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An Important Metal Complex in the Asymmetric Synthesis of α-Amino Acids. The Crystal and Molecular Structure of (−)$_{546}$-((*R*)-Alaninato)((6*R*,8*R*)-6,8-dimethyl-2,5,9,12-tetraazatridecane)cobalt(III) Bromide Trihydrate, (−)$_{546}$-[Co(*R*-ala)(1,5*R*,7*R*,11-Me$_4$-2,3,2-tet)]Br$_2$·3H$_2$O

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The crystal and molecular structures of (−)$_{546}$-((*R*)-alaninato)((6*R*,8*R*)-6,8-dimethyl-2,5,9,12-tetraazatridecane)cobalt(III) bromide trihydrate ((−)$_{546}$-[Co(*R*-ala)(1,5*R*,7*R*,11-Me$_4$-2,3,2-tet)]Br$_2$·3H$_2$O) (1), derived from (−)$_{546}$-[Co(AMM)(1,5*R*,7*R*,11-Me$_4$-2,3,2-tet)]$^+$ on decarboxylation, have been determined from three-dimensional X-ray counter data. In the above, AMM is an α-amino-α-methylmalonate ion. The compound crystallizes in an orthorhombic space group $P2_12_12_1$ with a=11.713 (1) Å, b=20.301 (2) Å, c=10.113 (2) Å, and Z=4. The structure was solved by the heavy-atom method followed by full-matrix least-squares and Fourier techniques. A refinement using 2168 reflections with $|F_o|>3[\sigma(F_o)]$ gave R=0.052. The absolute configuration of the complex cation is Λ in the β_2 form. The gauche conformations of two five-membered chelate rings for the tetramine are both δ, and the central six-membered chelate ring adopts a chair conformation with one methyl group axial and the other equatorial. All the secondary nitrogen atoms have S configurations except one of the terminal nitrogen atoms whose absolute configuration is R. The *N*-methyl group in an "out-of-plane" five-membered chelate ring is equatorial; however, the other in an "in-plane" five-membered chelate ring has an axial disposition. The alaninate ion coordinates to the cobalt via N and O atoms. The absolute configuration around the carbon center of the alanine was found to be R.

It is generally known that a chelated α-amino acidato ligand is not released from a cobalt(III) complex under mild basic conditions but results in epimerization of the α-carbon center.[1]

When [Co(*R* or *S*-ala)(1,5*R*,7*R*,11-Me$_4$-2,3,2-tet)]$^{2+}$, derived from [Co(AMM)(1,5*R*,7*R*,11-Me$_4$-2,3,2-tet)]$^+$ on decarboxylation, was warmed under mild basic conditions, the release of alanine with a retention of the asymmetric carbon center from the cobalt(III) complex was unprecedentedly observed. In the above, ala is the alaninate ion, 1,5*R*,7*R*,11-Me$_4$-2,3,2-tet is (6*R*,8*R*)-6,8-dimethyl-2,5,9,12-tetraazatridecane, and AMM is an α-amino-α-methylmalonate ion. On the basis of this novel reaction, we have developed a new cyclic system for the asymmetric synthesis of α-amino acids by using cobalt(III) complexes containing 1,5*R*,7*R*,11-Me$_4$-2,3,2-tet as a ligand.[2]

Some geometrical isomers, including the β_1 and β_2 modes,[3] are possible for mixed cobalt(III) complexes of an α-amino acid and a tetramine. It is difficult to assign the geometry of these compounds by AB (electronic absorption), CD, or NMR spectra. We found that while trying to establish an asymmetric synthesis of α-amino acids using chiral cobalt(III) complexes, it is important to confirm the structure of the complex [Co(ala)(1,5*R*,7*R*,11-Me$_4$-2,3,2-tet)]$^{2+}$, which easily releases alanine under mild basic conditions. Our purpose in undertaking an X-ray structure determination was to examine whether any specific stereochemical features could be observed to which the labile feature of the complex could be ascribed.

Experimental

Measurements. The electronic absorption (AB) spectra were recorded on a Shimadzu UV-210 spectrophotometer. The circular dichroism (CD) spectra were measured with a JASCO J-20 recording spectropolarimeter. Microanalyses were performed by Shonan Bunseki Center Co., Ltd.

Materials. All the reagents were of the best commercial grade and were used without further purification. 1,5*R*,7*R*,11-Me$_4$-2,3,2-tet was prepared by the previously reported method.[4]

Preparation of (−)$_{546}$-[Co(*R*-ala)(1,5*R*,7*R*,11-Me$_4$-2,3,2)]-(ClO$_4$)$_2$·H$_2$O (2). (−)$_{546}$-[Co(AMM)(1,5*R*,7*R*,11-Me$_4$-2,3,2-tet)]ClO$_4$·2.5H$_2$O[5] (100 mg) was dissolved into 10 ml of 1 mol dm^{-3} hydrochloric acid and warmed on a water bath for 1 h at 60 °C. The reaction mixture was then cooled and allowed to stand overnight at room temperature. The resulting wine red crystals were collected, washed with ethanol and ether, and dried in vacuo. They were then recrystallized from a minimum amount of warm water; yield, 30 mg. Anal. Calcd for $C_{14}H_{36}N_5O_{11}Cl_2Co$: C, 29.0; H, 6.25; N, 12.1%. Found: C, 29.0; H, 6.6; N, 12.2%. ^{1}H NMR (400 MHz; solvent D$_2$O; standard DSS) δ=1.20 (3H, d, *J* 7.02 Hz, C*H*$_3$–CH), 1.45 (3H, d, *J* 6.41 Hz, C*H*$_3$–CH), 1.53 (3H, d, *J* 7.02 Hz, C*H*$_3$–CH of ala), 1.90 (3H, s, C*H*$_3$–N), 2.16 (3H, s, C*H*$_3$–N), 2.65—3.03, 3.16—3.22, 3.30—3.40 (multiplets), 3.86 (1H, q, C*H*–CH$_3$ of ala).

Crystal Data and Intensity Measurements for (−)$_{546}$-[Co(*R*-ala)(1,5*R*,7*R*,11-Me$_4$-2,3,2-tet)]Br$_2$·3H$_2$O (1). Since the perchlorate obtained above was unsuitable for the X-ray

Table 1. Crystal Data and Experimental Conditions

Formula	$C_{14}H_{40}N_5O_5Br_2Co$
Molecular wt	577.24
Crystal shape	sphere (0.34 mm ϕ)
Space group	$P2_12_12_1$
a	11.713(1) Å
b	20.301(2) Å
c	10.113(2) Å
V	2404.6(6) Å^3
d(obsd)	1.59 g cm^{-3}
d(calcd)	1.60 g cm^{-3}
Z	4
λ	0.7107 Å (Mo $K\alpha$)
Abs coeff	44.4 cm^{-1}
Monochromator	LiF
Take off angle	5°
Method	$\omega-2\theta$ ($\theta-2\theta$, $2\theta\leq30°$)
Scan speed	2° min^{-1}
Bkgd counts	10 s
Stds	3 every 50 reflections
2θ limits	70°
No. of data	2345
No. of obsd data	2168 ($F_o\geq3\sigma(F_o)$)

crystallography, we have newly prepared the bromide as follows. The perchlorate obtained above was dissolved in water and converted to the bromide form by allowing it to pass through a Dowex 2-X8 anion-exchange-resin column (100—200 mesh, Br^- form). A pure bromide salt was obtained upon evaporation of the resultant solution to near-dryness. A wine-red powder was obtained, which yielded good wine-red crystals upon recrystallization from a minimum amount of an ethanol–water solution. Anal. Calcd for $C_{14}H_{40}N_5O_5Br_2Co$: C, 29.1; H, 7.0; N, 12.1; Br, 27.7%. Found: C, 30.0; H, 6.9; N, 12.6; Br, 28.5%. The AB and CD spectra of the bromide were almost identical with those of the perchlorate.

The crystal used in the data collection was shaped into a sphere of 0.34 mm in diameter. The crystallographic and experimental data are summarized in Table 1. The diffraction data were measured on a Rigaku AFC-5 diffractometer. Three standard reflections were monitored every 50 reflections and showed no variation in intensity, for which no correction was made. The standard Lorentz, polarization, and absorption corrections were applied.

Table 2. Final Positional Parameters and Their Estimated Standard Deviations (in Parentheses)

Atom	x	y	z
Co	0.05931(10)	0.08529(5)	0.30307(11)
N(1)	−0.0386(7)	0.1189(4)	0.4506(8)
N(2)	−0.0851(6)	0.0494(3)	0.2268(8)
N(3)	0.0452(6)	0.1681(3)	0.1983(8)
N(4)	0.2023(7)	0.1258(3)	0.3805(8)
N(5)	0.0922(7)	0.0021(4)	0.3956(8)
O(1)	0.1496(4)	0.0490(2)	0.1658(5)
O(2)	0.2526(5)	−0.0372(2)	0.1082(6)
C(1)	−0.1416(9)	0.0761(6)	0.4521(12)
C(2)	−0.1796(9)	0.0722(5)	0.3133(17)
C(3)	−0.1158(9)	0.0587(5)	0.0849(13)
C(4)	−0.1028(11)	0.1320(6)	0.0443(13)
C(5)	0.0115(9)	0.1606(5)	0.0545(10)
C(6)	0.1532(10)	0.2041(5)	0.2119(12)
C(7)	0.1936(13)	0.1974(6)	0.3486(14)
C(8)	0.1409(7)	−0.0466(4)	0.3014(11)
C(9)	0.1866(7)	−0.0107(4)	0.1816(8)
C(N1)	0.0108(10)	0.1275(6)	0.5918(9)
C(N4)	0.3133(8)	0.0989(4)	0.3389(11)
C(C3)	−0.0495(10)	0.0131(5)	−0.0106(11)
C(C5)	0.0099(11)	0.2317(5)	−0.0135(12)
C(C8)	0.2224(8)	−0.0950(4)	0.3689(9)
Br(1)	0.17318(10)	0.39421(5)	0.21294(15)
Br(2)A[a)]	0.32267(19)	0.24332(7)	0.65914(19)
Br(2)B	0.3853(9)	0.2264(3)	0.6158(9)
O(3)	0.0570(8)	0.4149(4)	0.9170(11)
O(4)	0.0778(9)	0.3216(5)	0.7087(14)
O(5)	0.0382(11)	0.3378(5)	0.4610(11)

a) Populations of Br(2)A and Br(2)B are 0.824(4) and 0.176(4), respectively.

Structure Solution and Refinement. The structure was solved by the heavy-atom method and refined by a block-diagonal least-squares method. Atomic scattering factors were taken from Ref. 6. Also, the weighting scheme

$$1/w = [\sigma(\text{count})]^2 + [0.015|F_o|]^2$$

was employed. Since the tetramine was derived from (R,R)-2,4-pentanediamine,[7)] the known absolute configurations of the asymmetric carbon atoms were used as internal reference asymmetric centers to determine the absolute configuration of the complex ion. The effects of anomalous dispersion were included in F_c; values of f' and f'' for Br, Co, O, N, and C were taken from Ref. 8. One of the two Br atoms, Br(2), was located at two positions. A model structure postulating the disorder of that bromine atom was refined by a full-matrix least-squares method. The thermal parameters of the subsidiary bromine atom were assumed to be the same as those of the main bromine atom. The population of the main and subsidiary bromine atoms were refined to 0.817 (6) and 0.183 (6), respectively. All the hydrogen atoms, except for those of the methyl groups and waters of crystallization, were located by assuming a tetrahedral coordination; they were all included in the final refinement with the isotropic temperature factors (R=0.054 and R'=0.054), where $R=\sum||F_o|-|F_c||/\sum|F_o|$ and $R'=(\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2)^{1/2}$. Hydrogen atom scattering factors were taken from a compilation of Stewart et al.[9)] The final positional parameters along with their standard deviations are listed in Table 2. Complications of the anisotropic thermal parameters as well as observed and calculated structure factors are deposited as Document No. 8638 at the office of the Editor of Bull. Chem. Soc. Jpn. The calculations were carried out on the Hitachi M-200H computer at the Computer Center of the Institute for Molecular Science with the Universal Crystallographic Computing Program System UNICS III.[10)]

Results and Discussion

Molecular Structure of (−)$_{546}$-β_2-[Co(*R*-ala)(1,5*R*,7*R*,11-Me$_4$-2,3,2-tet)]Br$_2$·3H$_2$O (1). The present structure determination of the important intermediate complex in the asymmetric synthetic system of α-alanine could establish that the cobalt ion is a slightly distorted octahedral center to which alanine is coordinated as a bidentate.

A detailed view of the complex cation is given in Fig. 1, and the intramolecular distances and bond angles are given in Tables 3 and 4. The geometry of the tetramine ligand, 1,5*R*,7*R*,11-Me$_4$-2,3,2-tet, is Λ-cisβ. The alaninato coordinates to a cobalt atom with N(5) and O(1) atoms in the β_2 form; the configuration of the asymmetric carbon is R. Consequently, the complex ion is represented as Λ-β_2-[Co(*R*-ala)(1,5*R*,7*R*,11-Me$_4$-2,3,2-tet)]$^{2+}$.

The arrangement of the groups around the secondary nitrogen atoms, N(1), N(2), N(3), and N(4),

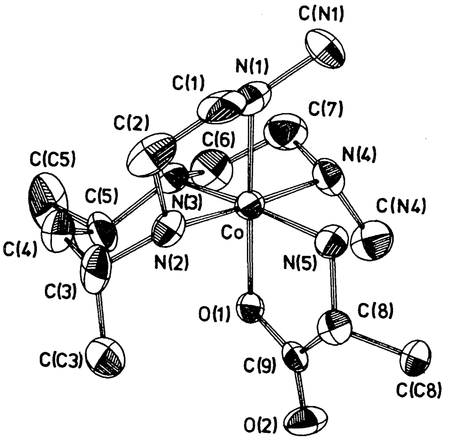

Fig. 1. ORTEP view of (−)$_{546}$-[Co(*R*-ala)(1,5*R*, 7*R*, 11-Me$_4$-2,3,2-tet)]$^{2+}$ ion with the atomic numbering scheme in an asymmetric unit.

Table 3. Bond Distances (*l*/Å) and Their Estimated Standard Deviations (in Parentheses)

Co–N(1)	2.002(15)
Co–N(2)	1.996(14)
Co–N(3)	1.995(13)
Co–N(4)	2.025(14)
Co–N(5)	1.969(14)
Co–O(1)	1.893(9)
N(1)–C(1)	1.486(27)
N(1)–C(N1)	1.552(25)
N(2)–C(2)	1.485(27)
N(2)–C(3)	1.491(24)
N(3)–C(5)	1.515(23)
N(3)–C(6)	1.467(24)
N(4)–C(7)	1.491(28)
N(4)–C(N4)	1.473(22)
N(5)–C(8)	1.488(22)
O(1)–C(9)	1.299(17)
O(2)–C(9)	1.199(18)
C(1)–C(2)	1.474(32)
C(3)–C(4)	1.550(30)
C(3)–C(C3)	1.549(28)
C(4)–C(5)	1.464(29)
C(5)–C(C5)	1.600(28)
C(6)–C(7)	1.468(32)
C(8)–C(9)	1.512(22)
C(8)–C(C8)	1.531(23)

Table 4. Bond Angles (ϕ/°) and Their Estimated Standard Deviations (in Parentheses)

N(1)–Co–N(2)	85.8(6)
N(1)–Co–N(3)	93.5(6)
N(1)–Co–N(4)	92.7(6)
N(1)–Co–N(5)	92.9(6)
N(1)–Co–O(1)	177.0(7)
N(2)–Co–N(3)	91.9(6)
N(2)–Co–N(4)	177.3(7)
N(2)–Co–N(5)	92.2(6)
N(2)–Co–O(1)	92.8(5)
N(3)–Co–N(4)	86.0(6)
N(3)–Co–N(5)	172.7(7)
N(3)–Co–O(1)	89.2(5)
N(4)–Co–N(5)	90.2(6)
N(4)–Co–O(1)	88.8(5)
N(5)–Co–O(1)	84.6(5)
Co–N(1)–C(1)	105.9(9)
Co–N(1)–C(N1)	120.7(8)
C(1)–N(1)–C(N1)	111.1(14)
Co–N(2)–C(2)	106.9(10)
Co–N(2)–C(3)	122.0(8)
C(2)–N(2)–C(3)	110.3(15)
Co–N(3)–C(5)	116.5(8)
Co–N(3)–C(6)	107.4(9)
C(5)–N(3)–C(6)	111.4(13)
Co–N(4)–C(7)	104.9(10)
Co–N(4)–C(N4)	118.0(8)
C(7)–N(4)–C(N4)	111.1(15)
Co–N(5)–C(8)	110.0(7)
Co–O(1)–C(9)	117.4(7)
N(1)–C(1)–C(2)	105.4(14)
N(2)–C(2)–C(1)	110.7(14)
N(2)–C(3)–C(4)	110.6(13)
N(2)–C(3)–C(C3)	113.9(13)
C(4)–C(3)–C(C3)	111.0(15)
C(3)–C(4)–C(5)	116.9(15)
N(3)–C(5)–C(4)	110.3(13)
N(3)–C(5)–C(C5)	109.0(12)
C(4)–C(5)–C(C5)	108.5(15)
N(3)–C(6)–C(7)	108.6(14)
N(4)–C(7)–C(6)	108.5(14)
N(5)–C(8)–C(9)	109.1(11)
N(5)–C(8)–C(C8)	112.4(11)
C(9)–C(8)–C(C8)	116.5(11)
O(1)–C(9)–O(2)	124.0(10)
O(1)–C(9)–C(8)	115.5(10)
O(2)–C(9)–C(8)	120.6(11)

are R, S, S, and S, respectively. The conformations of the three chelate rings of the tetramine are presented in Fig. 2-a,b,c. Both of the five-membered rings have a δ-gauche conformation with an equatorial methyl group on N(1) and an axial one on N(4). The central six-membered ring for the tetramine adopts a chair conformation with one methyl group axial, C(C3), and the other equatorial, C(C5).

The four Co–N distances of tetramine, Co–N(1), Co–N(2), Co–N(3), and Co–N(4), are not significantly different from one another, and the mean value (2.01 Å) is quite usual. The ring angles at the cobalt atom for the five-membered rings are 85.8 (6)° and 86.0 (6)° for N(1)–Co–N(2) and N(3)–Co–N(4), respectively. These are normal for cobalt(III) five-membered diamine chelate rings. The ring angle at the cobalt atom for a six-membered ring, N(2)–Co–N(3), is 91.9 (6)°. The average N–C and C–C distances of the membered nitrogen and carbon atoms are 1.49 and 1.48 Å, respectively.

The observed values of the Co–N(2)–C(3) and Co–N(3)–C(5) are 122.0 (8)° and 116.5 (8)°, significantly expanded from a tetrahedral configuration. This distortion is attributed to an interaction between the axial *C*-methyl group on C(3) and the apical O(1) atoms. The conformation of the six-membered chelate ring in the tetramine is represented diagrammatically in Fig. 3. The dihedral angles between the plane A and B (α), and B and C (β) are 35.8° and 59.0°, respectively. The value of α is considerably small, compared with a corresponding value of 40.6° in the [Co(ox)(*N*,*N'*-Me$_2$-*R*,*S*-2,3″,2-tet)]$^+$ ion,[11] which has no axial *C*-methyl group. However, it is similar to that of 36.4° in the [Co(ox)(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$ ion,[12] which has an axial *C*-methyl group. This small α value indicates a flattened structure of the six-membered ring. The magnitude of the ring flattening of the two complexes containing axial *C*-methyl groups, [Co(ox)-(5*R*,7*R*-Me$_2$-2,3,2-tet)]$^+$ and [Co(*R*-ala)(1,5*R*,7*R*,11-Me$_4$-2,3,2-tet)]$^+$, is the same in spite of a difference in the bidentate ligands, oxalato or alaninato, and additional *N*-methyl groups. Thus, although the conformation of the tetramine is not much different

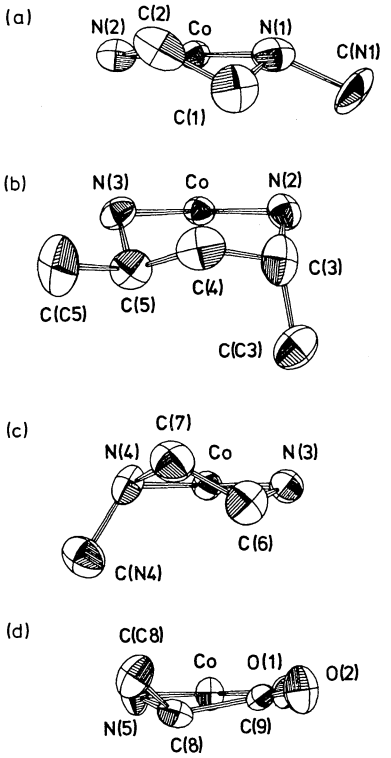

Fig. 2. A perspective drawing of the chelate rings. (a): The out-of-plane five-membered ring, (b): the central six-membered ring, (c): the in-plane five-membered ring, (d): the alaninato five-membered ring.

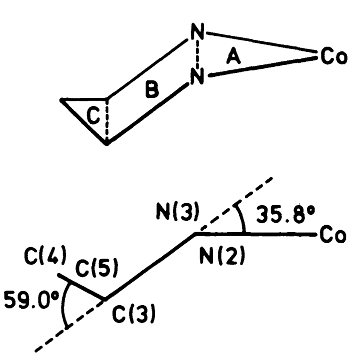

Fig. 3. The dihedral angles between the planes A and B, and between the planes B and C.

Table 5. Interatomic Nonbonded Distances (l/Å) between Methyl Groups and Other Atoms (Less than 3.5 Å) and Their Standard Deviations (in Parentheses)

C(N1)-Co	3.10(2)
C(N1)-N(4)	3.10(3)
C(N1)-N(5)	3.37(3)
C(N1)-C(1)	2.51(3)
C(N4)-Co	3.01(2)
C(N4)-N(5)	3.30(2)
C(N4)-O(1)	2.79(2)
C(N4)-C(6)	3.12(3)
C(N4)-C(7)	2.44(3)
C(N4)-C(9)	3.11(2)
C(C3)-N(2)	2.55(2)
C(C3)-O(1)	3.03(2)
C(C3)-C(4)	2.55(3)
C(C3)-C(5)	3.15(3)
C(C3)-C(9)	3.42(2)
C(C5)-N(3)	2.54(2)
C(C5)-C(4)	2.49(3)
C(C5)-C(6)	2.89(3)
C(C8)-N(5)	2.51(2)
C(C8)-O(2)	2.91(2)
C(C8)-C(9)	2.59(2)

from those of other analogous 2,3,2-tet complexes, the tetramine containing an R,R-2,4-pentanediamine unit is somewhat strained by nonbonded repulsions, including methyl substituents.

Close contacts between the N-methyl or C-methyl carbon atoms and other atoms in the complex (less than 3.5 Å) are listed in Table 5. Four close contacts between axial methyl groups and alaninato chelate ring, C(N4)–N(5) 3.30 (2) Å, C(N4)–C(9) 3.11 (2) Å, C(C3)–O(1) 3.03 (2) Å, and C(C3)–C(9) 3.42 (2) Å, were observed.

The conformation of the chelate ring for the alaninato is presented in Fig. 2-d. The five-membered ring has a slightly puckered pseudo-δ-gauche conformation (maximum deviation from the plane of best fit; N(5), 0.12 Å; C(8), 0.12 Å). In order to compare the structure of the alaninato chelate with those in reported alaninato–cobalt(III) complexes, the Cambridge Crystallographic Data File (XDC) was searched and alaninato–cobalt(III) complexes whose structures have been established on the basis of three-dimensional counter data were collected. Their selected distances, angles, and torsional angles are listed in Table 6. The bond lengths and angles in the present complex are normal compared with those in the reported complexes. The Co–N(5) distance is 1.969 (14) Å. This value is in the upper end of the reported range for the corresponding Co–N bonds (1.935—1.961 Å). The Co–O(1) distance is 1.893 (9) Å, which is normal for the Co–O bonds (the reported values are in the range 1.877—1.925 Å). The angle at the cobalt atom N(5)–Co–O(1) is 84.6 (5)°, while the reported values are in the range 83.4—86.3°. The angles Co–N(5)–C(8) and Co–O(1)–C(9) are 110.0 (7)° and 117.4 (7)°, while the reported values are in the range 106.1—110.8° and 114.3—116.8°, respectively. The torsional angle N(5)–C(8)–C(9)–O(1) is rather characteristic. The value is 17.6°; this is considerably smaller compared with those reported for the corresponding torsional angles (19.0—29.4°). This distortion is attributed to an interaction between the terminal N-methyl group in the tetramine part (C(N4)) and the carbon in the alanine part (C(9)). A similar distortion in the alaninato chelate has been observed in the Λ-β_2-[Co(S-ala)(S,S-pyht)]$^{2+}$ ion,[13] which has N-substituent on the terminal nitrogen of the tetramine that is similar to the present complex, whose torsional angle is 19.0°. We observed the release of alanine from the Λ-β_2-[Co(S-ala)(S,S-pyht)]$^{2+}$ ion when this complex was warmed under mild basic conditions; this is similar to the case of the [Co(R-ala)(1,5R,7R,11-Me$_4$-2,3,2-tet)]$^{2+}$ ion.

Thus, the present structure determination revealed that the important intermediate complex in the asymmetric synthetic system of α-alanine has the usual octahedral coordination geometry, although the conformation of the ligands are somewhat strained. The obtained results suggest that the labile feature of this complex should be ascribed to factors other than a stereochemical distortion of the alanine unit.

Description of the Unit Cell. The unit cell, Fig. 4, consists of four discrete complex cations, twelve bromine atoms (including eight disordered positions) and twelve waters of crystallization. In Table 7 are listed some of the important distances outside the

Table 6. Selected Distances, Angles, and Torsional Angles of Alaninato Chelates in Crystallographically Established Alaninato-Cobalt(III) Complexes

Complexes	Distances		Angles			Torsional Angles	R	Ref.
	d/Å		θ/°			ϕ/°		
	Co–N	Co–O	N–Co–O	Co–N–C	Co–O–C	N–C–C–O		
(+)$_{589}$-[Co(S-ala)(NH$_3$)$_2$-(NO$_2$)$_2$]	1.935$^{a)}$	1.919$^{a)}$	86.3$^{b)}$	108.8$^{b)}$	114.3$^{b)}$	27.2$^{b)}$	0.025	14
(−)-mer-[Co(S-ala)$_3$]·H$_2$O	1.942(10)	1.899(9)	85.2(4)	107.8(7)	114.4(8)	26.4(14)	0.075	15
	1.948(10)	1.880(8)	85.3(4)	108.2(8)	116.8(8)	23.7(16)		
	1.945(10)	1.877(9)	86.3(4)	109.2(8)	114.9(9)	29.4(15)		
[Co(R-ala)(NO$_2$)$_2$(tn)]	1.951$^{a)}$	1.910$^{a)}$	85.5$^{b)}$	109.5$^{b)}$	115.4$^{b)}$	24.1$^{b)}$	0.046	16
(+)$_{589}$-Ba[Co(R-ala)-(glygly)(NO$_2$)]Cl·4H$_2$O	1.961$^{a)}$	1.925$^{a)}$	83.4$^{b)}$	106.1$^{b)}$	116.4$^{b)}$	29.1$^{b)}$	0.045	17
[Co(S-OHBH$^{c)}$)(S-ala)·2H$_2$O	1.938(6)	1.912(5)	85.0(2)	108.2(4)	114.9(4)	19.1	0.059	18
Λ-β_2-[Co(R-ala)(S,S-pyht$^{d)}$)]-(ClO$_4$)$_2$·2H$_2$O	1.96(2)	1.90(1)	85.8(6)	110.8(9)	115.4(10)	19.0	0.056	13
Λ-β_2-[Co(R-ala)(1,5R,7R,11-Me$_4$-2,3,2-tet)]Br$_2$·3H$_2$O	1.969(14)	1.893(9)	84.6(5)	110.0(7)	117.4(7)	17.6	0.054	This work

a) XDC data. b) Calculated on the basis of the XDC data. c) α-N-(o-hydroxybenzyl)-L-histidinato. d) 1,7-bis(2(S)-pyrrolidyl)-2,6-diazaheptane.

Table 7. Intermolecular Hydrogen Bonds (Less than 3.5 Å)

A-H···B	A···B	A-H···B	Symmetry of atom B		
N(1)-Br(2)A	3.42(2)A	138.3°	$-1/2+X$,	$1/2-Y$,	$1-Z$
N(1)-Br(2)B	3.33(2)	150.7	$-1/2+X$,	$1/2-Y$,	$1-Z$
N(2)-Br(1)	3.37(1)	131.3	$-X$,	$-1/2+Y$,	$1/2-Z$
N(3)-Br(2)A	3.48(1)	173.6	$-1/2+X$,	$1/2-Y$,	$1-Z$
N(3)-Br(2)B	3.41(2)	165.2	$-1/2+X$,	$1/2-Y$,	$1-Z$
N(4)-O(2)	2.97(2)	141.5	$1/2-X$,	$-Y$,	$1/2+Z$
N(5)-O(2)	2.90(2)	162.9	$1/2-X$,	$-Y$,	$1/2+Z$
N(5)-O(3)	3.13(2)	147.8	$-X$,	$-1/2+Y$,	$3/2-Z$
O(3)-Br(1)	3.31(2)		X,	Y,	$1+Z$
O(3)-O(4)	2.84(3)		X,	Y,	Z
O(4)-Br(2)A	3.32(2)		X,	Y,	Z
O(4)-O(5)	2.57(3)		X,	Y,	Z
O(5)-Br(1)	3.18(2)		X,	Y,	Z
O(5)-Br(2)A	3.25(2)		$-1/2+X$,	$1/2-Y$,	$1-Z$
O(5)-Br(2)B	2.35(3)		$-1/2+X$,	$1/2-Y$,	$1-Z$

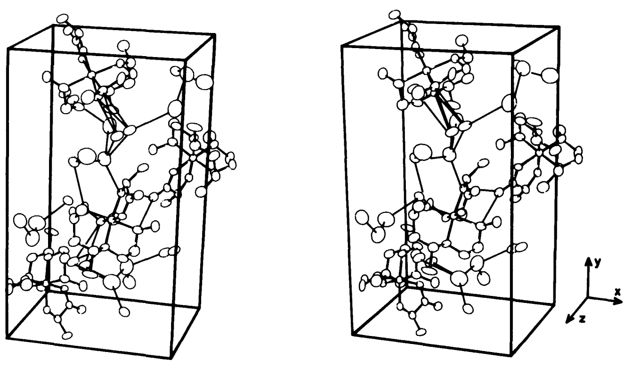

Fig. 4. Stereoscopic view of the unit cell contents showing the crystal packing.

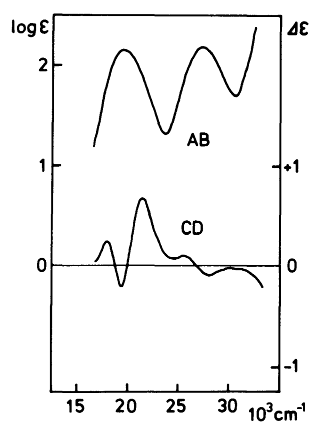

Fig. 5. Electronic absorption (AB) and circular dichroism (CD) spectra of $(-)_{546}$-[Co(R-ala) (1,5R,7R,11-Me$_4$-2,3,2-tet)]$^{2+}$.

Table 8. Electronic Absorption (AB) and Circular Dichroism (CD) Spectral Data of $(-)_{546}$-Λ-β_2-[Co(R-ala)(1,5R,7R,11-Me$_4$-2,3,2-tet)]$^{2+}$

AB	CD
$\tilde{\nu}/10^3$ cm^{-1} (log ε)	$\tilde{\nu}/10^3$ cm^{-1} ($\Delta\varepsilon$)
19.5 (2.15)	17.9 (+0.24)
	19.3 (−0.20)
	21.0 (+0.67)
27.3 (2.18)	25.5 (+0.10)
	28.0 (−0.08)

complex ion. Three water oxygen atoms, O(3), O(4), and O(5), and one bromide anion, Br(1), are aligned along the c-axis with distances of about 3 Å. O(4), O(5), and Br(2) (A or B) are aligned along the a-axis. There probably exists a network of hydrogen bonds between these water oxygens and the bromide anions. In addition of this network, there are N-H···Br and N-H···O hydrogen bonds between the complex ions and the water oxygen and bromide anion. An O(2) atom of the alaninato is linked to N(4) and N(5) by N-H···O hydrogen bonds at distances 2.97 (2) and 2.90 (2) Å, respectively.

Circular Dichroism and Absorption Spectra. The CD and AB spectra of $(-)_{546}$-Λ-β_2-[Co(R-ala)(1,5R,7R,11-Me$_4$-2,3,2-tet)]$^{2+}$ are shown in Fig. 5, and their spectral data are summarized in Table 8. It is often observed that the CD sign in the first absorption region is closely related to the absolute configurations for the dissymmetric cobalt complexes. For example, the sign of the dominant peak for the first absorption region is expected to be positive for a Λ configuration. However, the present complex has two positive and one negative cotton effects in the first absorption region. Therefore, it is difficult to assign the absolute configuration by means of CD spectroscopy.

The electronic absorption spectrum of the complex gives typical [CoN$_5$O]$^{2+}$ absorptions. The first absorption band of this complex is shifted by about 700 cm^{-1} to the lower-energy side compared to the alaninato complex of 2,3,2-tet. This indicates that an alkyl group substitution on the tetramine nitrogen causes a weakening of the ligand field. Since the present crystal structure does not show any significant stereochemical features for the coordinated alanine part, we believe that the labile feature of this complex is closely related to the strength of the ligand field. Studies are now in progress to clarify the labile feature of amino acidato cobalt(III) complexes while hoping to establish metal-assisted asymmetric reactions.

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