

**CRYSTAL AND MOLECULAR STRUCTURE OF DI- μ -PHENOXIDO-BIS-
[*N*-{(2-HYDROXYBENZYL)-(S)-ALANINATO- κ^3 -O,O',N}COPPER(II)].
A SIMPLE HOMODIMETALLIC MODEL FOR *N*-TERMINAL TYROSINE
COORDINATION WITH (S)-ALANINE AS A SECOND AMINO ACID
RESIDUE**

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Single-crystal X-ray diffraction study established the dimeric [Cu₂(ohb-(S)-Ala)₂] structure (ohb-(S)-Ala = *N*-(2-hydroxybenzyl-(S)-alaninate). The complex crystallizes in the tetragonal space group *P4*₃2₁2 with *a* = *b* = 8.849(1) Å, *c* = 24.913(2) Å, *V* = 1 950.8(3) Å³, *Z* = 8. The Cu(II) ion has distorted square-pyramidal geometry with the equatorial positions occupied by three oxygen and one nitrogen atom. Each copper atom is weakly coordinated at the apical position by carbonyl oxygen atom of the neighbouring molecule at the distance 2.329(2) Å. The Cu–Cu separation 3.0204(7) Å and the Cu–O3–Cu angle 100.8(1)° lead to antiferromagnetic coupling (at room temperature $\mu_{\text{eff}} = 1.35 \mu_{\text{B}}$). The O1–Cu–O3 angle (154.9(1)°) indicates distortion of the square pyramid toward a trigonal bipyramid ($\tau = 0.23$).

Key words: Chelates; Amino acids; Copper; X-Ray diffraction; *N*-Terminal tyrosine-like copper(II) complex.

Characteristic feature of many metalloproteins is the presence of tyrosine in dinuclear copper(II) or iron(III) units in their active sites^{1,2}. Suitable ligands modelling tyrosine coordination environments are *N*-(2-hydroxybenzyl)amino acids (ohb-aa). Recently we have studied cobalt(III) complexes of the [Co(ohb-(S)-aa)₂]ⁿ⁻ type (aa means amino acid anion) with the aim to assess ligand proximity effects in octahedral inert model tyrosine-like metal complexes³⁻⁵. In an attempt to extend our studies to the biologically relevant metals, we have prepared copper(II) complexes of the mentioned ligands. Recently⁶, copper(II) complexes containing *N*-(2-hydroxybenzyl)-(R,S)-alaninate and a heterocyclic nitrogen base have been described and structurally characterized. However, the structure of the homoleptic dinuclear copper(II) complex derived from the optically active alanine remains unresolved. Due to the increasing interest in phenoxide-bridged dinuclear Cu(II) units in biology, we report in this paper the structure of [Cu₂(ohb-(S)-Ala)₂].

EXPERIMENTAL

The *N*-(2-hydroxybenzyl)-(*S*)-alanine ligand was synthesized by the previously described method⁵. The copper(II) complex of this ligand was prepared by mixing stoichiometric quantities of the ligand (10 mmol), NaOH (20 mmol) and Cu(CH₃COO)₂·H₂O (10 mmol) in 100 ml of hot water. The resulting green precipitate was filtered off and crystals suitable for X-ray analysis deposited from the filtrate during several days. These were collected, washed successively with a small amount of cold water, acetone and air-dried. For C₁₀H₁₁CuNO₃ (256.7) calculated: 46.79% C, 4.32% H, 5.46% N; found: 46.82% C, 4.33% H, 5.49% N. The magnetic moment was determined at room temperature by the Faraday method (Cahn–Faraday magnetic balance). Diamagnetic corrections were made using Pascal constants⁷.

Crystal Structure Determination

The structure was solved by direct methods and anisotropically refined by full-matrix least-squares. Hydrogen atoms were located from the difference synthesis and expected geometry. All H atoms were refined isotropically. Absorption was neglected.

RESULTS AND DISCUSSION

Crystal data of [Cu₂(ohb-*S*)-Ala]₂ are given in Table I, bond distances and angles are collected in Table II. The structure of this complex is illustrated in Fig. 1 (only half of the complexes is symmetrically independent) and shows that copper atom possesses a square-planar NO₃ environment forming dinuclear unit through the two unsymmetrical deprotonated phenoxide bridges with the O3–Cu–O3' (–*y* + 1, –*x* + 1, –*z* + 1/2) angle 79.2(1)° and the Cu–Cu' separation 3.0204(7) Å. This bridging arrangement forms Cu₂O₂ core with slightly different Cu–O(phenoxide) bond lengths (Cu–O3 1.976(2) Å, Cu–O3' 1.944(2) Å). In addition, the bridged Cu–phenoxide bonds are somewhat shorter in comparison with the nonbridged Cu–O(phenoxide) coordination. Similarly, all four basal plane angles are different ranging from 79.2(1)° to 97.3(1)° in dependence on the respective ring size requirement. Angles about donor atoms are somewhat op-

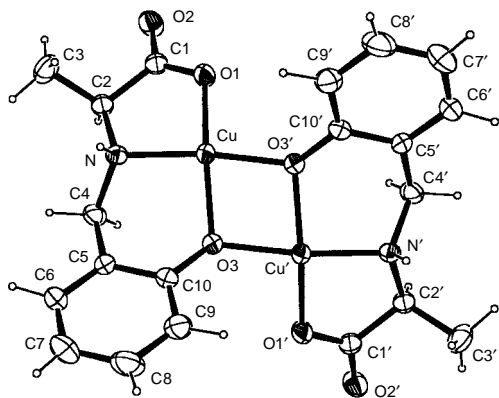


FIG. 1
Molecular structure of [Cu₂(ohb-*S*)-Ala]₂ showing the atomic numbering scheme

ened and exceed values for tetrahedral N and O coordination. A comparison of bond angles clearly shows that the deviations which are especially apparent from the Cu–N–C2 and C2–N–C4 angle values (Table II) are due to the presence of six-membered rings. As the O3–Cu–N–C2 ($-144.0(2)^\circ$) and O1–Cu–N–C4 ($140.1(2)^\circ$) dihedral angles indicate, chelate rings are not coplanar.

Each of the two copper atoms lies $0.302(2)$ Å above the same side of the O1–N–O3–O3' and O1'–N'–O3'–O3 plane and is axially coordinated to the O2'' ($x + 1/2, -y + 3/2, -z + 1/4$) carbonyl oxygen atom of the adjacent molecule in the *cis* arrangement at the distance $2.329(2)$ Å, with the O''–Cu–Cu'–O2'' dihedral angle ($-y + 3/2, x - 1/2, z - 1/4$) $-26.8(1)^\circ$.

TABLE I

Crystallographic data and structure refinement parameters for [Cu₂(ohb-(S)-Ala₂)]

Space group	$P4_32_12$
Crystal size, mm	$0.18 \times 0.18 \times 0.20$
Diffractometer and radiation used	Enraf–Nonius CAD4, CuK α = 1.54187 Å
Scan technique	$\omega/2\theta$
No. and θ range for lattice parameter refinement	25; 53.85 – 54.25°
h, k, l range	$-10 \rightarrow 0, -10 \rightarrow 10, -29 \rightarrow 0$
Standard reflections monitored in interval; intensity fluctuation; θ range	120 min; -1.7% ; 5.30 – 64.96°
Absorption coefficient, mm^{-1}	3.06
R_{int}	0.107
No. of unique reflections	1 662
Criterion for observed reflections	$I \geq 1.96\sigma(I)$
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2 + 2.207P]$, where $P = (F_o^2 + 2F_c^2)/3$
Parameters refined	181
Values of $R, wR(F^2), S$	0.045, 0.083, 1.141
Flack x parameter	0.00(4)
Ratio of max. least-squares shift to e.s.d. in the last cycle	<0.001
The largest difference peak and hole, $e \text{ \AA}^{-3}$	0.52, -0.78
Source of atomic scattering factors	SHELXL97 (ref. ⁸)
Programs used	SDP (ref. ⁹), SHELXS86 (ref. ¹⁰), SHELX97 (ref. ⁸)

TABLE II
Bond lengths (Å) and angles (°) for [Cu₂(ohb-(S)-Ala₂)]

Atoms	Distances	Atoms	Distances
Cu–N	1.978(2)	Cu–O3 ⁱ	1.944(2)
Cu–O2 ⁱⁱ	2.329(2)	Cu–O1	1.942(2)
O2–C1	1.233(4)	Cu–O3	1.976(2)
C5–C10	1.417(3)	O1–C1	1.285(3)
C1–C2	1.533(4)	O3–C10	1.336(4)
C4–C5	1.507(4)	C9–C10	1.382(5)
C6–C7	1.395(6)	C2–C3	1.533(4)
C8–C9	1.378(5)	C5–C6	1.365(4)
N–C2	1.486(3)	C7–C8	1.384(5)
N–C4	1.492(4)		
Atoms	Angles	Atoms	Angles
O1–Cu–O3 ⁱ	97.3(1)	O1–Cu–O3	154.9(1)
O3 ⁱ –Cu–O3	79.2(1)	O1–Cu–N	85.2(1)
O3 ⁱ –Cu–N	168.5(1)	O3–Cu–N	93.8(1)
O1–Cu–O2 ⁱⁱ	112.5(1)	O3 ⁱ –Cu–O2 ⁱⁱ	100.6(1)
O3–Cu–O2 ⁱⁱ	92.6(1)	N–Cu–O2 ⁱⁱ	88.8(1)
C1–O1–Cu	115.5(2)	C10–O3–Cu ⁱ	130.6(2)
C10–O3–Cu	118.7(2)	Cu ⁱ –O3–Cu	100.8(1)
C2–N–C4	114.4(2)	C2–N–Cu	109.9(2)
C4–N–C4	113.3(2)	O2–C1–O1	124.7(3)
O2–C1–C2	118.6(2)	O1–C1–C2	116.7(2)
N–C2–C1	111.0(2)	N–C2–C3	110.8(2)
C1–C2–C3	110.4(3)	N–C4–C5	110.4(2)
C6–C5–C10	119.3(3)	C6–C5–C4	121.7(2)
C10–C5–C4	119.0(3)	C5–C6–C7	121.8(3)
C8–C7–C6	118.4(3)	C9–C8–C7	120.7(3)
C8–C9–C10	120.9(3)	O3–C10–C9	122.3(2)
O3–C10–C5	118.8(2)	C9–C10–C5	118.9(3)

Symmetry code: (i) $-y + 1, -x + 1, -z + 1/2$ (symmetry generation of the complex); (ii) $x + 1/2, -y + 3/2, -z + 1/4$.

The geometries at both the Cu centers can be thus described as square pyramidal (4 + 1). Furthermore, the O1–Cu–O3 basal angle $154.9(1)^\circ$ indicates a significant distortion of the square pyramid toward a trigonal bipyramid. The amount of this distortion is indicated by the value of the trigonality¹¹ index $\tau = 0.23$, which for perfect square-planar and trigonal bipyramidal geometry approaches zero and unity¹¹, respectively. However, the number of structurally characterized copper(II) complexes belonging to this class is very limited^{6,12}. The paucity of data makes it difficult to evaluate the degree of trigonality as a function of a ligand structure. As can be expected, mononuclear [Cu(ohb-(R,S)-Ala)L] complexes (L = 1,10-phenanthroline or imidazole) with ligands L occupying the basal

TABLE III

Weighted least-squares planes through the starred atoms¹⁵. Equation of the plane: $m1*X + m2*Y + m3*Z = d$

Atom	<i>d</i>	<i>s</i>	<i>d/s</i>	(<i>d/s</i>) ²
Plane 1				
<i>m1</i> = 0.46934(0.00111)				
<i>m2</i> = -0.80513(0.00076)				
<i>m3</i> = -0.36260(0.00107)				
<i>D</i> = -6.88480(0.00646)				
N*	0.0000	0.0024	0.000	0.000
Cu*	0.0000	0.0004	0.000	0.000
O1*	0.0000	0.0023	0.000	0.000
C1	-0.2507	0.0030	-84.178	7 085.937
C2	-0.2630	0.0026	-99.849	9 969.815
	Sum (<i>d/s</i>) ² for starred atoms			0.000
Plane 2				
<i>m1</i> = 0.77492(0.00080)				
<i>m2</i> = -0.62232(0.00102)				
<i>m3</i> = -0.11058(0.00121)				
<i>D</i> = -3.97198(0.00948)				
O3*	0.0000	0.0022	0.000	0.000
Cu*	0.0000	0.0004	0.000	0.000
N*	0.0000	0.0025	0.000	0.000
C4	-0.3470	0.0032	-107.956	11 654.530
C5	0.6359	0.0031	205.863	42 379.410
C10	0.7399	0.0027	278.848	77 756.130
	Sum (<i>d/s</i>) ² for starred atoms			0.000

plane⁶ are closer to square-planar coordination ($\tau = 0.13$ and 0.007 , respectively). The bridged structure gives rise the magnetic moment 1.35 BM in the solid state at room temperature (for comparison, μ_{eff} of the dimeric $[\text{Cu}_2(\text{ohb}-(R,S)\text{-Ala})_2]$ was found⁶ to be $1.31 \mu_{\text{B}}$) which corresponds to the number of unpaired electrons 0.78 . Due to the pyramidal distortion, this reduction in the number of unpaired electrons corresponds, to the moderate antiferromagnetic coupling between Cu(II) atoms^{13,14}. This finding is in contrast with the normal magnetic moment found in the case¹² of $[\text{Cu}_2(\text{ohb-Gly})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$.

The *N*-(2-hydroxybenzyl)-(*S*)-alaninate ligand which retained, contrary to the results described in ref.⁶, its *S* configuration at the α -carbon atom during synthesis coordinates around copper in a stereospecific manner giving rise to *R* configuration of the nitrogen atom. A comparison of the O1-Cu-N-C2 ($10.8(2)^\circ$) and Cu-O3-C10-C5 ($49.1(3)^\circ$) dihedral angles shows that the six-membered rings are more puckered than the five-membered ones. Chelate ring conformations are consistent with the dihedral angles. The six-membered ring assumes asymmetric skew-boat conformation, while the presence of the carboxylate group in the ligand framework together with the *R* configuration of the nitrogen atom enforces an asymmetric envelope coordination onto the five-membered chelate ring (for carbon atom deviations, see Table III).

$[\text{Cu}_2(\text{ohb}-(S)\text{-Ala})_2]$ was isolated in the anhydrous form and only one intermolecular hydrogen bond between H1-N and $\text{O1}''$ atoms was detected ($\text{N}\cdots\text{O1}''$ distance $2.928(3)$ Å, $\text{H1-N}\cdots\text{O1}'$ distance $2.11(4)$ Å, $\text{H1-N}\cdots\text{O1}''$ angle $163(3)^\circ$). This bonding framework together with the $\text{Cu-O2}''$ bonds link the complexes in a three-dimensional network (*cf.* Fig. 2).

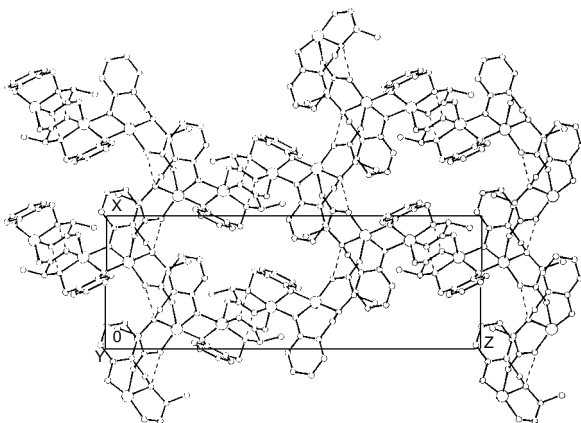


FIG. 2

Crystal packing diagram of $[\text{Cu}_2(\text{ohb}-(S)\text{-Ala})_2]$ (--- hydrogen bonds)

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