 (7)	C(11)	7031 (14)	−3382 (15)	517 (3)
N(1)	4216 (12)	590 (11)	551 (1)	C(12)	7463 (14)	−3162 (16)	786 (3)
N(2)	1895 (9)	−344 (9)	750 (1)	C(13)	6253 (14)	−2584 (12)	921 (2)
N(3)	3418 (10)	−2243 (10)	443 (1)	C(14)	3560 (13)	−917 (12)	1289 (1)
N(4)	5647 (9)	−1686 (9)	717 (1)	C(15)	3311 (12)	−2351 (12)	1193 (2)
N(5)	4136 (9)	−139 (8)	1067 (1)	C(16)	4409 (16)	−797 (16)	1529 (2)
O(1)	3244 (8)	−2542 (7)	949 (1)	O(3)	−365 (16)	2458 (15)	66 (2)
O(2)	3092 (8)	−3251 (8)	1351 (1)	O(4)	−1984 (14)	3984 (21)	116 (2)
C(1)	5004 (20)	941 (18)	361 (4)	O(5)	36 (18)	4184 (22)	327 (3)
C(2)	4721 (17)	2365 (15)	274 (2)	O(6)	−1457 (21)	2785 (23)	460 (2)
C(3)	3320 (15)	2596 (15)	362 (2)	O(7)	−651 (21)	−384 (13)	1237 (2)
C(4)	3084 (14)	1587 (13)	586 (2)	O(8)	−138 (18)	−2546 (12)	1306 (2)
C(5)	1789 (15)	794 (15)	555 (2)	O(9)	−1914 (15)	−1526 (20)	1480 (3)
C(6)	773 (11)	−1301 (15)	696 (1)	O(10)	46 (17)	−986 (16)	1625 (2)
C(7)	922 (14)	−2124 (15)	454 (2)	O(W1)	7389 (13)	559 (11)	867 (3)
C(8)	2124 (14)	−3026 (15)	446 (2)	O(W2)	8252 (25)	−172 (31)	228 (6)

(b) Final Anisotropic Thermal Parameters and Their Estimated Standard Deviations (in Parentheses)[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	3.08 (10)	2.78 (9)	2.30 (7)	0.05 (8)	0.50 (6)	0.29 (6)
Cl(1)	6.9 (2)	13.0 (4)	3.2 (1)	2.7 (3)	−0.6 (2)	−2.0 (2)
Cl(2)	5.6 (2)	4.6 (2)	4.5 (1)	1.3 (1)	0.1 (1)	0.1 (1)
N(1)	5.1 (6)	4.7 (6)	2.9 (4)	1.5 (5)	1.6 (5)	1.3 (4)
N(2)	3.4 (5)	4.5 (5)	2.0 (4)	−0.8 (4)	0.3 (4)	0.3 (4)
N(3)	3.1 (5)	3.7 (5)	2.6 (4)	−0.2 (4)	0.5 (4)	−0.8 (4)
N(4)	4.1 (5)	2.2 (4)	4.0 (5)	1.0 (3)	0.6 (4)	0.6 (4)
N(5)	3.5 (5)	2.4 (4)	2.8 (4)	0.5 (4)	0.3 (4)	0.2 (3)
O(1)	3.3 (4)	2.7 (3)	2.5 (3)	−0.3 (3)	1.2 (3)	−0.0 (3)
O(2)	4.9 (4)	3.1 (4)	2.7 (3)	−0.2 (3)	1.1 (3)	0.3 (3)
C(1)	8.7 (12)	5.1 (10)	13.7 (15)	1.0 (10)	6.3 (11)	3.2 (11)
C(2)	7.5 (11)	4.9 (9)	5.0 (8)	−1.3 (8)	1.0 (7)	3.1 (7)
C(3)	6.4 (8)	6.9 (9)	0.8 (5)	1.3 (7)	0.7 (5)	1.7 (5)
C(4)	5.4 (8)	4.1 (7)	1.7 (4)	1.7 (7)	1.7 (5)	1.9 (4)
C(5)	5.3 (8)	5.8 (9)	1.5 (5)	1.5 (7)	1.1 (5)	0.8 (5)
C(6)	3.8 (6)	6.8 (8)	1.6 (5)	−0.7 (7)	1.8 (4)	−0.1 (5)
C(7)	4.1 (8)	6.3 (9)	3.9 (7)	−1.4 (7)	0.6 (6)	0.6 (6)
C(8)	3.4 (7)	6.0 (9)	3.1 (6)	−1.0 (7)	−0.6 (5)	−1.7 (6)
C(9)	5.8 (9)	3.8 (7)	4.2 (7)	0.1 (7)	2.4 (6)	−1.3 (5)
C(10)	3.9 (7)	4.3 (8)	5.7 (8)	1.2 (6)	1.5 (6)	−0.1 (6)
C(11)	3.5 (8)	4.4 (8)	12.9 (14)	2.0 (7)	1.4 (9)	−2.8 (9)
C(12)	2.6 (7)	5.7 (9)	9.4 (11)	0.4 (6)	0.8 (8)	0.5 (9)
C(13)	3.1 (6)	3.8 (6)	5.9 (7)	0.3 (6)	1.0 (6)	1.6 (5)
C(14)	4.7 (7)	3.5 (7)	2.2 (4)	−0.2 (6)	1.2 (4)	1.7 (4)
C(15)	3.3 (6)	3.2 (6)	3.4 (6)	−0.3 (5)	0.8 (5)	−0.4 (5)
C(16)	8.7 (10)	7.2 (10)	3.0 (5)	−2.8 (8)	−2.8 (6)	1.7 (6)
O(3)	15.4 (12)	12.3 (10)	8.1 (8)	5.6 (9)	−1.7 (8)	−5.4 (8)
O(4)	11.4 (10)	27.5 (20)	5.0 (6)	10.8 (13)	−3.1 (6)	−3.6 (9)
O(5)	12.7 (12)	22.6 (20)	16.0 (14)	−3.5 (14)	−3.3 (11)	−7.5 (15)
O(6)	20.0 (17)	30.5 (23)	3.8 (6)	1.9 (18)	3.8 (9)	0.4 (10)
O(7)	27.4 (21)	7.5 (8)	4.4 (6)	2.3 (10)	1.4 (10)	−0.0 (6)
O(8)	18.7 (14)	6.3 (7)	8.9 (8)	7.2 (9)	1.8 (8)	−0.4 (6)
O(9)	9.1 (9)	18.8 (16)	15.7 (13)	−2.8 (11)	7.5 (9)	−6.6 (12)
O(10)	19.4 (14)	12.5 (11)	7.7 (8)	6.8 (11)	−6.6 (9)	−1.7 (8)
O(W1)	9.5 (9)	5.3 (6)	20.8 (15)	−1.0 (6)	−7.0 (9)	−2.3 (7)
O(W2)	6.2 (15)	14.2 (23)	16.1 (27)	3.1 (16)	1.4 (16)	7.3 (20)

[a] Parameters have the form $\exp[-0.25(a^{*2}h^2B_{11} + b^{*2}k^2B_{22} + c^{*2}l^2B_{33} + 2a^*b^*hkB_{12} + 2a^*c^*hlB_{13} + 2b^*c^*klB_{23})]$.

anisotropic thermal parameters to all the atoms except for hydrogen atoms, converged with $R_1 = 0.056$ and $R_2 = 0.067$. The "goodness-of-fit" defined by $(\sum w(|F_o| - |F_c|)^2/(m - n))^{1/2}$ was 2.38, where m is the number of observations and n is the number of variables. Refinement in the Δ configuration with the space group $P4_32_12$ converged with $R_1 = 0.060$ and $R_2 = 0.071$. Thus, the choice of Λ configuration is justified to greater than the 99% significance level according to Hamilton's R factor test.[14] A final difference Fourier map had as its prominent features several peaks 1.6 e/Å^3 in the neighborhood of the cobalt and chlorine atoms. The atomic scattering factors and the corrections for anomalous dispersion of Co and Cl were taken from ref 15. Final atomic parameters and their estimated standard deviations are listed in Table I. The calculations of the absorption correction, the Fourier synthesis, the full-matrix least-squares analysis, and drawings of the crystal and molecular structures were carried out on a HITAC 8700/8800 computer at the computer center of this university using the INCOR, ANSFR-2, FLS-4, and ORTEP2 programs of the UNICS system, respectively.

Description and Discussion of the Structure

The observed structure of the complex ion is represented in Figure 1. The absolute configuration of the cation is Λ, as deduced from the known absolute configuration of the

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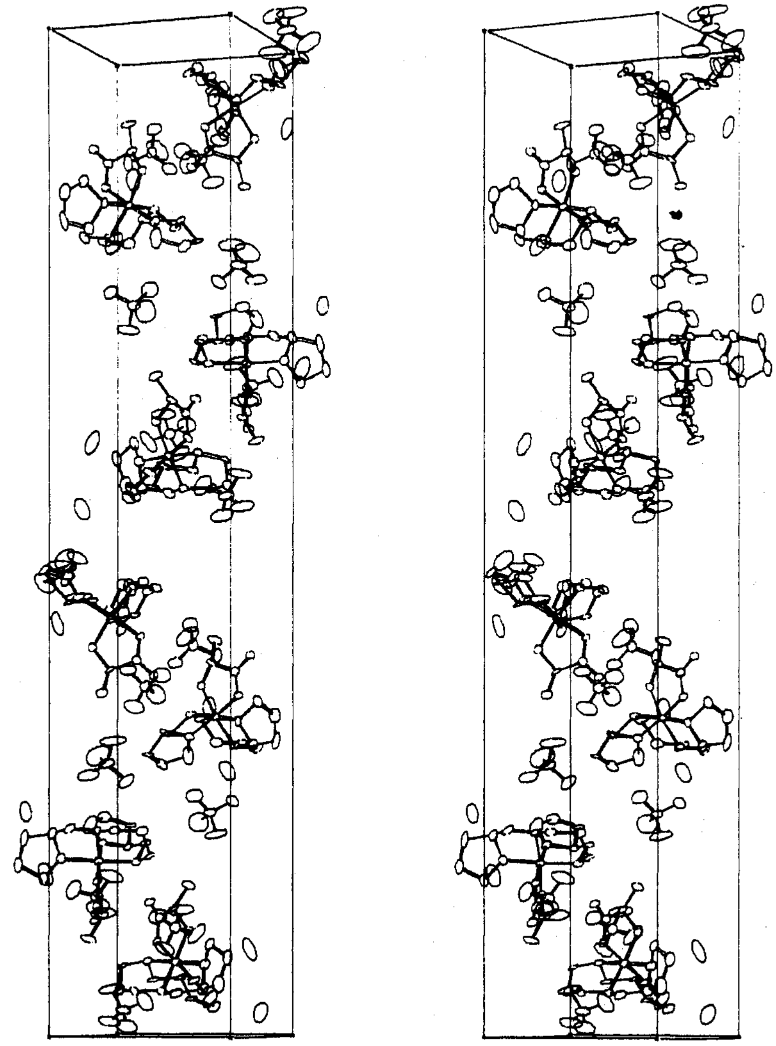

Figure 2. Stereoscopic illustration of the unit cell contents.

Table II. Bond Distances (Å) and Their Estimated Standard Deviations (in Parentheses)

Co–N(1)	1.98 (2)	C(3)–C(4)	1.57 (3)
Co–N(2)	1.98 (2)	C(4)–C(5)	1.52 (3)
Co–N(3)	2.01 (2)	C(6)–C(7)	1.52 (3)
Co–N(4)	2.00 (2)	C(7)–C(8)	1.50 (4)
Co–N(5)	1.96 (2)	C(9)–C(10)	1.47 (4)
Co–O(1)	1.90 (1)	C(10)–C(11)	1.54 (4)
N(1)–C(1)	1.32 (4)	C(11)–C(12)	1.50 (4)
N(1)–C(4)	1.51 (3)	C(12)–C(13)	1.51 (4)
N(2)–C(5)	1.53 (3)	C(14)–C(15)	1.54 (3)
N(2)–C(6)	1.50 (3)	C(14)–C(16)	1.53 (3)
N(3)–C(8)	1.51 (3)	Cl(1)–O(3)	1.39 (3)
N(3)–C(9)	1.49 (3)	Cl(1)–O(4)	1.38 (3)
N(4)–C(10)	1.53 (3)	Cl(1)–O(5)	1.36 (4)
N(4)–C(13)	1.52 (3)	Cl(1)–O(6)	1.41 (4)
N(5)–C(14)	1.52 (3)	Cl(2)–O(7)	1.36 (3)
O(1)–C(15)	1.30 (3)	Cl(2)–O(8)	1.38 (3)
O(2)–C(15)	1.24 (3)	Cl(2)–O(9)	1.32 (3)
C(1)–C(2)	1.52 (5)	Cl(2)–O(10)	1.38 (3)
C(2)–C(3)	1.49 (4)		

Table III. Bond Angles (Deg) and Their Estimated Standard Deviations (in Parentheses)

N(1)–Co–N(2)	86.0 (8)	C(1)–N(1)–C(4)	111.2 (23)
N(1)–Co–N(3)	97.0 (8)	C(5)–N(2)–C(6)	107.1 (16)
N(1)–Co–N(4)	90.2 (8)	C(8)–N(3)–C(9)	108.7 (17)
N(1)–Co–N(5)	90.8 (8)	C(10)–N(4)–C(13)	105.0 (16)
N(1)–Co–O(1)	175.6 (9)	N(1)–C(1)–C(2)	111.5 (21)
N(2)–Co–N(3)	93.8 (7)	C(1)–C(2)–C(3)	103.0 (22)
N(2)–Co–N(4)	175.8 (8)	C(2)–C(3)–C(4)	105.9 (18)
N(2)–Co–N(5)	90.3 (7)	N(1)–C(4)–C(3)	102.6 (15)
N(2)–Co–O(1)	91.3 (7)	N(1)–C(4)–C(5)	106.1 (15)
N(3)–Co–N(4)	85.0 (7)	C(3)–C(4)–C(5)	112.4 (17)
N(3)–Co–N(5)	171.5 (8)	N(2)–C(5)–C(4)	104.7 (15)
N(3)–Co–O(1)	86.6 (7)	N(2)–C(6)–C(7)	115.4 (15)
N(4)–Co–N(5)	91.4 (7)	C(6)–C(7)–C(8)	115.1 (17)
N(4)–Co–O(1)	92.7 (7)	N(3)–C(8)–C(7)	111.9 (16)
N(5)–Co–O(1)	85.8 (6)	N(3)–C(9)–C(10)	108.6 (16)
Co–N(1)–C(1)	138.4 (16)	N(4)–C(10)–C(9)	107.4 (16)
Co–N(1)–C(4)	107.8 (10)	N(4)–C(10)–C(11)	104.2 (16)
Co–N(2)–C(5)	108.7 (10)	C(9)–C(10)–C(11)	113.8 (20)
Co–N(2)–C(6)	117.9 (9)	C(10)–C(11)–C(12)	107.3 (20)
Co–N(3)–C(8)	116.2 (10)	C(11)–C(12)–C(13)	105.6 (20)
Co–N(3)–C(9)	108.2 (11)	N(4)–C(13)–C(12)	102.2 (16)
Co–N(4)–C(10)	109.0 (10)	N(5)–C(14)–C(15)	106.4 (13)
Co–N(4)–C(13)	120.7 (10)	N(5)–C(14)–C(16)	112.9 (14)
Co–N(5)–C(14)	110.8 (9)	C(15)–C(14)–C(16)	115.8 (16)
Co–O(1)–C(15)	115.4 (10)	O(1)–C(15)–O(2)	123.0 (14)
		O(1)–C(15)–C(14)	118.0 (14)
		O(2)–C(15)–C(14)	118.8 (15)

asymmetric carbon atoms of the tetraamine ligand, derived from L-proline and L-alaninato as internal reference asymmetric centers. This same result comes from the determination of absolute configuration by the anomalous dispersion of X-rays. And it is also consistent with the assignment on the basis of the circular dichroism.[11] The tetraamine ligand and amino acidato are coordinated to a cobalt atom in the Λ-cis-β_2 geometry. The arrangement of the group around the secondary nitrogen atoms of the inner amines are both *R* configuration, and those of the terminal amines are both *S*. The unit cell (Figure 2) includes eight complex cations, sixteen perchlorate anions, and sixteen positions of water molecules.

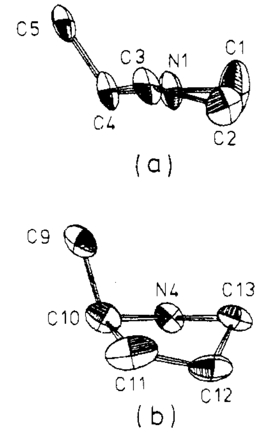

Figure 3. Perspective drawings of the pyrrolidine rings: (a) "out-of-plane" pyrrolidine ring; (b) "in-plane" pyrrolidine ring.[16] The rings are viewed down along a bisector of the C–N–C angle. Ellipsoids enclose 30% probability.

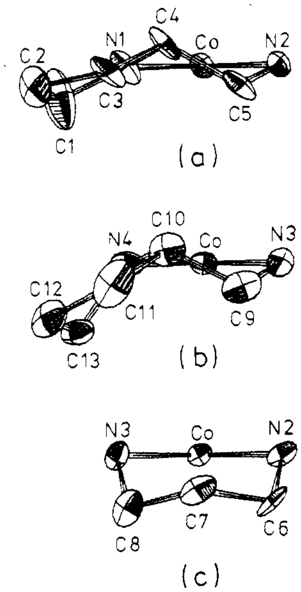

Figure 4. Perspective drawings of the chelate rings: (a) "out-of-plane" five-membered ring;[16] (b) "in-plane" five-membered ring;[16] (c) central six-membered ring. The rings are viewed down along a bisector of the N–Co–N angle. Ellipsoids enclose 30% probability.

Intramolecular bond distances and bond angles are given in Tables II and III, respectively.

It is noteworthy that in the apical pyrrolidine ring N(1)–C(1) bond (1.32 (4) Å) is abnormally short as the C–N single bond, and Co–N(1)–C(1) angle (138.4 (1.6)°) is significantly larger than the regular tetrahedral value. A possible reason for these unusual values is discussed below.

Yet other substantial deviations from the nominal bond angle values are observed. The N(1)–Co–N(3) angle is 97.0 (8)°, which is consistent with the corresponding value (97.9 (2)°) observed in the oxalate complex, Λ-β-[Co(ox)(*SS*-pyht)]$^{+}$.[7] The observed values of the Co–N(2)–C(6), Co–N(3)–C(8), and Co–N(4)–C(13) are 117.9 (9), 116.2 (1.0), and 120.7 (1.0)°, respectively, which also significantly expanded from the tetrahedral.

The angles at the cobalt to the five-membered chelate ring donors are 86.0 (8) and 85.0 (7)° for N(1)–Co–N(2) and N(3)–Co–N(4), respectively, and to the six-membered chelate ring donors is 93.8 (7)°. In the alaninato chelate ring the angle at the cobalt for the five-membered chelate ring N(5)–Co–O(1) is 85.8 (6)°, which is normal for cobalt(III) amino acidate chelate ring.[2,3]

Table IV. Least-Squares Planes[a]

		eq of plane:[b] $aX + bY + cZ = d$			
plane	atoms in plane	*a*	*b*	*c*	*d*
1	N(1), C(1), C(3), C(4)	−0.5624	−0.5580	−0.6102	4.4780
2	N(4), C(10), C(11), C(12)	−0.6294	0.7085	0.3192	1.1370

atoms	dev from plane 1, Å	atoms	dev from plane 2, Å
N(1)	0.017	N(4)	−0.010
C(1)	−0.012	C(10)	0.018
C(3)	0.009	C(11)	−0.017
C(4)	−0.015	C(12)	0.009
C(2)	−0.366	C(13)	0.586

[a] These unweighted least-squares planes were calculated with a program DAPH written by Dr. Ashida. [b] The coordinates *X*, *Y*, and *Z* are expressed in angstroms referred to the crystal axes *a*, *b*, and *c*.

Table V. Selected Torsional Angles (Deg)

Five-Membered Chelate Rings			
Co–N(1)	16.6	Co–N(3)	17.5
N(1)–C(4)	44.2	N(3)–C(9)	42.5
C(4)–C(5)	55.5	C(9)–C(10)	51.0
C(5)–N(2)	41.5	C(10)–N(4)	35.5
N(2)–Co	14.2	N(4)–Co	9.8
Six-Membered Chelate Ring			
Co–N(2)	39.5	C(7)–C(8)	65.6
N(2)–C(6)	51.7	C(8)–N(3)	60.6
C(6)–C(7)	61.4	N(3)–Co	44.1
Pyrrolidine Rings			
N(1)–C(1)	12.2	N(4)–C(10)	25.9
C(1)–C(2)	22.8	C(10)–C(11)	2.8
C(2)–C(3)	23.2	C(11)–C(12)	21.4
C(3)–C(4)	16.9	C(12)–C(13)	37.0
C(4)–N(1)	3.0	C(13)–N(4)	38.8
Alaninato Ring			
Co–N(5)	12.5	C(15)–O(1)	9.7
N(5)–C(14)	18.8	O(1)–Co	1.9
C(14)–C(15)	19.0		

Perspective drawings of the pyrrolidine rings are represented in Figure 3. As Figures 3 and 4 show, the anisotropic thermal motions of the atoms in the apical pyrrolidine ring, in which abnormally large deviations from the nominal bond distance and bond angle were observed, were quite large.

The pyrrolidine ring has two conformational states designated as "envelope" and "half-chair" because of the flexibility of the ring.[17] The pyrrolidine ring fused with the five-membered chelate ring is substantially strained. Further, the apical pyrrolidine ring has some nonbonded repulsions with the other ligand. The nonbonded interatomic distances are 2.29 Å between the NH protons of the N(1) and that of the N(5) atom, and 2.24 Å between the NH proton of the N(5) atom and the methyne proton of the C(4) atom. The conformations of the pyrrolidine ring of the proline (or prolinato ligand) and *SS*-pyht, which have been determined by X-ray diffraction studies, are quite different from one another.[3,7,18] In *cis*-β-(oxalato)(1,7-bis(2(*S*)-pyrrolidyl)-2,6-diazaheptane)cobalt(III) complex one of the pyrrolidine rings is "half-chair" and the other is not typical but is close to "envelope" form. Thus there are various conformations of the pyrrolidine ring.

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(16) The "plane" is defined by the cobalt atom and the three nitrogen atoms N(2), N(3), and N(4) of the tetraamine.[4,5]

(17) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Interscience: New York, 1965; p 201.

(18) (a) DeTar, D. F.; Luthura, N. P. *J. Am. Chem. Soc.* **1977**, *99*, 1232. (b) Ito, T.; Marumo, F.; Saito, Y. *Acta Crystallogr., Sect. B* **1971**, *27*, 1062. (c) Mathieson, A. M.; Welsh, H. K. *Acta Crystallogr.* **1952**, *5*, 599.

Table VI. Intermolecular Contacts (to 3.4 Å)

atom 1	atom 2	dist, Å	symmetry of atom 2
N(4)	O(W1)	2.94 (3)	x, y, z
C(13)	O(W1)	3.34 (3)	x, y, z
O(3)	O(W2)	3.08 (6)	$x - 1, y, z$
O(6)	O(W1)	3.29 (4)	$x - 1, y, z$
O(6)	O(W2)	3.20 (6)	$x - 1, y, z$
O(7)	O(W1)	2.91 (4)	$x - 1, y, z$
N(3)	O(4)	3.01 (3)	$y, x, -z$
C(9)	O(4)	3.14 (4)	$y, x, -z$
O(W2)	O(W2)	3.27 (8)	$y + 1, x - 1, -z$
O(2)	N(2)	2.96 (2)	$-x + {}^1/_2, y - {}^1/_2, -z + {}^1/_4$
O(2)	N(5)	2.94 (2)	$-x + {}^1/_2, y - {}^1/_2, -z + {}^1/_4$
O(2)	C(4)	3.19 (3)	$-x + {}^1/_2, y - {}^1/_2, -z + {}^1/_4$
O(2)	C(5)	3.27 (3)	$-x + {}^1/_2, y - {}^1/_2, -z + {}^1/_4$
O(2)	C(14)	3.21 (3)	$-x + {}^1/_2, y - {}^1/_2, -z + {}^1/_4$
O(2)	O(7)	3.35 (3)	$-x + {}^1/_2, y - {}^1/_2, -z + {}^1/_4$
C(13)	O(7)	3.37 (4)	$-x + {}^1/_2, y - {}^1/_2, -z + {}^1/_4$
O(8)	N(5)	2.85 (3)	$-x + {}^1/_2, y - {}^1/_2, -z + {}^1/_4$
O(8)	O(W1)	3.40 (4)	$-x + {}^1/_2, y - {}^1/_2, -z + {}^1/_4$
O(9)	O(W1)	3.05 (4)	$-x + {}^1/_2, y - {}^1/_2, -z + {}^1/_4$

If the energy difference among the conformers is small enough, it seems to be possible that the pseudorotation of the ring occurs. We assume that the large deviations from the nominal bond distance and bond angle values in the "out-of-plane" pyrrolidine ring are apparent ones due to the thermal motions involving the pseudorotation of the pyrrolidine ring. The large anisotropic thermal motion of the C(1) atom suggests that the observed position of this atom is the average one.

Least-squares planes through the four atoms of the pyrrolidine rings are given in Table IV. The conformations of the pyrrolidine rings are not identical with each other, though the rings are in "envelope-like" forms. The atom, which is out of the plane formed by the remaining four atoms, is not the same one.[18] The torsional angles cited in Table V also show this.

Conformations of the five-membered chelate rings and the six-membered chelate ring for the tetraamine are presented in Figure 4. The five-membered chelate rings both have the δ-gauche conformation, which is a contrast to "envelope-like" chelate rings observed in *cis*-β-(oxalato)(1,7-bis(2-(*S*)-pyrrolidyl)-2,6-diazaheptane)cobalt(III) complex.[7] The six-membered chelate ring has a distorted chair conformation, which is approximately similar to those of the related compounds.[4-7]

The molecular packing is illustrated in Figure 2, and some nonbonded distances are given in Table VI. There are two possible hydrogen bonds formed between two amino nitrogen atoms and a carboxylic oxygen atom, which hold together the cations in a spiral along the unique axis (N(2)···O(2) = 2.96 Å, N(5)···O(2) = 2.94 Å). The N(4)···O(W1) and N(5)···O(8) are certainly hydrogen bonds. Other possible hydrogen bonds involve N(3), the perchlorate anion, and the water molecule and form a three-dimensional network.

In the crystal structure of the complex cation no significant nonbonded interaction between the tetraamine and alaninato is observed, which is consistent with the result that this isomer, the (*R*)-alaninato complex, is the predominant one over the (*S*)-alaninato complex at equilibrium of the epimerization.[11] In the case of the Λ-β_2-[Co(*S*-ala)(*SS*-pyht)]$^{2+}$, it is presumed that there are some nonbonded interactions between *SS*-pyht and alaninato. The relation between the structure and the stereoselectivity on the epimerization will be discussed in detail elsewhere on the basis of the strain energy minimization technique.[11b]

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Registry No. $(+)_{589}$-β_2-[Co(*R*-ala)(*SS*-pyht)]$(ClO_4)_2 \cdot 2H_2O$, 73365-62-5.

Supplementary Material Available: A listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.