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Contribution from Ames Laboratory—USDOE and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Crystal and Molecular Structure of [α-*N*-(*o*-Hydroxybenzyl)-L-histidinato](L-alaninato)cobalt(III) Dihydrate[1]

KENNETH E. VOSS, ROBERT J. ANGELICI,* and ROBERT A. JACOBSON*

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The crystal and molecular structure of [α-*N*-(*o*-hydroxybenzyl)-L-histidinato](L-alaninato)cobalt(III) dihydrate has been determined by three-dimensional X-ray analysis. The compound crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 13.188$ (2) Å, $b = 18.140$ (2) Å, $c = 7.842$ (1) Å, and $Z = 4$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures to a final discrepancy factor $R = 0.059$ for 3553 observed reflections ($I_{\mathrm{obsd}} \geq 3\sigma_I$). The geometry around the cobalt ion is distorted octahedral. The α-*N*-(*o*-hydroxybenzyl)-L-histidinato ligand is tetradentate, bonding through the imidazole nitrogen, carboxylate oxygen, secondary amino nitrogen, and phenolate oxygen atoms. The histidinate fragment of the tetradentate ligand occupies one face of the coordination octahedron with the phenolate oxygen of the *o*-hydroxybenzyl substituent occupying the position trans to the histidinate carboxyl oxygen. The bidentate L-alaninate ligand is attached with its amino nitrogen trans to the imidazole nitrogen and its carboxylate oxygen trans to the secondary amino nitrogen of the tetradentate ligand. The L-alaninato five-membered chelate ring adopts the conformation of an asymmetric envelope.

Introduction

A realization of the importance of transition metal ions in biological processes[1] has led to a dramatic growth in the number of investigations of interactions between amino acids and transition metal ions. As part of a program designed to investigate stereoselective effects that might occur in mixed (ternary) transition metal complexes of optically active amino acids, we have synthesized the potentially tetradentate α-*N*-(*o*-hydroxybenzyl)-L-histidine ligand (L-OHBH) as well as its mixed Co(III) complexes, [(L-OHBH)(AA)Co$^{\mathrm{III}}$], where AA = L-, D-, DL-alaninate, or α-aminoisobutyrate.[2] In these complexes the tridentate histidine portion of the L-OHBH ligand could, because of geometric constraints, occupy only a face of the coordination octahedron; however, examination of molecular models indicated that the phenolate oxygen of the *o*-hydroxybenzyl group could coordinate trans to either the carboxylate oxygen or imidazole nitrogen donor atoms of the histidinate fragment. In addition, the orientation of the other amino acidate ligand in the coordination sphere was unknown. In order to interpret spectral features of this and related complexes,[2] an investigation of the structure of [(L-OHBH)(L-Ala)Co$^{\mathrm{III}}$]·2H_2O was undertaken.

Experimental Section

Preparation. The preparation, purification, and characterization of [Co(L-OHBH)(L-Ala)]·2H_2O are described elsewhere.[2]

Crystal Data. The crystals were obtained, by recrystallization from hot water, in the form of dark red prismatic rods. A single crystal of approximate dimensions 0.2 × 0.2 × 0.4 mm was chosen and mounted on the end of a glass fiber with Duco cement. The crystal was placed on a four-circle diffractometer and initial ω-oscillation photographs were taken using a Polaroid cassette. The photographs indicated that the crystal was indeed single, and from these photographs the coordinates of 15 reflections were then input into our automatic indexing program.[3] The reduced cell and reduced cell scalars that resulted from this program indicated orthorhombic symmetry. Subsequent Polaroid oscillation pictures around each of the three axes in turn verified the presence of *mmm* Laue symmetry. Observed layer line spacings agreed, within experimental error, with those predicted for this cell by the indexing routine. A least-squares refinement of the lattice constants based on the $\pm 2\theta$ measurements of 17 strong high-angle reflections determined by left–right, top–bottom beam splitting on the previously aligned four-circle diffractometer (Mo Kα radiation, λ 0.709 54 Å), at 25 °C, yielded $a = 13.188$ (2), $b = 18.140$ (2), and $c = 7.842$ (1) Å.

Collection and Reduction of X-ray Intensity Data. Data were collected at room temperature using an automated four-circle diffractometer designed and built in the Ames Laboratory and previously described by Rohrbaugh and Jacobson.[4] Within a 2θ sphere of 50° ($(\sin \theta)/\lambda = 0.596$ Å^{-1}) all data in the hkl and $hk\bar{l}$ octants were measured. Of these 3880 reflections, 3553 had $I_{\mathrm{obsd}} \geq 3\sigma_I$ and were considered observed. The estimated deviations in the structure factors were calculated by the finite difference method.[5]

The intensity data were then corrected for Lorentz–polarization effects, but no absorption correction was made ($\mu = 9.84$ cm^{-1}). The maximum transmission factor was less than 0.82 while the minimum exceeded 0.67. The estimated error in each intensity was calculated by

$$\sigma_I^2 = C_{\mathrm{T}} + 2C_{\mathrm{B}} + (0.03C_{\mathrm{T}})^2 + (0.03C_{\mathrm{B}})^2$$

where C_{T} and C_{B} represent the total count and background count, respectively, and the factor 0.03 represents an estimate of nonstatistical errors.

Solution and Refinement of Structure. Observed systematic extinctions of $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, and $00l$, $l = 2n + 1$, uniquely determine the space group to be $P2_12_12_1$. The position of the cobalt atom was obtained by analysis of a three-dimensional Patterson function. The remaining atoms were found by successive structure factor[6] and electron density map calculations.[7] In addition to positional parameters for all nonhydrogen atoms, the anisotropic

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Table I. Final Atom Positional[a] and Thermal Parameters[b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	5185.6 (0.6)[c]	1302.8 (0.4)	3752 (1)	41.5 (0.5)	16.8 (0.3)	72 (0.1)	−1.1 (0.3)	5.2 (0.7)	−3.8 (0.5)
O1	4828 (4)	2031 (2)	5392 (6)	61 (3)	22 (1)	106 (7)	3 (2)	−4 (5)	−5 (3)
O2	5552 (6)	2715 (3)	7426 (8)	116 (5)	29 (2)	145 (9)	7 (3)	−27 (6)	−22 (4)
O3	5526 (4)	568 (2)	2125 (6)	57 (3)	19 (1)	86 (7)	−1 (1)	−10 (4)	5 (3)
O4	4074 (4)	1595 (3)	2341 (6)	54 (3)	22 (1)	110 (8)	0 (2)	0 (4)	12 (3)
O5	2479 (4)	1302 (3)	1688 (8)	52 (3)	31 (2)	203 (11)	3 (2)	−48 (5)	19 (4)
O6	5235 (6)	540 (4)	−1494 (7)	119 (5)	42 (2)	132 (9)	−24 (3)	4 (7)	7 (4)
O7	397 (6)	751 (4)	1816 (9)	102 (5)	33 (2)	232 (13)	−7 (3)	−17 (7)	9 (4)
N1	6085 (5)	1978 (3)	2635 (7)	63 (4)	21 (2)	81 (9)	0.6 (2)	3 (5)	6 (3)
N2	6716 (6)	2690 (4)	652 (8)	84 (5)	25 (2)	118 (10)	−6 (3)	33 (6)	8 (4)
N3	6225 (4)	1049 (3)	5377 (7)	45 (3)	22 (2)	99 (9)	−2 (2)	−8 (5)	1 (3)
N4	4211 (4)	655 (3)	4836 (7)	44 (3)	27 (2)	94 (9)	−1 (2)	−15 (5)	9 (4)
C1	5573 (6)	2214 (4)	6366 (9)	77 (5)	22 (2)	80 (10)	−3 (3)	−7 (7)	5 (4)
C2	6549 (6)	1762 (4)	6149 (10)	65 (5)	25 (2)	118 (11)	−12 (3)	−11 (8)	0.2 (5)
C3	7316 (8)	2176 (5)	5067 (12)	83 (7)	40 (3)	133 (13)	−30 (4)	−14 (8)	10 (6)
C4	6936 (6)	2323 (4)	3286 (10)	59 (5)	26 (2)	147 (14)	−14 (3)	−4 (7)	4 (5)
C5	7322 (7)	2768 (4)	2049 (11)	83 (6)	27 (2)	131 (14)	−19 (3)	19 (8)	3 (5)
C6	5966 (6)	2215 (4)	1032 (9)	70 (5)	22 (2)	104 (11)	4 (3)	16 (7)	9 (4)
C7	7034 (6)	567 (4)	4666 (11)	41 (4)	31 (2)	146 (14)	−1 (3)	−5 (7)	−4 (5)
C8	6565 (5)	−138 (4)	4011 (10)	37 (4)	26 (2)	127 (12)	6 (2)	7 (6)	5 (5)
C9	6861 (7)	−821 (5)	4633 (11)	67 (5)	32 (3)	145 (13)	25 (3)	10 (7)	4 (5)
C10	6408 (7)	−1460 (5)	3980 (13)	80 (6)	28 (3)	210 (17)	17 (3)	22 (9)	13 (6)
C11	5710 (6)	−1415 (4)	2678 (12)	58 (5)	24 (2)	216 (17)	−1 (3)	26 (8)	5 (6)
C12	5407 (5)	−739 (4)	2064 (10)	43 (4)	23 (2)	154 (12)	5 (2)	22 (6)	−2 (4)
C13	5827 (5)	−83 (4)	2745 (8)	35 (4)	21 (2)	90 (10)	3 (2)	10 (5)	6 (4)
C14	3288 (5)	1191 (3)	2462 (8)	52 (4)	19 (2)	86 (10)	6 (2)	−18 (6)	−2 (4)
C15	3360 (5)	538 (4)	3642 (10)	39 (4)	23 (2)	130 (12)	−3 (2)	−18 (7)	13 (5)
C16	2375 (7)	361 (7)	4569 (15)	42 (5)	69 (5)	237 (21)	−18 (4)	−12 (9)	48 (9)

[a] The positional parameters are presented in fractional unit cell coordinates (×10^4). [b] The β_{ij} (×10^4) are defined by $T = \exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$. [c] In this and the following table, estimated standard deviations are given in parentheses for the least significant figures.

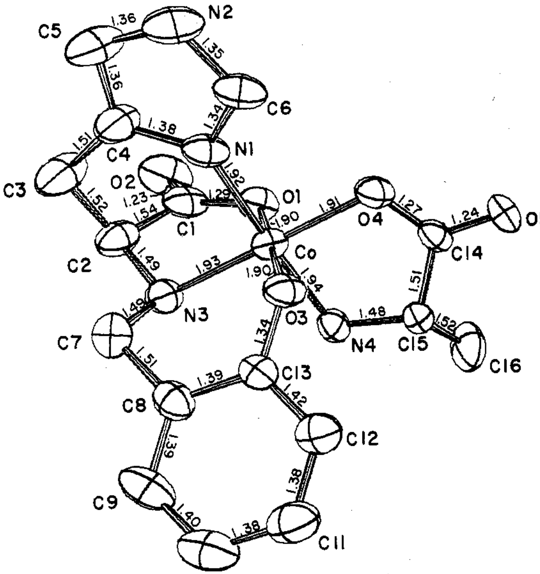

Figure 1. View of [Co(L-OHBH)(L-Ala)]·2H_2O showing 50% probability ellipsoids and bond distances. Distances and standard deviations for bonds involving the cobalt atom are also given in Table II. Standard deviations for the remaining distances are 0.01 Å.

thermal parameters for those atoms were refined by a full-matrix least-squares procedure,[6] minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$, to a final conventional discrepancy factor of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.059$. The largest ratio of parameter shift to standard deviation in the final refinement cycle was 0.07, and examination of observed and calculated structure factors revealed no appreciable extinction effects. The scattering factors used were those of Hanson et al.,[8] modified for the real and imaginary parts of anomalous dispersion.[9]

The final positional and thermal parameters are listed in Table I. The standard deviations were calculated from the inverse matrix of the final least-squares cycle.[10] Bond lengths and bond angles are listed in Figure 1 and Table II. A listing of the final observed and calculated structure factor amplitudes is available as supplementary material.

Table II. Selected Interatomic Distances (Å) and Angles (deg) for [Co(L-OHBH)(L-Ala)]·2H_2O

(a) Distances[a]

Co-N1	1.917 (6)	Co-O1	1.903 (4)
Co-N3	1.927 (5)	Co-O3	1.899 (4)
Co-N4	1.938 (6)	Co-O4	1.912 (5)

(b) Angles

O1-Co-O3	179.1 (3)	C13-C8-C7	118.0 (7)
N1-Co-N4	176.7 (3)	C13-C8-C9	120.7 (7)
N3-Co-O4	173.9 (3)	C12-C11-C10	120.4 (7)
O1-Co-O4	90.5 (2)	C11-C10-C9	120.4 (8)
O1-Co-N1	91.1 (2)	C10-C9-C8	119.4 (8)
O1-Co-N3	84.0 (2)	C9-C8-C7	121.3 (7)
O1-Co-N4	87.7 (2)	C8-C7-N3	109.4 (6)
N1-Co-N3	90.8 (2)	C7-N3-Co	113.7 (5)
N1-Co-O4	91.9 (2)	C7-N3-C2	117.3 (5)
N3-Co-N4	92.1 (2)	C2-N3-Co	105.4 (4)
N4-Co-O4	85.0 (2)	Co-N1-C6	124.2 (5)
N4-Co-O3	91.5 (2)	Co-N1-C4	128.5 (5)
O3-Co-O4	89.3 (2)	C4-N1-C6	107.3 (6)
N1-Co-O3	89.7 (2)	N1-C6-N2	109.1 (7)
N3-Co-O3	96.2 (2)	C6-N2-C5	108.6 (6)
Co-O4-C14	114.9 (4)	N2-C5-C4	107.0 (7)
O4-C14-O5	124.7 (6)	C5-C4-N1	108.0 (7)
O4-C14-C15	116.6 (6)	C5-C4-C3	129.9 (8)
O5-C14-C15	118.8 (6)	N1-C4-C3	122.1 (7)
C14-C15-C16	113.9 (7)	C4-C3-C2	112.6 (7)
C14-C15-N4	108.9 (5)	C3-C2-C1	110.9 (6)
C16-C15-N4	112.1 (7)	C3-C2-N3	113.1 (6)
Co-N4-C15	108.2 (4)	C2-C1-O1	115.9 (6)
Co-O3-C13	116.4 (4)	C2-C1-O2	119.2 (7)
O3-C13-C12	119.2 (6)	C1-C2-N3	105.5 (6)
O3-C13-C8	122.0 (6)	C1-O1-Co	113.0 (5)
C13-C12-C11	120.2 (7)		

[a] Distances not involving the cobalt atom are given in Figure 1.

Description and Discussion of the Structure

The crystal structure of [α-*N*-(*o*-hydroxybenzyl)-L-histidinato](L-alaninato)cobalt(III) dihydrate consists of

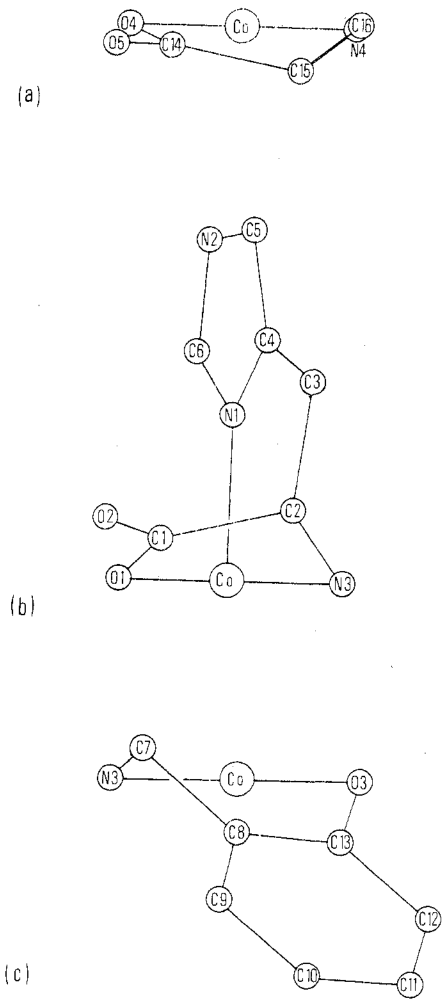

Figure 2. Chelate ring conformations in [Co(L-OHBH)(L-Ala)]·$2H_2O$. In each case a reference plane is defined by the cobalt atom and the two donor atoms; the view is that down the bisector of the angle formed by these three atoms at the cobalt atom.

discrete molecules having somewhat distorted octahedral coordination geometry about the cobalt atom. In addition, the two waters of hydration provide crystalline stability through a network of hydrogen bonding.

The histidine portion of the L-OHBH ligand is attached to the cobalt atom through its imidazole nitrogen (N1), carboxylate oxygen (O1) and α-amino nitrogen (N3) in a manner similar to that found for histidine in bis(L-histidinato)cobalt(II) monohydrate[12] and bis(L-histidinato)nickel(II) monohydrate.[13] In addition to the histidine unit which occupies one triangular face of the coordination octahedron, the phenolate oxygen atom (O3) of the *o*-hydroxybenzyl group is attached to the cobalt atom and occupies the coordination position trans to the carboxylate oxygen (O1). The two remaining coordination positions about the cobalt atom are filled by the chelating L-alaninate ligand. The α-amino nitrogen (N4) of this bidentate amino acid occupies the position trans to the coordinated imidazole nitrogen (N1), and the L-alaninate carboxylate oxygen (O4) is attached in the position trans to the secondary amino nitrogen (N3). The absolute configuration about the cobalt atom was assigned on the basis of the known configurations of the optically active amino acids used in the preparation of the compound.

The bond distances observed within the ligands compare quite well with average values previously determined for coordinated aliphatic amino acidates and histidinate.[14] The two types of C–O distances in the carboxylate groups are evident. The C–O distances (C1–O1 = 1.288 (9) Å, C14–O4 = 1.273 (8) Å) to the coordinating oxygen atoms are significantly longer than those (C1–O2 = 1.232 (9) Å, C14–O5 = 1.244 (9) Å) to the uncoordinated "carbonyl-type" oxygens, in agreement with observations in other amino acid complexes.[15-17] The Co–(donor atom) bond distances, Co–N4 (1.938 Å), Co–N3 (1.927 Å), Co–O1 (1.903 Å), and Co–O4 (1.912 Å), are comparable to cobalt–primary amino nitrogen,[15,18-22] cobalt–secondary amino nitrogen,[16,23-25] and cobalt–carboxylate oxygen distances[15-26] found in a number of other cobalt(III)–amino acidate, –amino polycarboxylate, or –dipeptide complexes. Similarly, the distance observed for the Co–O3 bond, 1.899 Å, falls within the range of cobalt–phenolate oxygen bond distances reported for several cobalt(III)–bis(salicylideniminato) complexes.[27-29] To the best of our knowledge this molecule is the first example of a Co(III) complex containing a histidine group which has been characterized by an X-ray structural investigation; hence, there are no literature values to compare with the Co–N1(imidazole) distance of 1.917 Å.

The angular distortions about the cobalt atom from ideal octahedral geometry are significant. The largest deviations from 90° occur for the angles O1–Co–N3, 84.0°, N4–Co–O4, 85.0°, and N3–Co–O3, 96.2°. These deviations can best be explained as the result of the constraints imposed upon the coordination geometry by the chelate rings present. The contractions of the first two angles above from ideality are consistent with values reported for other five-member amino acidate chelate rings attached to cobalt(III).[15-26] The oversized N3–Co–O3 angle, on the other hand, would seem the natural result of a six-member chelate ring possessing restricted flexibility due to the presence of sp^2 hybridization at C8 and C13.

The cobalt atom deviates by only 0.03 Å from the plane described by the imidazole ring (N1–C6–N2–C5–C4). Furthermore, the angle formed between the plane of the imidazole ring and the Co–N1 bond is only 1.4°. In other known structures containing the histidinate ligand bonded to a transition metal ion the corresponding angle has been found to be as large as 10.0°,[14] and the metal ion has been found

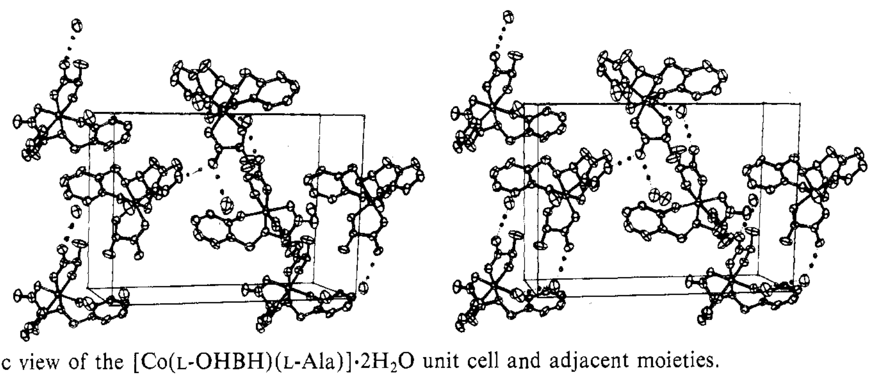

Figure 3. Stereographic view of the [Co(L-OHBH)(L-Ala)]·$2H_2O$ unit cell and adjacent moieties.

to be, characteristically, not coplanar with the imidazole ring. Equations of least-squares planes, torsional angles, and deviations of selected atoms from these planes are given in the supplementary material.

Projections of fragments of the molecule are shown in Figure 2. The relative atomic positions in these projections result from the least-squares planes calculations and are given to show the general conformations of the chelate rings.

X-ray structural studies of a number of α-amino acid complexes have shown the five-membered chelate rings to exist in either of two possible conformations: (1) a planar or slightly puckered conformation or (2) an asymmetric-envelope conformation.[14,30] In [Co(L-OHBH)(L-Ala)]·2H_2O the L-alaninate chelate ring (Figure 2a) is found to be in the latter of these two possible conformations. The chelate ring is bent in such a fashion as to displace the α carbon, C15, from the O4–Co–N4 plane in the direction of the phenolate oxygen, O3, and the phenyl ring (see Figure 1) and to bring the β carbon, C16, very nearly into the plane defined by O4–Co–N4 (i.e., C16 is equatorial relative to the chelate ring). The L-alaninate chelate ring exhibits a torsional angle O4–C14–C15–N4 of 19.1° which falls within the 0–30° range of values observed for the corresponding angle of coordinated α-amino acids in a number of other X-ray structural studies.[30]

The asymmetric-envelope conformation is also evident in the L-histidinate portion of the L-OHBH ligand (Figure 2b) and is imposed by the attachment of the imidazole side chain to the cobalt atom at N1. The bending observed in the five-membered chelate ring is opposite to that observed in the L-alaninate chelate ring in the sense that in this case, the β carbon atom, C3, is far removed from the plane defined by O1, N3, and Co (i.e., C3 is axial relative to the chelate ring). The torsional angle O1–C1–C2–N3 of 22.7° falls within the normal range of values noted above.

The projection of the chelate ring formed by the *o*-hydroxybenzyl group is shown in Figure 2c, and the puckered conformation is evident.

In addition to the asymmetric centers in the ligands at atoms C2 and C15, the coordination of the L-OHBH ligand to the metal ion gives rise to an asymmetric secondary nitrogen atom, N3, which has the *S* absolute configuration. Angular distortion is observed at this nitrogen atom with the angle C7–N3–C2, 117.3°, deviating significantly from the regular tetrahedral value, 109.5°, to be expected for a strain-free secondary nitrogen atom. The distortion of this angle, again, appears to be due to the constraining forces of the chelate rings.

An examination of molecular models shows that an *R* absolute configuration at the asymmetric nitrogen atom would allow atoms C3 and C7 to be nearly trans about the C2–N3 bond axis as compared with the torsional angle C7–N3–C2–C3 of 45.3° for the observed *S* configuration. However, an *R* configuration at N3 would bring the phenyl ring and the methylene protons of the *o*-hydroxybenzyl group into a position near the amino protons of the L-alaninate ligand which presumably makes this configuration at N3 less stable.

A stereographic view of the unit cell and adjacent moieties of [Co(L-OHBH)(L-Ala)]·2H_2O is shown in Figure 3. The view is one looking into the face of the unit cell defined by the *a* and *b* axes. Extensive intermolecular hydrogen bonding though the waters of crystallization occurs in the crystal. Apparent hydrogen bonding interactions are shown as dotted lines in Figure 3. The water oxygen atom, O6, is within hydrogen bonding distance (2.86 Å) of the phenolate oxygen, O3, of the complex molecule (see Figure 1). Similarly, the water oxygen atom, O7, lies 2.92 Å from the carboxylate oxygen, O5, of the L-alaninate ligand. In addition to these apparent interactions, O6 is situated 2.82 Å from an oxygen atom, corresponding to O7, of a water molecule associated with an adjacent moiety and 2.93 Å from the secondary nitrogen atom, corresponding to N3, in another adjacent molecule. The water oxygen atom, O7, also interacts with the O2 oxygen atom in the L-OHBH ligand of an adjacent molecule. One other apparent hydrogen bonding interaction involves direct interaction of the L-alaninate carboxyl oxygen, O5, with an imidazole nitrogen, corresponding to N2, of an adjacent molecule.

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Registry No. [Co(L-OHBH)(L-Ala)]·2H_2O, 66373-82-8.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes and of least-squares planes and torsional angles (11 pages). Ordering information is given on any current masthead page.

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