STRUCTURAL CHARACTERIZATION OF BIS[*N*-(*o*-HYDROXYBENZYL-(*S*)-LEUCINATO)]COBALTATE(III) ANION. TYROSINE-LIKE MODEL COMPLEX WITH STRUCTURALLY INEQUIVALENT CHELATE RINGS

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$[Co(NH_3)_4(H_2O)_2]OH$. $[Co(ohb-(S)-Leu)_2]$. $2 H_2O$ (ohb, *o*-hydroxybenzyl) was characterized by single-crystal X-ray diffraction which shows that both ligands in the $[Co(ohb-(S)-Leu)_2]^-$ anion assume *facial* coordination mode with all donor atoms *trans* to each other, proposed on the basis of UV-VIS and ^{13}C NMR spectroscopy, with *R,S* configuration of secondary N atoms. Compound crystallizes in the tetragonal space group $I4_1$ with unit cell dimensions $a = 22.173(7)$, $c = 13.270(2)$ Å, $V = 6\ 524$ Å^3, $Z = 4$. Structural data show that both ligands are not equivalent. Bond angles and bond lengths depend on whether secondary N atoms adopt *R* or *S* configuration. The average bond lengths are shorter when the ohb-(*S*)-Leu ligand coordinates with (N)*R* configuration.
Key words: Tyrosine-like metal complex; *o*-Hydroxybenzyl-(*S*)-leucinato ligand; $[Co(ohb-(S)-Leu)_2]^-$ structure.

Tyrosine plays an important role in several iron containing metalloproteins where it comprises, together with other ligating amino acids, the active sites[1]. Since the amino acid residues proximal to tyrosine are not identical in these metalloproteins (cf. transferrins[2]), it can be thus expected that they will exhibit different second order influence on metal binding sites. In order to explore the metal coordination sphere ligand proximity effect, substitutionally inert model bis[*N*-(*o*-hydroxybenzyl-amino-acidato)]cobaltate(III) complexes of homologous tridentate ligands with invariant donor atom sets mimicking tyrosine coordination have been prepared and characterized[3]. It has been found that chiroptical and some other properties vary systematically with the number of ligand carbon atoms; leucine complex has deviated showing for example double the number of carbon atom NMR resonances and unexpectedly more negative reduction potential than other complexes of electrophilic ligands.

This study of molecular and crystal structure of the [Co(*o*-hydroxybenzyl-(*S*)-leucinato)₂]⁻ anion ([Co(ohb-(*S*)-Leu)₂]⁻; ohb, *o*-hydroxybenzyl) has been undertaken primarily to verify the geometry of complexes already described, structure of which has been

tentatively assigned on the basis of electronic absorption and ^{13}C NMR spectroscopies and to obtain more details which could explain different leucine complex behaviour.

EXPERIMENTAL

^{13}C NMR spectra (δ, ppm) were recorded in $(CD_3)_2SO$ on a Bruker AM 400 equipment with DMSO as internal standard. Optical spectra in the UV and visible regions were measured with a Specord M 40 spectrophotometer. Circular dichroism spectra were obtained with a Jobine Mark V Dichrograph.

Preparation [Co(NH$_3$)$_4$(H$_2$O)$_2$]OH . [Co(ohb-(S)-Leu)$_2$] . 2 H$_2$O

This compound, contrary to a previously described method[3], was prepared using $Na_3[Co(NO_2)_6]$ as a cobalt(III) source. Solid $Na_3[Co(NO_2)_6]$ (4.04 g, 10 mmol) was gradually added together with a small portion of activated charcoal to a solution containing ohb-(S)-Leu (4.74 g, 20 mmol) and NaOH (1.60 g, 40 mmol) in water (200 ml). The mixture was stirred and heated to 50–60 °C for 1 h. The resulting brown solution was filtered while hot. To the filtrate solid $[Co(NH_3)_6]Cl_3$ (2.67 g, 10 mmol) was immediately added and khaki colored product that deposited was filtered off, washed successively with water and methanol. Methanolic filtrate was set aside for crystallization and deep brown crystalls that deposited were washed with water and air dried. For $C_{52}H_{93}N_8Co_3O_{17}$ (1 278.9) calculated: 48.83% C, 7.33% H, 8.76% N; found: 48.88% C, 7.10% H, 8.70% N.

Crystal Structure Determination

The structure was solved by direct methods and anisotropically refined by full matrix least squares. Hydrogen atom parameters were found from the expected geometry, difference synthesis and were not refined. The C11–C13 and C24–C26 atoms of isopropyl groups were isotropically refined assuming their ideal geometry. Absorption was neglected. Crystallographic data together with atomic coordinates and isotropic thermal parameters for non-hydrogen atoms are presented in Tables I and II.

RESULTS AND DISCUSSION

[Co(ohb-(S)-aa)$_2$]$^-$ anion (aa means amino acid anion) can exist in fifteen isomeric forms (nine of them are *facial* and six *meridional*). From those, only *facial*-all-*trans* isomers were isolated and identified[3]. Attempts to obtain *facial*-all-*trans* Na[Co(ohb-(S)-Leu)$_2$] isomer in the crystalline form suitable for X-ray analysis were unsuccessful so that this isomer was isolated as [Co(NH$_3$)$_4$(H$_2$O)$_2$]OH[Co(ohb-(S)-Leu$_2$]$_2$. 2 H$_2$O salt. Its visible ($\nu_{max} = 26.667$ cm^{-1}, $\varepsilon = 1\ 392$ mol^{-1} cm^{-1}; $\nu_{max} = 15.272$ cm^{-1}, $\varepsilon = 306$ mol^{-1} cm^{-1} in DMSO) and CD spectra (Fig. 1) resemble those of Na[Co(ohb-aa)$_2$] complexes (aa is glycine, (S)-α- alanine, isobutyric acid, (S)-norvaline and (S)-valine) confirming that these already described complexes[3] have the same *facial*-all-*trans* geometry. Furthermore, the similarity in the CD spectra indicates also coincidence of the significant structural features. The ^{13}C NMR spectrum (spectral assignments are based on ^{1}H-^{13}C heteronuclear correlation with the APT) which displays double signals for each carbon atom (Table III) is, as can be expected, analogous to that of Na[Co(ohb-(S)-Leu)$_2$] (ref.[3]). Double the number of signals was ascribed to a sterically

forced deviations of the two ohb(*S*)-Leu ligands from their equivalent positions[3]. It follows from these similarities that the [Co(ohb-(*S*)-Leu)$_2$]$^-$ anion can serve (taking different structural environments of the two leucine ligands into account) as a structural model for other *facial*-all-*trans* Na[Co(ohb-aa)$_2$] complexes.

Structure Description

As can be seen from Fig. 2, the crystal structure of [Co(NH$_3$)$_4$(H$_2$O)$_2$]OH[Co(ohb-(*S*)-Leu)$_2$]$_2$. 2 H$_2$O possess extensive and complex network of hydrogen bonds (Table IV) linking four anions into squares with channels packed by [Co(NH$_3$)$_4$(H$_2$O)$_2$]OH^{2+} cations. Furthermore, the two [Co(ohb-(*S*)-Leu)$_2$]$^-$ anions in every group of four anions are possibly hold together through hydrophobic interaction between the leucine CH$_3$

TABLE I
Crystallographic data for [Co(NH$_3$)$_4$(H$_2$O)$_2$]OH[Co(ohb-(*S*)-Leu)$_2$]$_2$. 2 H$_2$O and structure refinement parameters

Space group	*I*4$_1$
Crystal dimensions	0.35 × 0.30 × 0.25 mm
Diffractometer and radiation used	Enraf–Nonius CAD4 MoKα = 0.71073 Å
Scan technique	$\omega/2\theta$
No. and θ range of reflections for lattice parameter refinement	17; 14.91–18.70°
Range of *h*, *k* and *l*	0→23, 0→23, –14→14
Standard reflections monitored in interval; intensity fluctuation	120 min; –1.2%
Total number of reflections measured	3 574
2θ range	0–44°
Value of R_{int}	0.054
No. of unique observed reflections	2 007
Criterion for observed reflections	$I \geq 1.96\sigma(I)$
Function minimized	$\sum w\,(F_o^2 - F_2^2)^2$
Weighting scheme	$w = 1/[\sigma^2(F_o)^2 + (0.0457P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Parameters refined	333
Value of R	0.060
Value of $wR(F^2)$	0.122
Value of S	0.918
Flack *x* parameter	–0.03(4)
Ratio of max. least-squares shift to e.s.d. in the last cycle	0.003
Max. and min. heights in final map	0.39, –0.31 e/Å^3
Source of atomic scattering factors	SHELXL93 (ref.[4])
Programs used	SDP (ref.[5]), SHELXS86 (ref.[6]), PARST (ref.[7])

TABLE II

Atomic coordinates (. 10^4) and equivalent isotropic thermal parameters (. 10^3) for non-hydrogen atoms. The isotropic equivalent parameter is defined as $U_{eq} = 1/3 \sum \sum U_{ij} a_i a_j \mathbf{a}_i^* \mathbf{a}_j^*$

Atom	x	y	z	U_{eq}, Å^2
Co1	–115(1)	2494(1)	–1039(7)	56(1)
Co2	0	5000	–44(7)	53(1)
O1	–211(4)	1837(3)	–1947(9)	62(2)
O2	–570(3)	2063(3)	–70(10)	71(2)
O3	–673(4)	1565(4)	–3330(9)	83(3)
O4	–24(3)	3153(3)	–155(9)	59(2)
O5	340(4)	2928(4)	–2019(9)	71(2)
O6	472(4)	3460(4)	1231(9)	76(3)
N1	–810(5)	2835(4)	–1721(10)	75(3)
N2	580(4)	2134(4)	–335(10)	62(3)
N3	362(4)	5518(4)	981(11)	80(3)
N4	–320(4)	4446(4)	–1085(11)	67(3)
C1	–1382(6)	2799(6)	–1043(13)	78(4)
C2	–1541(6)	2177(7)	–807(11)	70(4)
C3	–2109(6)	1903(10)	–991(13)	108(6)
C4	–2254(9)	1336(10)	–651(15)	108(6)
C5	–1824(9)	1035(8)	–196(15)	112(6)
C6	–1256(7)	1251(7)	66(11)	77(4)
C7	–1105(6)	1826(7)	–286(12)	69(4)
C8	–597(6)	1944(5)	–2664(14)	64(4)
C9	–913(6)	2522(5)	–2691(12)	67(3)
C10	–742(7)	2882(5)	–3573(13)	101(5)
C11	–1058(8)	3511(7)	–3681(14)	198(9)
C12	–1746(10)	3383(15)	–3843(27)	315(17)
C13	–868(14)	3720(15)	–4764(15)	288(15)
C14	1135(5)	2227(5)	–880(11)	61(3)
C15	1273(5)	2853(6)	–1157(11)	63(3)
C16	1810(7)	3114(7)	–915(12)	87(4)
C17	1967(7)	3685(8)	–1291(14)	93(5)
C18	1574(8)	3993(7)	–1905(13)	84(4)
C19	1035(7)	3732(6)	–2164(11)	77(4)
C20	877(6)	3155(6)	–1786(11)	63(3)
C21	357(6)	3071(6)	585(12)	60(3)
C22	560(5)	2430(5)	695(11)	57(3)
C23	1125(3)	2311(3)	1375(7)	83(4)
C24	978(7)	2315(9)	2531(8)	173(8)
C25	1607(8)	2085(9)	2912(17)	179(8)
C26	557(12)	1769(11)	2790(22)	252(13)
O7	–551(3)	–814(3)	2(7)	130(4)
OW1	–745(3)	5481(4)	–71(10)	88(3)
OW2	0	10000	1366(7)	330(19)
OW3	0	5000	–3239(7)	185(9)

groups and the aromatic system of the neighboring anion (CH_3-phenolate distance is 3.3314 Å). From the two ohb-(*S*)-leucinato ligands coordinated around cobalt(III) in each anion, only those with the *S* configuration of the secondary N atoms (vide infra) may be involved in this interaction.

The molecular structure of the anion and numbering scheme is shown in Fig. 3 and Table V lists selected bond lengths and bond angles. As follows from the data obtained, the O–Co–N angles associated with the five-membered chelate rings are 85.1(4)° and
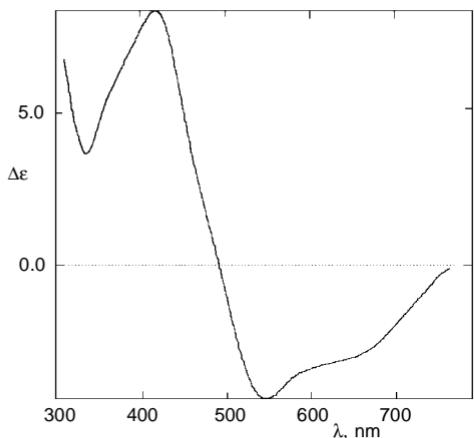

Fig. 1
Circular dichroism spectrum of $[Co(NH_3)_4(H_2O)_2]OH[Co(ohb-(S)-Leu)_2]_2$. 2 H_2O in DMSO solution
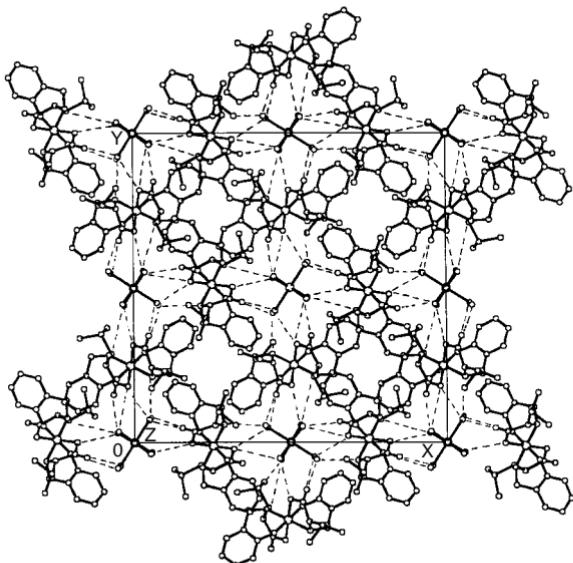
Fig. 2
Crystal packing diagram of $[Co(NH_3)_4(H_2O)_2]OH[Co(ohb-(S)-Leu)_2]_2$. 2 H_2O

85.8(4)° while those associated with the six-membered chelate rings are 95.3(4) and 96.3(4)°. These values suggest that both tridentate ligands with all-*trans* N_2O_4 donor set atoms surround the cobalt atom in a somewhat distorted octahedral fashion. The angle expanding six-membered chelate rings coordinate, similarly as in other cases[8,9] with the preference in the same plane. Phenolate rings assume *anti*-conformation.

Each of the two ohb-(*S*)-Leu ligands has two chiral centers, i.e. carbon atom with *S* configuration and secondary N atom configuration of which being probably determined by steric interactions. Most serious are those arising from the intraligand steric crowding between the *sec*-butyl group of the leucine part of ligand and hydrogen atom of the benzyl –CH$_2$–N– ligand moiety (Dreiding scale stereomodels suggest that the structure with *R,R* configuration of secondary atoms experiences the least severe nonbonded interactions between *sec*-butyl groups which increase gradually in the series *R,R* < *R,S* < *S,S**). Results of X-ray analysis presented here show that the secondary N atoms adopt *R* and *S* configuration which together with the donor atoms arrangement possesses to the [Co(ohb-(*S*)-Leu)$_2$]$^-$ anion idealized C_i point symmetry and consequently this anion has no configurational chirality. Its optical activity (Fig. 2) derives thus from different vici-
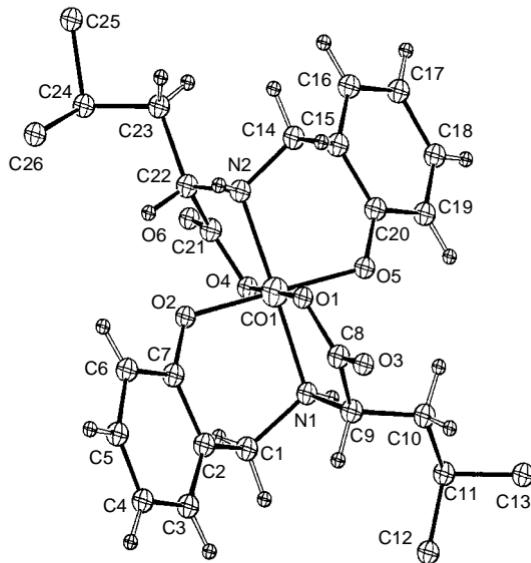
Fig. 3

Molecular structure of [Co(ohb-(*S*)-Leu)$_2$]$^-$ anion showing the atom-labelling scheme

* Recent study[10] of a structurally related [Co(ohb-aa)$_2$]$^{3-}$ complexes (aa is (*S*)-aspartic or (*S*)-glutamic acid anion) using molecular mechanics indicates that the minimized energy differences between *facial*-all-*trans* isomers with *R* and *S* secondary N atom configuration represents only minor contribution to an overal stability of isomers. The calculations carried out for *facial* isomers show the following order of stablity: *R,R* > *S,S* ≥ *R,S*.

nal, conformational and other uncommon effects connected undoubtedly with the coordination of rigid fused six-membered chelate rings[3,9,11] which contribute strongly to overal rotational strength. It should be pointed out in this connection that the CD spectra pattern and rotational strength of both T_{1g} and T_{2g} transitions observed for [Co(ohb-(S)-aa)$_2$]$^{n-}$ complexes (aa are amino acid anions including aminodicarboxylic acids[10]) do not depend on whether the complex has inherent chirality or not. From this it follows that the cobalt atom chirality does not dominate in these and similar complexes[11] to overall optical activity, contrary to other in the literature described common chiral complexes[12].

Both five- and six-membered fused chelate rings of the ohb-(S)-Leu framework formed by the ligands which tend to keep isolated chelate rings nearly planar, deviate from the planarity and assume asymmetric envelope (λ, δ) and asymmetric boat (λ, δ) conformations. As follows from Table VI, degree of these deviations varies both with

TABLE III
^{13}C NMR spectrum (δ, ppm) of [Co(NH$_3$)$_4$(H$_2$O)$_2$]OH[Co(ohb-(S)-Leu)$_2$] . 2 H$_2$O

α-C	β-C	γ-C	δ-C		CH$_2$–N	CO$_2^-$	C$_{ipso}$–CH$_2$	C$_{ipso}$–O
58.8	37.0	23.7	21.8	23.0	46.4	180.7	125.2	164.8
60.6	42.7	24.4	21.9	23.2	51.2	182.4	124.7	166.9

TABLE IV
Hydrogen bonding distances (Å) and angles (°) for [Co(NH$_3$)$_4$(H$_2$O)$_2$]OH{Co(ohb-(S)-Leu)$_2$]$_2$. 2 H$_2$O^a

Hydrogen bonds	Donor...Acceptor	H...Acceptor	Donor–H...Acceptor
N4–H1N4...O4	3.190(13)	2.325(8)	158.5(8)
N4–H2N4...OW3	3.191(21)	2.333(9)	173.0(6)
N2–H1N2...O7^i	2.982(11)	2.085(11)	168.2(10)
N4–H3N4...O3^{ii}	2.793(13)	1.906(9)	176.6(7)
OW1–H1W1...O1^{ii}	2.983(12)	2.007(9)	179.6(6)
OW1–H2W1...O6^{iii}	2.978(14)	1.972(9)	178.0(5)
N3–H1N3...O4^{iii}	3.395(14)	2.563(8)	155.7(6)
O7–H1O7...O6^{iv}	2.868(13)	1.868(13)	178.4(7)
N3–H2N3...O1^{iv}	3.388(21)	2.593(9)	148.0(9)
N3–H3N3...O7^{iv}	3.298(13)	2.468(7)	154.9(7)

^{a} For atom-labelling scheme see Fig. 3. Symmetry code (i) –x, –y, z; (ii) –y, $x + 0.5$, $z + 0.25$; (iii) –x, –y + 1, z; (iv) y –0.5, –x, z –0.25.

TABLE V

Selected bond distances (Å) and angles (°) for [Co(NH$_3$)$_4$(H$_2$O)$_2$]OH[Co(ohb-(S)-Leu)$_2$]$_2$. 2 H$_2$O. For symmetry code i see Table IV

Atoms	Distances	Atoms	Distances
Co1–O4	1.887(7)	Co1–O2	1.893(9)
Co1–O1	1.903(8)	Co1–O5	1.907(9)
Co1–N1	1.940(9)	Co1–N2	1.963(9)
Co2–N3^i	1.953(9)	Co2–N3	1.953(9)
Co2–OW1	1.966(8)	Co2–OW1^i	1.966(8)
Co2–N4	1.980(9)	Co2–N4^i	1.980(9)
O1–C8	1.301(14)	O2–C7	1.328(13)
O3–C8	1.233(13)	O4–C21	1.308(13)
O5–C20	1.329(13)	O6–C21	1.243(13)
N1–C9	1.481(13)	N1–C1	1.56(2)
N2–C14	1.439(12)	N2–C22	1.509(13)
C1–C2	1.46(2)	C2–C3	1.42(2)
C2–C7	1.42(2)	C3–C4	1.37(2)
C4–C5	1.31(2)	C5–C6	1.39(2)
C6–C7	1.40(2)	C8–C9	1.46(2)
C9–C10	1.47(2)	C11–C12	1.568(8)
C11–C13	1.567(8)	C11–C10	1.568(8)
C14–C15	1.47(2)	C15–C16	1.36(2)
C15–C20	1.39(2)	C16–C17	1.40(2)
C17–C18	1.38(2)	C18–C19	1.37(2)
C19–C20	1.42(2)	C21–C22	1.50(2)
C22–C23	1.566(12)	C24–C23	1.568(8)
C24–C25	1.568(8)	C24–C26	1.568(8)

Atoms	Angles	Atoms	Angles
O4–Co1–O2	91.5(3)	O4–Co1–O1	179.1(3)
O2–Co1–O1	89.1(3)	O4–Co1–O5	88.6(3)
O2–Co1–O5	179.8(4)	O1–Co1–O5	90.8(3)
O4–Co1–N1	94.1(4)	O2–Co1–N1	95.3(4)
O1–Co1–N1	85.1(4)	O5–Co1–N1	84.5(4)
O4–Co1–N2	85.8(4)	O2–Co1–N2	83.9(4)
O1–Co1–N2	94.9(4)	O5–Co1–N2	96.3(4)
N1–Co1–N2	179.2(5)	N3^i–Co2–N3	91.6(6)

TABLE V
(*Continued*)

Atoms	Angles	Atoms	Angles
N3^i–Co2–OW1	89.2(4)	N3–Co2–OW1	92.2(4)
N3^i–Co2–OW1^i	92.2(4)	N3–Co2–OW1^i	89.2(4)
OW1–Co2–OW1^i	177.9(6)	N3^i–Co2–N4	88.5(4)
N3–Co2–N4	176.4(4)	OW1–Co2–N4	91.4(4)
OW1^i–Co2–N4	87.2(4)	N3^i–Co2–N4^i	176.4(4)
N3–Co2–N4^i	88.5(4)	OW1–Co2–N4^i	87.2(4)
OW1^i–Co2–N4^i	91.4(4)	N4–Co2–N4^i	91.6(6)
C8–O1–Co1	113.3(7)	C7–O2–Co1	121.9(8)
C21–O4–Co1	115.3(8)	C20–O5–Co1	120.5(7)
C9–N1–C1	110.6(10)	C9–N1–Co1	110.2(7)
C1–N1–Co1	110.9(7)	C14–N2–C22	115.2(9)
C14–N2–Co1	112.3(7)	C22–N2–Co1	103.9(6)
C2–C1–N1	111.7(10)	C3–C2–C7	116.9(14)
C3–C2–C1	125.7(14)	C7–C2–C1	117.3(12)
C4–C3–C2	123(2)	C5–C4–C3	117(2)
C4–C5–C6	127(2)	C5–C6–C7	116.6(14)
O2–C7–C6	120.1(14)	O2–C7–C2	119.8(13)
C6–C7–C2	119.9(13)	O3–C8–O1	119.2(11)
O3–C8–C9	121.1(14)	O1–C8–C9	119.7(12)
C8–C9–C10	112.0(11)	C8–C9–N1	108.4(11)
C10–C9–N1	113.4(10)	C9–C10–C11	116.2(14)
C21–C11–C13	101(2)	C12–C11–C10	107(2)
C13–C11–C10	103(2)	N2–C14–C15	115.3(9)
C16–C15–C20	119.3(13)	C16–C15–C14	121.8(12)
C20–C25–C14	118.4(11)	C15–C16–C17	121(2)
C18–C17–C16	120.1(14)	C19–C18–C17	119(2)
C18–C19–C20	120.5(14)	O5–C20–C15	121.6(12)
O5–C20–C19	118.8(13)	C15–C20–C19	119.5(13)
O6–C21–O4	123.6(11)	O6–C21–C22	122.0(11)
O4–C21–C22	113.6(12)	C21–C22–N2	108.7(10)
C21–C22–C23	117.2(9)	N2–C22–C23	115.3(9)
C22–C23–C24	113.3(9)	C23–C24–C25	97.4(12)
C23–C24–C26	110(2)	C25–C24–C26	102(2)

TABLE VI
Weighted least-squares planes through the starred atoms[14]

Plane 1
$m1 = -0.61568(0.00467)$
$m2 = -0.43785(0.00470)$
$m3 = 0.65515(0.00415)$
$D = -1.73906(0.02762)$

Atom	d	s	d/s	$(d/s)^2$
O4*	0.0000	0.0091	0.000	0.000
CO1*	0.0000	0.0022	0.000	0.000
N2*	0.0000	0.0115	0.000	0.000
C21	–0.2086	0.0133	–15.692	246.254
C22	–0.6801	0.0121	–56.334	3 173.572
	Sum $(d/s)^2$ for starred atoms			0.000

Plane 2
$m1 = -0.60111(0.00504)$
$m2 = -0.45956(0.00483)$
$m3 = 0.65382(0.00390)$
$D = -1.85794(0.02848)$

Atom	d	s	d/s	$(d/s)^2$
O1*	0.0000	0.0086	0.000	0.000
CO1*	0.0000	0.0022	0.000	0.000
N1*	0.0000	0.0133	0.000	0.000
C9	0.3822	0.0146	26.173	685.010
C8	0.1816	0.0129	14.130	199.663
	Sum $(d/s)^2$ for starred atoms			0.000

Plane 3
$m1 = 0.07098(0.00713)$
$m2 = -0.77428(0.00362)$
$m3 = -0.62884(0.00427$
$D = -5.14914(0.01456)$

Atom	d	s	d/s	$(d/s)^2$
N1*	0.0000	0.0133	0.000	0.000
CO1*	0.0000	0.0023	0.000	0.000
O2*	0.0000	0.0096	0.000	0.000
C1	0.4233	0.0174	24.342	592.516
C2	–0.5688	0.0175	–32.424	1 051.327
C7	–0.6548	0.0138	–47.297	2 236.984
	Sum $(d/s)^2$ for starred atoms			0.000

TABLE VI
(*Continued*)

Plane 4
$m1 = -0.03338(0.00558)$
$m2 = -0.79059(0.00286)$
$m3 = -0.61144(0.00366)$
$D = -5.20757(0.01087)$

Atom	d	s	d/s	$(d/s)^2$
N2*	0.0000	0.0114	0.000	0.000
CO1*	0.0000	0.0023	0.000	0.000
O5*	0.0000	0.0090	0.000	0.000
C14	−0.2469	0.0133	−18.575	345.039
C15	0.6257	0.0152	41.210	1 698.256
C20	0.6018	0.0138	43.583	1 899.487
Sum $(d/s)^2$ for starred atoms				0.000

Plane 5
$m1 = -0.05056(0.00457)$
$m2 = -0.78363(0.00225)$
$m3 = -0.61917(0.00276)$
$D = -5.16725(0.00980)$

Atom	d	s	d/s	$(d/s)^2$
N1*	0.0323	0.0133	2.432	5.917
O2*	−0.0171	0.0096	−1.782	3.176
N2*	0.0240	0.0114	2.102	4.419
O5*	−0.0148	0.0090	−1.636	2.676
C1	0.4728	0.0173	27.269	743.591
C2	−0.5301	0.0176	−30.198	911.947
C7	−0.6490	0.0138	−46.947	2 203.996
Sum $(d/s)^2$ for starred atoms				16.189

Plane 6
$m1 = -0.05056(0.00449)$
$m2 = -0.78363(0.00218)$
$m3 = -0.61917(0.00267)$
$D = -5.16725(0.00969)$

Atom	d	s	d/s	$(d/s)^2$
N1*	0.0323	0.0133	2.432	5.917
O2*	−0.0171	0.0096	−1.782	3.176
N2*	0.0240	0.0114	2.102	4.419
O5*	−0.0148	0.0090	−1.636	2.676
C14	−0.2090	0.0133	−15.725	247.262
C15	0.6568	0.0152	43.287	1 873.726
C20	0.6057	0.0138	43.816	1 919.856
Sum $(d/s)^2$ for starred atoms				16.189

the secondary N atom configuration and chelate ring size. S configuration of secondary N

atom in comparison with R one (N1 atom) forces five-membered chelate ring α-CH atom more away from the planarity diminishing the above mentioned intraligand non-bonding interaction. On the other hand, more skewed structure, especially as far as benzyl –CH_2–N– group is concerned, corresponds to six-membered chelate ring with R stereogonic secondary N1 center. Consistent with the different degree of chelate rings puckering in dependence on the secondary N atom configuration is a ring strain which manifests itself in different values of endocyclic angles.

Structural inequality described which is a characteristic structural feature of the [Co(ohb-(S)-Leu)$_2$]$^-$ anion becomes more apparent when the corresponding chelate ring bond angles and bond distances are compared (Table V). This rather unsymmetrical structure is believed to arise from different already mentioned factors related to the chelate ring size, conformations and also to a different chiral environments induced by the coordination of the two nonbridged, spatially independent diastereoisomeric ligands. This is supported by the inspection of bond angles and lengths in a structurally related *cis*-(N)-[N,N'-bis(*o*-hydroxybenzyl)(ethylenediamine-N,N'-diacetato)]ironate(III) anion[13] with R and S secondary N atom configurations which are, although this ethylene-bridged structure exerts severe strains (within the experimental errors), the same. Consistent with the mentioned internal ring strain which seems to be a major factor in energy differences in the coordination of ligands with (R)-N1 and (S)-N2 centers are the Co-donor atom distances which reflect different strength of Co–O and Co–N interactions. Inspection of data given in Table V suggests that all cobalt-donor atom interactions are stronger when tridentate ligand coordinates with R secondary N atom configuration (N1 atom). Inequality of the Co-donor atom bond strength may be one of the reasons of different [Co(ohb-(S)-Leu)$_2$]$^-$ behaviour[3] in comparison with other [Co(ohb-aa)$_2$]$^-$ homologous complexes. From the comparison of C7–O2–Co (121.9(8)°) and C20–O5–Co (120.5(7)°) angles it follows that the phenolate Co–O5 bond which is a part of the chelate ring with (S)-N configuration (N2 atom) has somewhat more p character which may be consistent with longer and weaker cobalt–phenolate bond.

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