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The Crystal and Molecular Structure of (*N*-Benzyl-L-alaninato)-[*N*,*N′*-ethylenebis(*α*-methylsalicylideneaminato)]-cobalt(III) Trihydrate

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The crystal and molecular structure of the title complex $(-)_{435}$-Δ_{RS}-β_2(mer)-[Co(α-Me-sal$_2$en)(*N*-Bz-L-ala)]·3H_2O, has been determined by single crystal X-ray analysis. The crystals are orthorhombic, space group $P2_12_12_1$, with unit cell dimensions $a=19.247(8)$, $b=14.162(4)$, $c=10.329(4)$ Å, and $Z=4$. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares technique, using 1624 independent reflections, to the final *R*-value of 0.080. The molecular structure is of a Δ_{RS}-*cis*-β_2(mer) type in which two coordination sites of a distorted octahedron are occupied by the *N*-Bz-L-ala group and the others by the quadridentate α-Me-sal$_2$en Schiff-base ligand in a nonplanar configuration. The Co–O and Co–N bon lengths, 1.938(12) and 1.989(15) Å respectively, of the *N*-Bz-L-ala group are significantly longer than the usual values. The molecule is distinctly strained as shown by the bond angles of the ligands and those of the cobalt(III) coordination polyhedron. The water molecules form a hydrogen bonded chain linking phenolate and carboxylate oxygens of different molecules along the crystallographic c axis.

The crystal structures of Schiff-base metal complexes have been studied extensively.[1] However, there are only a few structures in which the quadridentate Schiff-base ligands took a nonplanar configuration.[2–6] Recently, studies of several metal complexes with quadridentate Schiff-base ligands in *cis*-configuration have shown that they exhibit stereoselective effects in coordinating optically active amino acids.[7,8] In order to elucidate these effects more clearly, we have synthesized a series of mixed complexes of the type [Co(*α*-Me-sal$_2$en)(AA)] where *α*-Me-sal$_2$en is the dianion of the quadridentate *N*,*N′*-ethylenebis(*α*-methylsalicylideneaminato) ligand and AA is the anion of one of the following amino acids: *N*-methyl-L-alanine, *N*-benzyl-L-alanine (abbreviated as *N*-Bz-L-ala), and *N*-benzyl-*N*-methyl-L-alanine.[9] This paper reports the result of an X-ray diffraction study of the crystal and molecular structure of $(-)_{435}$-[Co(*α*-Me-sal$_2$en)(*N*-Bz-L-ala)]·3H_2O, which is the predominant isomer at equilibrium conditions.

Experimental

Preparation of Compound. $(-)_{435}$-*cis*-β_2(mer)-[Co(*α*-Me-sal$_2$en)(*N*-Bz-L-ala)]·3H_2O was prepared by a method described elsewhere.[9] From a mixed solution of methanol and water (1 : 1), dark green crystals were obtained. Found: C, 58.36; H, 6.10; N, 7.29%. Calcd for $C_{28}H_{30}CoN_3O_4$·2.5H_2O: C, 58.33; H, 6.12; N, 7.29% and for $C_{28}H_{30}CoN_3O_4$·3H_2O: C, 57.43; H, 6.20; N, 7.18%. From comparison with the X-ray result, these values suggest that a partial dehydration occurred. $(M)_{435}=-4.38\times10^{4\circ}$ ($c=1.0\times10^{-3}$ mol dm^{-3}; chloroform solution).

Crystallographic-data Collection. The size of the crystal used for the X-ray measurement was 0.35×0.28×0.17 mm^3. The systematic absences for $h00(h=2n+1)$, $0k0(k=2n+1)$, $00l(l=2n+1)$ indicated the space group $P2_12_12_1$. The determination of cell dimensions and the collection of intensity data were carried out on a Rigaku AFC-5 automated four-circle diffractometer with Mo *Kα* radiation ($\lambda=0.71069$ Å) monochromated by a graphite plate. The unit cell dimensions were refined by a least-squares method with 20 reflections ($2\theta>22°$). The crystal data were as follows: orthorhombic, space group $P2_12_12_1$, $a=19.247(8)$, $b=14.162(4)$, $c=10.329(4)$ Å, $D_m=1.35$ g cm^{-3} (by flotation in a $ZnCl_2$ solution), $Z=4$, and $D_c=1.38$ g cm^{-3}. The intensity data were collected in the ω-2θ scan mode up to $2\theta=50°$ with the scan rate of 8°/min (50 kV, 170 mA). The scan range was $(1.2+0.5\tan\theta)°$. Of the 2119 unique observed reflections, 1624 reflections with $|F_o|\geq3\sigma(F_o)$ were used for the structure determination. Corrections for the absorption effect were neglected (μ(Mo *Kα*)$=6.9$ cm^{-1}).

Determination and Refinement of Crystal Structure

The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. Three kinds of water molecules were found from a difference Fourier map after the other non-hydrogen atoms were located. The refinement using anisotropic

Table 1. Positional and thermal parameters

Atom	*x*	*y*	*z*	B_{eq} or B/Å^2
Co	0.3644(1)	0.2109(1)	0.4979(2)	2.40
OA1	0.3222(6)	0.0981(8)	0.4266(11)	3.80
OA2	0.3292(7)	−0.0008(9)	0.2636(12)	4.73
OS1	0.2939(5)	0.2793(8)	0.4148(10)	3.28
OS2	0.4061(5)	0.3230(7)	0.5582(10)	2.64
NA1	0.4207(6)	0.2120(11)	0.3364(12)	3.11
NS1	0.3099(7)	0.1391(9)	0.5933(13)	2.80
CA1	0.3509(10)	0.0699(14)	0.3237(16)	4.19
CA2	0.4115(10)	0.1228(12)	0.2610(16)	3.66
CA3	0.4803(10)	0.0642(12)	0.2670(16)	4.93
CA4	0.4064(11)	0.2988(13)	0.2515(20)	2.91
CA5	0.4525(9)	0.3062(11)	0.1330(14)	2.34
CA6	0.4192(8)	0.2982(10)	0.0144(13)	3.66
CA7	0.4578(8)	0.3096(12)	−0.0988(15)	3.72
CA8	0.5256(9)	0.3282(12)	−0.0953(16)	3.62
CA9	0.5592(8)	0.3297(12)	0.0271(15)	3.52
CA10	0.5221(8)	0.3192(13)	0.1414(16)	3.64
CE1	0.3303(9)	0.1188(13)	0.7301(14)	3.37
CE2	0.3924(9)	0.0670(12)	0.6698(19)	3.88
CS11	0.2582(7)	0.3406(10)	0.4774(16)	2.74

Table 1. (Continued)

Atom	x	y	z	B_{eq} or B/Å^2
CS12	0.2323(9)	0.4194(12)	0.4066(19)	3.71
CS13	0.1917(11)	0.4829(14)	0.4608(19)	5.42
CS14	0.1721(11)	0.4834(13)	0.5938(24)	5.85
CS15	0.1960(9)	0.4067(14)	0.6618(19)	4.41
CS16	0.2383(8)	0.3365(12)	0.6122(15)	2.76
CS17	0.2595(8)	0.2531(13)	0.6887(15)	3.33
CS18	0.2228(9)	0.2348(13)	0.8113(16)	3.96
CS21	0.4754(9)	0.3304(12)	0.5550(14)	3.21
CS22	0.5022(10)	0.4204(12)	0.5343(13)	3.80
CS23	0.5737(9)	0.4321(13)	0.5239(17)	4.29
CS24	0.6178(9)	0.3528(13)	0.5370(17)	4.17
CS25	0.5909(8)	0.2689(15)	0.5625(17)	4.04
CS26	0.5192(8)	0.2511(13)	0.5731(18)	2.73
CS27	0.4935(8)	0.1629(11)	0.6196(14)	3.43
CS28	0.5391(10)	0.1019(14)	0.7028(25)	5.62
OW1	0.2618(7)	0.0577(9)	0.0360(12)	5.92
OW2	0.2291(10)	0.2365(14)	0.1545(15)	9.37
OW3	0.1523(12)	0.4080(20)	0.0377(25)	15.42
H(NA1)	0.468(7)	0.225(10)	0.355(13)	1.60
H(CA2)	0.405(7)	0.141(11)	0.148(15)	1.38
H1(CA3)	0.468(10)	0.000(14)	0.229(20)	5.54
H2(CA3)	0.501(8)	0.054(11)	0.357(15)	1.55
H3(CA3)	0.521(8)	0.106(12)	0.207(17)	2.77
H1(CA4)	0.351(8)	0.295(12)	0.218(15)	2.63
H2(CA4)	0.413(8)	0.352(12)	0.297(16)	1.24
H(CA6)	0.368(8)	0.286(11)	0.006(18)	3.03
H(CA7)	0.433(7)	0.311(10)	−0.171(13)	1.40
H(CA8)	0.561(10)	0.335(14)	−0.160(19)	4.97
H(CA9)	0.607(7)	0.328(10)	0.024(15)	1.83
H(CA10)	0.551(11)	0.319(15)	0.211(22)	6.75
H(CS12)	0.244(8)	0.423(11)	0.304(16)	2.47
H(CS13)	0.178(9)	0.529(13)	0.415(19)	4.71
H(CS14)	0.141(8)	0.520(11)	0.637(15)	2.22
H(CS15)	0.185(8)	0.403(12)	0.753(16)	2.93
H1(CS18)	0.243(10)	0.175(13)	0.853(18)	4.90
H2(CS18)	0.230(9)	0.291(13)	0.872(18)	4.64
H3(CS18)	0.175(10)	0.226(15)	0.798(20)	6.30
H1(CE1)	0.286(7)	0.075(10)	0.750(14)	1.31
H2(CE1)	0.348(7)	0.145(11)	0.828(15)	1.69
H1(CE2)	0.375(9)	0.007(12)	0.612(16)	2.85
H2(CE2)	0.423(9)	0.035(14)	0.749(18)	4.50
H(CS22)	0.467(8)	0.476(11)	0.526(16)	3.11
H(CS23)	0.597(8)	0.499(11)	0.506(18)	3.68
H(CS24)	0.670(8)	0.361(11)	0.533(15)	2.39
H(CS25)	0.623(7)	0.227(10)	0.573(14)	1.17
H1(CS28)	0.587(9)	0.124(14)	0.715(18)	3.81
H2(CS28)	0.522(9)	0.111(14)	0.807(19)	4.65
H3(CS28)	0.538(9)	0.034(13)	0.684(18)	4.29
H1(OW1)	0.283(9)	0.031(14)	0.113(19)	a)
H2(OW1)	0.246(10)	0.010(13)	−0.007(18)	a)
H1(OW2)	0.250(8)	0.248(12)	0.225(16)	a)
H2(OW2)	0.241(11)	0.173(15)	0.109(21)	a)
H1(OW3)	0.177(11)	0.345(15)	0.082(23)	a)
H2(OW3)	0.110(9)	0.402(13)	0.004(21)	a)

$B_{eq}=8\pi^2(U_{11}+U_{22}+U_{33})/3$. The anisotropic thermal parameters for the non-hydrogen atoms have been preserved by the Chemical Society of Japan.

a) These values were fixed at $B=6.0$/Å^2 during the least-squares calculations.

thermal parameters for the non-hydrogen atoms reduced the R value (defined as $\sum||F_o|-|\sum|F_c||/\sum|F_o|$) to 0.097. At this stage, all the hydrogen atoms were located from a difference Fourier map. The final refinement including the contribution of these hydrogen atoms with isotropic temperature factors converged to the R value of 0.080. The effect of the anomalous dispersion of the Co atom was included in the calculation.[10] The final difference map showed no peaks higher than 0.5 electrons/Å^3. Atomic scattering factors were taken from Ref. 10. All the computations were carried out by a HITAC M-180 computer at the Hiroshima University Information Processing Center. The computer programs used were FOUR-MMM[11] and HBLS-IV with a slight modification.[12] An ORTEP drawing was carried out by a computer system XTL in a Syntex R3 automated diffractometer.[13] The final atomic parameters are summarized in Table 1 with averaged isotropic temperature factors. The anisotropic thermal parameters and complete lists of the $|F_o|$ and $|F_c|$ values have been preserved by the Chemical Society of Japan (Document No. 8222).

Results and Discussion

The projections of the crystal structure along the c and b axes with the numbering scheme are shown in Figs. 1 and 2. The crystals are built up of discrete [Co(α-Me-sal$_2$en)(N-Bz-L-ala)] molecules and waters of crystallization.

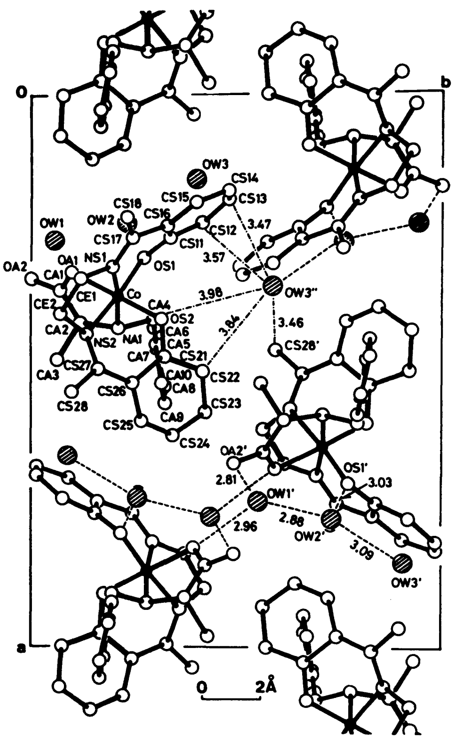

Fig. 1. A perspective drawing of the contents of the unit cell viewed down the c axis. The hydrogen bonds are indicated by bloken lines. Hydrogen atoms are omitted for clarity.

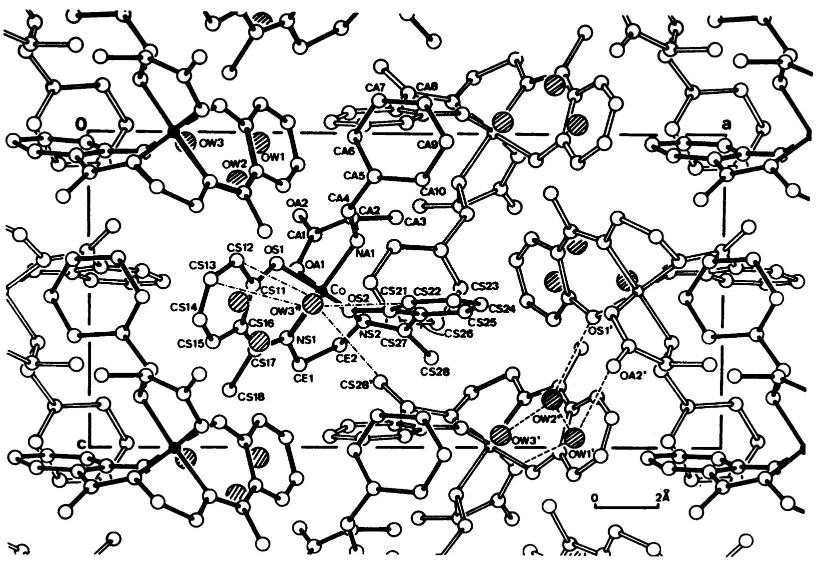

Fig. 2. A perspective drawing of the contents of the unit cell viewed down the b axis with the numbering scheme.

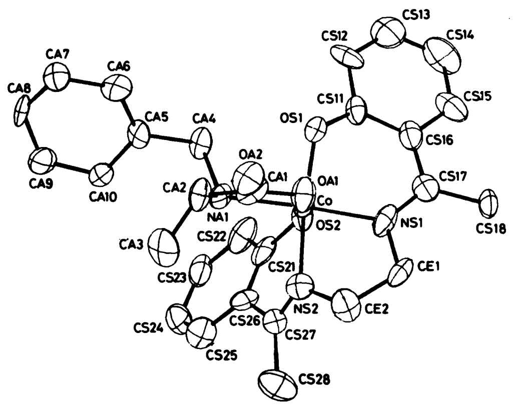

Fig. 3. An ORTEP drawing of the complex molecule. All atoms are drawn with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Molecular Structure. The ORTEP drawing of the complex molecule is shown in Fig. 3 where the thermal ellipsoids are depicted with a 50% probability. The molecular structure of [Co(α-Me-sal$_2$en)(*N*-Bz-L-ala)] has a close resemblance to that of [Co(α-Me-sal$_2$en)(L-isoleu)].[6] The *N*-benzyl-L-alaninate anion is nitrogen- and oxygen-bonded bidentate, and the α-methyl-sal$_2$en group has the *cis*-β_2 configuration[14] of a quadridentate ligand. The co-ordination polyhedron around the central cobalt atom is a meridional N_3O_3 structure in which the oxygen atom(OA 1) of the *N*-Bz-L-ala group is situated on the *trans* position of the oxygen atom(OS 2) of the phenolate moiety sal(2).

The absolute configuration of the complex molecule is Δ[15] as deduced from the known absolute configuration of the asymmetric carbon atom of the L-alaninato skeleton as an internal reference.[16] The arrangement of the group around the nitrogen atom(NA 1) of the *N*-benzyl-L-alaninato ligand is an *R* configuration and those around the asymmetric carbon atom(CA 2) is an *S* configuration. Thus, the structure of the complex molecule is denoted as Δ_{RS}-*cis*-β_2(mer) type.

Bond lengths and bond angles in the complex molecule are listed in Table 2 together with their estimated standard deviations. The Co–O and Co–N bond lengths of α-Me-sal$_2$en ligand are in agreement with those in the nonplanar [Co(salen)(acac)] derivatives within the experimental error.[2,3] The corresponding distances of the *N*-Bz-L-ala group, Co–OA1 1.938(12) and Co–NA1 1.989(15) Å, are significantly longer than those reported in Co(III) amino acidato chelates; Co–O$_{av.}$ 1.885(9) and Co–N$_{av.}$ 1.945(10) Å in (−)-mer-[Co(L-ala)$_3$][17] and Co–O 1.892(7) and Co–N 1.920(9) Å for L-phenylalaninato group in [Co(acac)$_2$(L-phala)].[18]

The bond angles around the cobalt atom are approximately in agreement with those in [Co(salen)(acac)][3] and [Co(salen)(bzacac)].[2] The chelate angle for the *N*-Bz-L-ala group, OA1–Co–NA1 85.2(6)°, is normal.

A perspective drawing of the complex molecule projected down the axis through the middle point of NS1-NS2 atoms and the cobalt atom is depicted in Fig. 4. Bailay *et al.* mentioned that the strain of the *cis*-β_2 type salen ligand is apparent in: (i) Angular strain in the "en" chelate ring, (ii) the nonplanar coordination geometry around the azomethine nitrogens, and (iii) the angular strain in the salicylideneamine moiety sal(2).[2] The highly strained conformational state about the "en" ring and the coordination geometry around the azomethine nitrogens (NS1 and NS2) are clearly shown in Fig. 4. The strain in the sal(2) moiety is also noticed by comparison with the sal(1) moiety in Fig. 4 and the sal(2) moiety in Fig. 3.

Calligaris *et al.* showed another representation for giving the degree of strain in these molecules.[3] Based on their representation, the angles between the planes passing through sal(1), sal(2), and the ala moieties, and the planes of the three equatorial planes of the octahedron around the cobalt atom are illustrated in Fig. 5.

Table 2. Bond distances and angles (e.s.d.'s in parentheses)

Bond distances (l/Å)

Co–OA1	1.938(12)	CA4–NA1	1.535(22)	CS13–CS14	1.425(32)	CS27–CS28	1.503(31)
Co–OS1	1.872(12)	CA4–CA5	1.514(23)	CS14–CS15	1.372(32)	CS27–CS26	1.427(23)
Co–OS2	1.885(10)	CA5–CA6	1.388(24)	CS15–CS16	1.384(27)	CS26–CS21	1.418(23)
Co–NA1	1.989(15)	CA6–CA7	1.395(25)	CS16–CS11	1.445(24)	CS26–CS25	1.406(25)
Co–NS1	1.911(14)	CA7–CA8	1.332(25)	CS16–CS17	1.478(25)	CS25–CS24	1.323(28)
Co–NS2	1.887(13)	CA8–CA9	1.420(25)	CS17–CS18	1.472(26)	CS24–CS23	1.414(28)
CA1–OA1	1.263(23)	CA9–CA10	1.388(25)	CS17–NS1	1.303(23)	CS23–CS22	1.391(27)
CA1–OA2	1.250(24)	CA10–CA5	1.356(25)	CE1–NS1	1.440(23)	CS22–CS21	1.391(26)
CA1–CA2	1.530(27)	CS11–OS1	1.281(20)	CE1–CE2	1.535(26)	CS21–OS2	1.337(20)
CA2–CA3	1.564(28)	CS11–CS12	1.424(25)	CE2–NS2	1.473(23)		
CA2–NA1	1.494(24)	CS12–CS13	1.315(28)	CE27–NS2	1.310(22)		

Bond angles (ϕ/°)

OA1–Co–NA1	85.2(6)	CA2–NA1–CA4	111.0(13)	CS17–NS1–CE1	120.3(15)
OS1–Co–NS1	91.8(6)	NA1–CA4–CA5	114.4(13)	Co–NS1–CS17	120.6(12)
OS2–Co–NS2	90.0(5)	CA4–CA5–CA6	115.9(15)	Co–NS1–CE1	113.1(11)
NS1–Co–NS2	83.0(6)	CA10–CA5–CA4	122.5(15)	NS1–CE1–CE2	110.9(15)
OA1–Co–OS1	87.1(5)	CA10–CA5–CA6	121.6(16)	CE1–CE2–NS2	105.1(14)
OA1–Co–NS1	90.4(6)	CA5–CA6–CA7	119.0(16)	CE2–NS2–CS27	121.4(14)
OA1–Co–NS2	91.8(6)	CA6–CA7–CA8	121.5(17)	Co–NS2–CE2	109.6(11)
OS1–Co–OS2	91.4(5)	CA7–CA8–CA9	118.3(16)	Co–NS2–CS27	126.4(12)
OS1–Co–NA1	90.4(6)	CA8–CA9–CA10	121.4(16)	NS2–CS27–CS28	121.5(17)
OS2–Co–NA1	92.2(5)	CA9–CA10–CA5	118.0(17)	NS2–CS27–CS26	118.9(15)
OS2–Co–NS1	92.3(5)	Co–OS1–CS11	120.4(11)	CS28–CS27–CS26	119.5(16)
NA1–Co–NS2	94.7(6)	OS1–CS11–CS12	117.3(15)	CS27–CS26–CS25	121.6(15)
OA1–Co–OS2	176.9(5)	OS1–CS11–CS16	126.9(15)	CS27–CS26–CS21	122.1(15)
OS1–Co–NS2	174.7(6)	CS16–CS11–CS12	115.7(15)	CS21–CS26–CS25	115.6(15)
NA1–Co–NS1	175.0(6)	CS11–CS12–CS13	121.7(18)	CS26–CS25–CS24	124.1(18)
Co–OA1–CA1	113.4(12)	CS12–CS13–CS14	124.8(20)	CS25–CS24–CS23	119.9(19)
OA1–CA1–OA2	121.7(18)	CS13–CS14–CS15	113.6(21)	CS24–CS23–CS22	119.5(18)
OA1–CA1–CA2	122.3(17)	CS14–CS15–CS16	125.2(20)	CS23–CS22–CS21	119.2(18)
OA2–CA1–CA2	116.0(17)	CS15–CS16–CS11	118.9(16)	CS22–CS21–CS26	121.7(16)
CA1–CA2–CA3	111.6(16)	CS15–CS16–CS17	122.6(16)	OS2–CS21–CS22	116.5(15)
CA1–CA2–NA1	106.5(15)	CS11–CS16–CS17	118.3(15)	OS2–CS21–CS26	121.9(14)
NA1–CA2–CA3	109.1(15)	CS16–CS17–CS18	118.0(16)	Co–OS2–CS21	118.9(10)
Co–NA1–CA2	111.5(11)	CS16–CS17–NS1	121.7(16)		
Co–NA1–CA4	112.8(10)	CS18–CS17–NS1	120.3(16)		

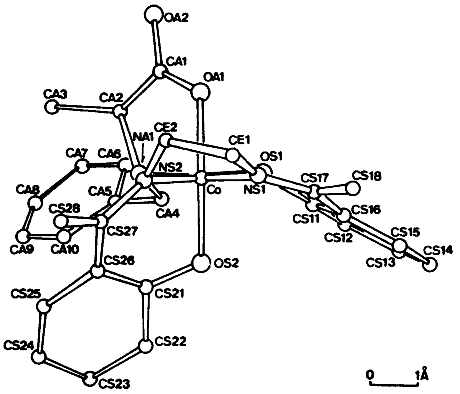

Fig. 4. Structure of the complex molecule viewed down the axis through the middle point of NS1-NS2 atoms and the cobalt atom.

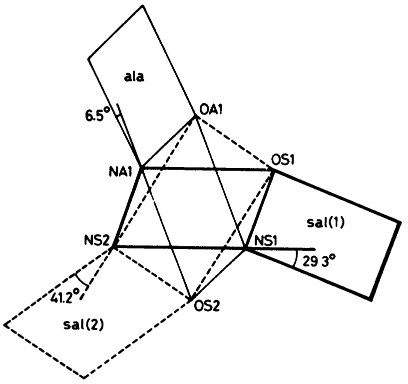

Fig. 5. A schematic drawing of the dihedral angles between the least-squares planes.

Comparison between these values, which are summarized in Table 3, and those found in [Co(salen)(acac)], 5.0, 29.3, and 17.9° for sal(1), sal(2), and acac respectively, indicates that the strain caused by the *cis*-β_2-salen skeleton in the present complex is distinctly higher than that in [Co(salen)(acac)].

The coordination of the bulky *N*-benzyl-L-alaninato ligand is probably responsible for this difference, as evidenced by the long Co–O and Co–N bond distances in the *N*-Bz-L-ala group. Two short intramolecular

Table 3. Distances of atoms from least-squares planes and dihedral angles between the planes

Least-aquares planes

Plane (1)		Plane (2)		Plane (3)	
Co	−0.040 Å	Co	−0.015 Å	Co	0.006 Å
OS1	−0.015	OA1	−0.037	OA1	0.034
NA1	0.035	OS1	0.087	OS2	0.029
NS1	0.039	OS2	−0.078	NA1	−0.034
NS2	−0.019	NS2	0.052	NS1	−0.034
Sal (1)		Sal (2)		Ala	
OS1	0.070 Å	OS2	0.027 Å	OA1	−0.020 Å
NS1	−0.146	NS2	0.159	OA2	0.059
CS11	0.001	CS21	0.001	NA1	0.058
CS12	−0.021	CS22	−0.047	CA1	−0.028
CS13	−0.008	CS23	−0.012	CA2	−0.067
CS14	−0.035	CS24	0.046		
CS15	0.009	CS25	0.032		
CS16	0.010	CS26	0.011		
CS17	0.127	CS27	−0.207		

Dihedral angles between the planes

Plane (1)	-Sal (1)	29.3°	Plane (2)	-Plane(3)	86.3°
	-Plane(2)	88.1		-Sal(1)	71.1
	-Plane(3)	88.6		-Ala	87.6
	-Sal(2)	60.5	Plane (3)	-Ala	6.5
	-Ala	89.5		-Sal(1)	67.2
Plane (2)	-Sal(2)	41.2		-Sal(2)	70.0

Plane equations: each plane is represented by $lx'+my'+nz'+p=0$ with respect to the orthogonal axes, where x', y', and z' are coordinates in Å.

	Plane(1)	Plane(2)	Plane(3)	Sal(1)	Sal(2)	Ala
l	−0.418	−0.608	−0.715	−0.808	−0.028	−0.665
m	−0.848	−0.043	0.547	−0.538	−0.192	0.522
n	−0.324	0.793	−0.435	−0.240	−0.981	−0.534
p	7.097	0.297	5.626	7.795	6.779	5.734

nonbonded contacts are found between the methylene carbon atom(CA4) of *N*-Bz-L-ala group and the oxygen atoms of the α-Me-sal$_2$en ligand: CA4–OS1 2.760(21) and CA4–OS2 3.187(20) Å.

A new question thus arises. Why the fairly bulky amino nitrogen atom of *N*-Bz-L-ala(NA1) coordinates in the somewhat crowded position which is *trans* to the nitrogen atom NS1 in the equatorial plane instead of in the less crowded position *trans* to the apical oxygen atom(OS2)?

In relation to this, it is noteworthy that the structure of chloro(pyridine)[*N*,*N*′-tetramethylenebis(salicylideneaminato)]rhodium(III), in which the sal$_2$trien group acts as a quadridentate chelated ligand and takes a common *cis*-β type structure, belongs to the meridional coordination about the arrangement of mononegative coordination atoms(Cl$^-$, O$^-$, O$^-$) and the neutral nitrogen atoms(N(py), N(sal$_2$trien), N(sal$_2$trien)).[5] In the structure of μ-peroxo-bis{[3,3′-bis(salicylideneamino)dipropylaminato]cobalt(III)}, again the coordination around the cobalt atom takes a meridional N_3O_3 type.[19] Moreover, our X-ray studies on $(-)_{435}$-(L-isoleucinato)[*N*,*N*′-ethylenebis(α-methylsalicylideneaminato)]cobalt(III) $1.5H_2O$ has clearly shown that the structure is Λ_L-*cis*-β_2-mer(N_3O_3) type.[6] Therefore, as far as we know, all the structures of the related complexes so far determined by X-ray analyses are of meridional type. Thus, it can be inferred that the preference for the meridional coordination plays an important role in determining the molecular structures of these complexes.

There were many studies on the stereoselectivity or stereospecificity of [Co(N_4)(AA)] complexes with a chiral amino acid.[20] In comparison with these *cis*-β_2-[Co(N_4)(AA)] complexes, the stereoselectivity of *cis*-β_2-type cobalt(III) Schiff-base complexes is surprisingly high: for example, in the present *N*-Bz-L-ala complex, the stereoselectivity for the Λ_{RS}-*cis*-β_2(mer) configuration is almost 100%.[9] Recently, Yamaguchi *et al.* reported that the structure of $(+)_{589}$-[Co(*R*-ala)(*SS*-pyht)]$^{2+}$, which is the predominant isomer at the equilibrium conditions, is a Λ_R-*cis*-β_2 type.[21] The complex has no significant nonbonded interaction between the tetramine moiety and the alaninato ligand. In contrast to this, our present cobalt(III) Schiff-base complex has several significant nonbonded interactions between the α-Me-sal$_2$en moiety and the *N*-Bz-L-ala group though this isomer is the most favorable one at the equilibrium conditions.[9] The intramolecular nonbonded distances are as follows: CA4–OS1 2.760(21), CA4–Co 2.947(17), CA4–OS2 3.187(20), NA1–CA10 3.190(24), NA1–CS21 3.003(23) and NA1–CS26 3.143(22) Å.

If the absolute configuration around the *N*-Bz-L-amino nitrogen atom(NA1) changes from *R* to *S* and remaining part of the molecule is fixed, several abnormally short contacts appear around the methylene

TABLE 4. INTERMOLECULAR DISTANCES AND ANGLES

Hydrogen bond distances and bonding modes			
D–H···A	D···A(l/Å)	H···A(l/Å)	D–H···A(ϕ/°)
OW1–H1(OW1)···OA2	2.81(2)	1.84(20)	171(18)
OW1–H2(OW1)···OA1$^{\mathrm{i}}$	2.96(2)	2.14(19)	161(18)
OW2–H1(OW2)···OS1	3.03(2)	2.18(16)	174(15)
OW2–H2(OW2)···OW1	2.88(2)	1.85(22)	177(19)
OW3–H1(OW3)···OW2	3.09(3)	1.98(23)	175(19)
Selected intermolecular distances (l/Å)			
CS21···CA7$^{\mathrm{ii}}$	3.60(3)	CS18···OA2$^{\mathrm{iv}}$	3.50(2)
CS26···CA8$^{\mathrm{ii}}$	3.60(2)	OA2···CS23$^{\mathrm{v}}$	3.64(2)
CS27···CA7$^{\mathrm{ii}}$	3.64(3)	CA3···CA10$^{\mathrm{v}}$	3.60(3)
CS14···CA6$^{\mathrm{iii}}$	3.65(3)	CS25···CS11$^{\mathrm{vi}}$	3.60(3)
CE1···OA2$^{\mathrm{iv}}$	3.51(2)	CS28···CS13$^{\mathrm{vi}}$	3.60(3)
Selected intermolecular distances around OW3 atom (l/Å)			
OW3$^{\mathrm{iii}}$···OS2	3.98(3)	OW3$^{\mathrm{iii}}$···CS13	3.47(3)
···CS22	3.84(3)	···CS14	3.76(4)
···CS12	3.57(3)	···CS28$^{\mathrm{vii}}$	3.46(4)

Roman numerals as superscripts refer to the following equivalent positions, relative to the reference atom at (x,y,z): i$(1/2-x, -y, -1/2+z)$, ii$(x, y, 1+z)$, iii$(1/2-x, 1-y, 1/2+z)$, iv$(1/2-x, -y, 1/2+z)$, v$(1-x, -1/2+y, 1/2-z)$, vi$(1/2+x, 1/2-y, 1-z)$, vii$(1-x, 1/2+y, 3/2-z)$. D; Hydrogen donor, A; hydrogen acceptor.

carbon atom(CA4) of the *N*-Bz moiety. The shortest intramolecular distance calculated in this Λ_{SS} model is only 2.10 Å for CA4–CS26(sal(2)). On contrast to this, the inversion of the absolute configuration around the α-carbon atom(CA2) of *N*-Bz-L-ala group from *S* to *R* introduces a fairly small repulsive effect. The shortest distance in this Λ_{RR} model is 2.64 Å for CA2(R)–CA4. Thus, our presumption about the thermodynamic stabilities among the diastereoisomers of the present complex,[9] $\Lambda_{RS} \gg \Lambda_{RR} > \Lambda_{SS}$, can be verified clearly.

Crystal Packing and Water of Crystallization. The selected intermolecular distances including the hydrogen bonding modes are summarized in Table 4. Three water molecules of crystallization(OW1, OW2, and OW3) make a columnar structure around the two-fold screw axis along the c-direction, and provide crystalline stability by forming strong hydrogen bonds. The hydrogen bonding network of these water molecules, including three other oxygen atoms(two(OA1 and OA2) come from the *N*-Bz-L-ala group and one(OS1) from the sal(1) moiety), is shown in Fig. 1 and Fig. 2 by the dotted lines.

Three benzene rings are present in this molecule. The packing modes around these benzene rings in the present crystal are as follows: (i) The benzene ring of the sal(1) moiety has close contacts with the water molecule OW3(see Table 4), and (ii) the remaining two benzene rings(one comes from the *N*-Bz-L-ala and the other from the sal(2) of the α-Me-sal$_2$en) are stacked nearly perpendicular to each other along the crystallographic c axis.

The intermolecular bond distances around the water molecule OW3 are summarized in Table 4. It is interesting to note that this water molecule lies nearly on a line which passes through the central cobalt atom and the middle point of the OS1 and OS2 oxygen atoms as shown in Fig. 2. Therefore, the central area of the OS1–Co–OS2 plane is covered with the water molecule OW3, and this water molecule prohibits other molecules from approaching along this direction.

The packing feature around the water molecule OW3 is also responsible for the thermal dehydration behavior of this crystal. The elemental analysis shows that partial dehydration should occur in this crystal. There are strong interactions around the water molecules OW1 and OW2 as shown in Table 4. In contrast, only one short contact is found around the OW3; OW3–OW2 3.09(3) Å. Additionally, the averaged isotropic temperature factor for OW3 ($B_{\mathrm{eq}}=15.4$ Å^{-2}) is considerably larger than those obtained for OW1(5.9) and OW2(9.4). Thus, it can be concluded that the partial dehydration mainly occurs at the position of OW3.

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