

The Crystal Structure of Aqua-bis(*N*-salicylidene- β -alaninato)dicopper(II) Monohydrate

PER-ERIK WERNER,^a ALADÁR VALENT,^b VOLRATH ADELSKÖLD^a and OĽGA ŠVAJLENOVÁ^b

^aDepartment of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden and ^bDepartment of Inorganic and Organic Chemistry, Faculty of Pharmacy, Komenský University, Kalinčiaková 8, 83232 Bratislava, Czechoslovakia

The crystal structure of aqua-bis(*N*-salicylidene- β -alaninato)dicopper(II) monohydrate, $[(C_{10}H_9NO_3-CuH_2O)(C_{10}H_9NO_3Cu)]H_2O$, has been determined by X-ray diffraction methods. The structure has been determined and refined in the triclinic space group $P\bar{1}$ with the unit cell dimensions $a=12.581(4)$ Å, $b=10.339(4)$ Å, $c=8.156(3)$ Å, $\alpha=92.04(3)^\circ$, $\beta=95.36(3)^\circ$, $\gamma=77.44(3)^\circ$. Intensity data were collected on a diffractometer with $CuK\alpha$ radiation. The final R index for 1004 "observed" reflections is 0.060. The asymmetric unit contains two differently coordinated copper atoms in a dimeric molecule; the copper–copper distance being 3.028(3) Å. The copper atoms are bridged by two phenolic oxygens. One copper atom has a distorted square-pyramidal, and the other one a distorted square-planar coordination. The five-coordinated copper is bound to a water molecule in the apical direction at a distance of 2.295(11) Å. The dimeric structure proposed on the basis of magnetic behaviour has been confirmed by the results of the crystal structure determination.

The metal complexes of Schiff bases derived from salicylaldehyde and amino acids^{1,2,3} have received comparatively little attention in spite of their apparent usefulness as models for the more complicated metal – pyridoxal – amino acid systems, which are intermediates in biologically important transamination reactions.⁴ Earlier, some crystal structures of the copper(II) complexes derived from salicylaldehyde and amino acids have been solved.

Carlisle *et al.*⁵ have prepared the *N*-salicylidene-L-valinatocopper(II) complex and on the basis of magnetic properties described the structure as tetrameric. They suggest that the magnetic state

may be closely approximated by considering any in-plane spin-spin coupling. Švajlenová *et al.*⁶ have prepared the aqua-*N*-salicylidene- β -alaninato-copper(II) complex, which has a subnormal value of its magnetic moment even at room temperature ($\mu_{eff}=0.91$ B.M.). This value of μ_{eff} eliminates the possibility of H_2O bonded "in-plane" together with donor atoms of the Schiff base. Molecular water could be coordinated only by a weak bond in an axial direction, without influence on the superexchange mechanism in the basal square plane. In order to obtain more information about these aspects, we decided to determine the crystal structure of the title compound.

EXPERIMENTAL

Aqua-bis(*N*-salicylidene- β -alaninato)dicopper(II) monohydrate was prepared by reaction of β -alanine (5×10^{-2} mol), copper(II) acetate monohydrate (5×10^{-2} mol), and salicylaldehyde (5×10^{-2} mol) in boiling aqueous ethanol (50 ml ethanol + 60 ml H_2O). The mixture was stirred and heated for 90 min. The dark green crude product was obtained by cooling the solution. The compound was recrystallized from hot aqueous ethanol. Carbon, nitrogen and hydrogen were determined by micro-analytical methods. The results of the analysis were: C 44.3 %, N 5.0 % and H 4.0 %, which are in good agreement with the calculated values: C 44.04 %, N 5.14 % and H 4.07 % for the formula $C_{20}H_{18}N_2O_6Cu_2(H_2O)_2$.

A crystal of approximate dimensions $0.05 \times 0.15 \times 0.6$ mm³ was selected for X-ray analysis. Data were collected with a Philips PW1100 four-circle diffractometer, equipped with a graphite mono-

Table 1. Crystal data.

Aqua-bis(<i>N</i> -salicylidene- β -alaninato)dicopper(II) monohydrate monohydrate $[(C_{10}H_9NO_3CuH_2O)-(C_{10}H_9NO_3Cu)]H_2O$; F. W. = 545.5	
Space group $P\bar{1}$ (No. 2); $Z = 2$	
$a = 12.581(4) \text{ \AA}$	$\alpha = 92.04(3)^\circ$
$b = 10.339(4)$	$\beta = 95.36(3)$
$c = 8.156(3)$	$\gamma = 77.44(3)$
$D_x = 1.757 \text{ g cm}^{-3}$	
$\mu(\text{CuK}\alpha) = 7.9 \text{ cm}^{-1}$	

chromator to reflect CuK α radiation. Lattice parameters were determined by least-squares refinement of the θ values for 25 centered reflections. Crystal data are given in Table 1.

Intensities were measured by the $\theta-2\theta$ scan mode ($\theta_{\max} = 50^\circ$) at a speed of $0.9^\circ \text{ min}^{-1}$ in θ and a scan width of 1.5° . The background was measured at each end of the interval for half the scan time. 1004 independent reflections were considered as observed according to the criterion $I \geq 3\sigma(I)$. Three reflections were monitored periodically during the data collection and showed no sign of crystal deterioration. The data were corrected for Lorentz and polarization effects, but not for absorption ($\mu = 7.9 \text{ cm}^{-1}$).

Calculations were carried out with the SHELX program system.⁷ The figures were drawn with the PLUTO 78 program.⁸ Scattering factors were taken from *International Tables for X-Ray Crystallography*.⁹ Anomalous dispersion was taken into account.

STRUCTURE DETERMINATION AND REFINEMENT

A Patterson synthesis favoured the centrosymmetric space group $P\bar{1}$ and yielded the Cu positions. Fourier syntheses revealed the positions of the other non-hydrogen atoms. Initially, the structure was least-squares refined isotropically. Next, all H atoms except for those of the crystal water molecules were introduced geometrically, and the structure was refined with Cu anisotropic and the rest of the non-hydrogen atoms isotropic. The H atoms were treated as riding on the corresponding C atoms, with fixed bond length (1.08 \AA) and with the same thermal parameters as the C atoms. In the final cycles of refinement the weighting scheme $w = 1/[\sigma^2(F_o) + (0.023 F_o)^2]$ was employed. There were no changes larger than 0.06σ in any of the 139 parameters varied in the final refinement cycle. The final unweighted R factor was 0.060, and $R_w =$

$[\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2} = 0.059$. The attempt to locate hydrogen linked to the two water oxygen atoms from the difference Fourier map calculated after refinement was unsuccessful.

A list of observed and calculated structure factors are obtainable from the authors on request.

RESULTS AND DISCUSSION

The atomic coordinates and isotropic thermal parameters are given in Table 2. The numbering scheme of the asymmetric unit is shown in Fig. 1. The crystal water oxygen O8, not directly bound to copper, is omitted in the figure.

Table 2. Atomic coordinates ($\times 10^4$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$). $T = \exp(-8\pi^2 U \sin^2 \theta / \lambda^2)$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (\AA^2)
Cu1	3052(2)	2973(2)	2238(3)	38
Cu2	2684(2)	5724(2)	839(3)	38
C1	4879(13)	4342(15)	2654(19)	35(5)
C2	5470(13)	5196(16)	1975(20)	43(5)
C3	6518(13)	5210(16)	2627(19)	41(4)
C4	7049(15)	4351(17)	3867(22)	56(6)
C5	6461(14)	3520(17)	4482(21)	47(5)
C6	5408(14)	3469(16)	3882(20)	41(5)
C7	4852(13)	2670(16)	4722(20)	44(5)
C8	6568(16)	8324(18)	4554(22)	64(6)
C9	2951(15)	479(18)	4456(24)	67(7)
C10	1965(16)	1051(18)	3441(23)	57(6)
C11	1412(12)	3923(15)	-725(19)	30(5)
C12	1393(12)	2613(15)	-1248(19)	33(5)
C13	697(13)	2362(17)	-2523(20)	42(5)
C14	-52(13)	3388(16)	-3364(21)	48(5)
C15	-17(13)	4684(16)	-2854(19)	38(5)
C16	708(12)	4956(15)	-1607(18)	31(5)
C17	661(13)	6337(16)	-1257(19)	38(5)
C18	1260(13)	8237(16)	-35(22)	51(6)
C19	2264(14)	8709(18)	-415(22)	52(6)
C20	3250(15)	8253(18)	677(22)	53(6)
N1	3896(11)	2407(12)	4240(16)	41(4)
N2	1396(10)	6785(13)	-281(16)	41(4)
O1	3847(8)	4382(9)	2021(12)	35(3)
O2	2119(8)	4147(9)	501(12)	31(3)
O3	1916(9)	2045(11)	2494(13)	50(4)
O4	1200(10)	439(13)	3288(15)	72(4)
O5	3346(9)	7174(11)	1520(13)	49(4)
O6	3995(10)	8908(11)	927(14)	62(4)
O7	3977(9)	1505(11)	413(13)	52(4)
O8	9010(13)	1197(16)	4108(20)	126(6)

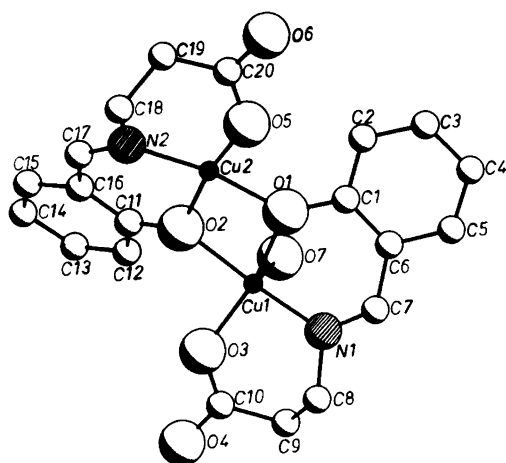


Fig. 1. The conformation of the title compound and the numbering of the atoms. Crystal water not bound to copper is omitted.

Two copper(II) ions and two tridentately coordinated *N*-salicylidene- β -alaninato (L^-) ions form a binuclear complex, where one of the copper(II) ions is also bound to a water molecule, ($CuLH_2O$) (CuL). Thus, one copper(II) ion ($Cu1$) exhibits a distorted square-pyramidal coordination, whereas the other ($Cu2$) is approximately square-coordinated. The copper atoms are bridged by two phenolic O atoms, with a copper–copper distance of 3.028(3) Å. The remaining two coordination sites in the square planes are occupied by a N atom and a carboxylate O atom. The fifth site in the coordination sphere around $Cu1$ is occupied by a water molecule at a distance of 2.295 Å in the apical direction. Thus, the dimeric structure that could be predicted from the magnetic measurement is confirmed by the structure determination. The coordination distances and angles around the Cu atoms are given in Table 3. As can be seen from the table, the bonds between the five-coordinated copper, $Cu1$, and the bridging oxygen atoms are somewhat longer than the corresponding bonds around $Cu2$.

The displacements of Cu from least-squares planes through the basal coordination planes are given in Table 4. The angle between the planes is 33°, cf. the stereo view in Fig. 2.

The displacement of $Cu1$ from its coordination plane is 0.25 Å, which is somewhat larger value than found in related complexes: 0.14 Å in the glycinate,¹⁰

Table 3. Bond distances (Å) and angles (°) around the Cu atoms.

Cu1–N1	1.900(14)	Cu2–N2	1.920(13)
Cu1–O1	1.960(10)	Cu2–O2	1.917(9)
Cu1–O2	2.013(10)	Cu2–O1	1.986(10)
Cu1–O3	1.917(11)	Cu2–O5	1.909(10)
Cu1–O7	2.295(11)		
N1–C7	1.312(21)	N2–C17	1.314(20)
N1–C8	1.494(23)	N2–C18	1.482(20)
Cu1–O1–Cu2	100.3(5)	Cu1–O2–Cu2	100.8(5)
O1–Cu1–O2	76.3(4)	O1–Cu2–O2	77.9(4)
O1–Cu1–N1	91.4(5)	O2–Cu2–N2	91.9(5)
N1–Cu1–O3	96.3(6)	N2–Cu2–O5	95.7(5)
O2–Cu1–O3	92.1(5)	O1–Cu2–O5	94.2(4)
O1–Cu1–O3	162.7(5)	O2–Cu2–O5	170.5(5)
N1–Cu1–O2	161.2(5)	N2–Cu2–O1	169.4(5)
O1–Cu1–O7	96.6(4)		
O2–Cu1–O7	95.3(4)		
O3–Cu1–O7	97.2(5)		
N1–Cu1–O7	100.3(5)		

0.17–0.18 Å in threoninate¹¹ and 0.18–0.20 Å in the phenylalaninate¹² complex. On the other hand, the square coordinated $Cu2$ is situated only 0.08 Å from its coordination plane.

In Cu(II) complexes formed with salicylaldehyde and amino acids, the bond between N and C atoms of the amino acid or the bond between the N and C atoms of the aldehyde part are sometimes shorter than a normal single or double bond, respectively. This finding was first discussed by Ueki *et al.*¹⁰ They suggested that the bond distances around

Table 4. Displacements (Å) of the atoms from least-squares planes in $[(C_{10}H_9NO_3CuH_2O)-(C_{10}H_9NO_3Cu)]H_2O$ defined by:

Plane I: O1, O2, O3, N1

Plane II: O1, O2, O5, N2

Atom	Plane I	Atom	Plane II
O1	–0.014(10)	O1	0.016(10)
O2	0.013(10)	O2	–0.016(10)
O3	–0.012(10)	O5	–0.014(10)
N1	0.012(13)	N2	0.014(13)
Cu1	–0.252(3)	Cu2	0.075(3)
O7	–2.546(11)		

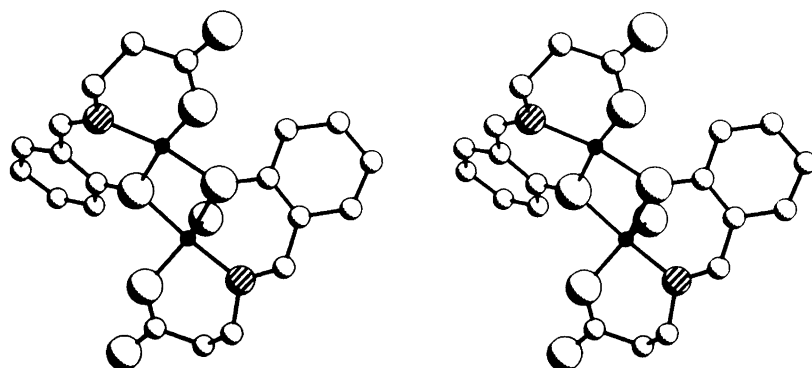


Fig. 2. Stereoscopic view of aqua-bis(*N*-salicylidene- β -alaninato)dicopper(II).

the nitrogen atom may give a clue to the reaction mechanism in the nonenzymatic transamination reactions. The reaction mechanism proposed by Metzler *et al.*⁴ was concerned with the migration of the double bond around the nitrogen atom. However, in the present structure, as well as in the valinato¹³ and the threoninato¹¹ complexes, no

significant deviations from normal single and double bond distances are found (*cf.* Table 3).

The projection of the crystal structure along the *c* axis is shown in Fig. 3. The neighbouring molecules are connected by intermolecular hydrogen bonding between water and carboxylate oxygen. Thus, the binuclear complexes are connected by four hydrogen

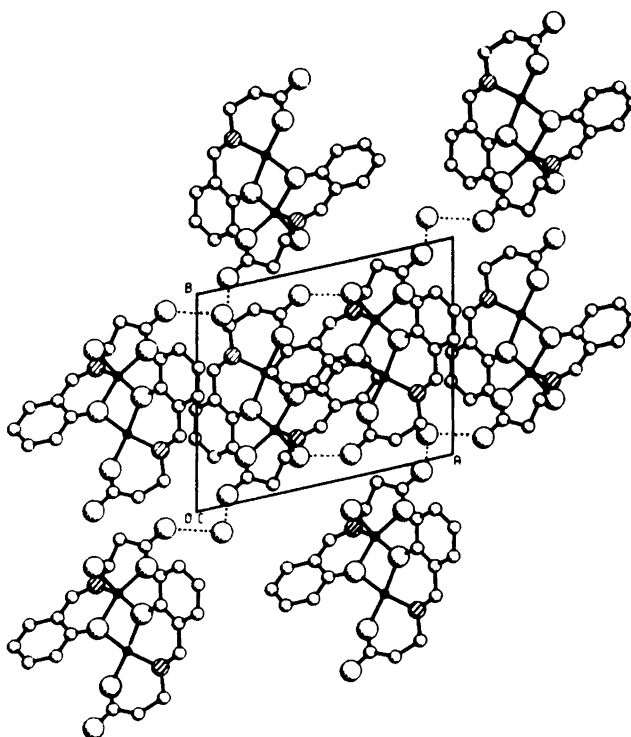


Fig. 3. Projection of the crystal structure along the *c* axis. Broken lines indicate hydrogen bonds.

Table 5. Hydrogen bond distances (Å).

O7 ⁱ —H···O6	2.727(15)
O7 ⁱⁱ —H···O6	2.811(15)
O8 ⁱⁱⁱ —H···O4	2.832(20)
O8 ^{iv} —H···O4	2.827(21)

Symmetry code

- | | |
|---------------------|---------------------|
| (i) $x, 1+y, z$ | (iii) $x-1, y, z$ |
| (ii) $1-x, 1-y, -z$ | (iv) $1-x, -y, 1-z$ |

bonds in a three-dimensional network. The hydrogen bond distances between the two non-equivalent water molecules and the carboxylate oxygen atoms are given in Table 5. It is unlikely that a direct electron exchange between the copper atoms operates in the present structure where the copper—copper distance is as long as 3.028(3) Å. The situation is similar to that discussed by Barclay and Hoskins¹⁴ for acetylacetone-mono(*o*-hydroxyanil)-copper(II), where the coordination around the copper atoms in a dimeric unit is also square—pyramidal around one of the copper atoms and square-planar around the other one, just as in the present structure.

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