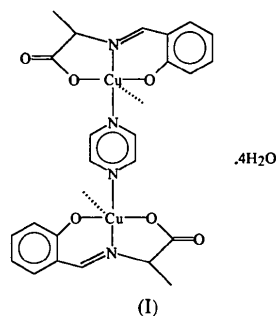


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molecules are connected through the second N atom of the pyrazine to form binuclear copper units, and are further linked through the above-mentioned apical coordinations into chains parallel to [100]. The water molecules help to form a hydrogen-bonding network between the chains. All copper polyhedra and the molecular axis are oriented parallel.

Comment

Recently, we reported the monomeric structure of pyrazine(*N*-salicylidene- α -amino-2-methylpropanato)-copper(II) (Warda, 1997), in which the pyrazine ligand acts as a monodentate ligand. In this communication, we report the title structure, (I), which has a bidentate pyrazine ligand.



Acta Cryst. (1998). **C54**, 302–304

Polymeric μ, μ' -Pyrazine-*N, N'*-bis(*N*-salicylidene-*R, S*-alaninato)copper(II) Tetrahydrate†

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Abstract

The Cu^{II} atom in the title compound, [Cu₂(C₁₀H₉NO₃)₂(C₄H₄N₂)₂].4H₂O, adopts a square-pyramidal coordination with the three donor atoms of the *N*-salicylidene-*R, S*-alaninato Schiff base dianion and one N atom of the pyrazine ligand bound in the basal plane. The axial position is occupied by a phenolato O atom of a symmetry-related ligand at an apical distance of 2.396 (2) Å. The

The Cu^{II} atoms adopt a (4+1) square-pyramidal geometry, with the three donor atoms of the tridentate Schiff base (TSB) *N*-salicylidene-*R, S*-alaninato dianion (ONO²⁻ chelator) and one N atom of the pyrazine ligand in the basal plane. All the equatorial copper distances are in the normal range.

The apical coordination site is occupied by the O1ⁱ atom of a neighbouring molecule, with a Cu—O1ⁱ distance of 2.396 (2) Å [symmetry code: (i) 1 - x, 1 - y, -z]. The apical distance is the most variable in this class of complex. The Cu atom is displaced from the basal plane by 0.136 (1) Å towards the apical ligand.

The pyrazine ring (pzn) lies on an inversion centre, oriented to the basal plane (O1, O2, N1, N2) at an angle of 30.4 (4)°; it acts as a bidentate ligand joining two CuTSB molecules to form pzn(CuTSB)₂, with a Cu—N2 distance of 2.053 (2) Å. The overall effect of the dual linkage of monomers (*via* pyrazine N and TSB O atoms) is to form chains parallel to [100] with composition [pzn(CuTSB)₂]_∞.

The chains are stabilized through hydrogen bonding with water molecules. The H atoms of two O4 water molecules and two O5 build an eight-membered ring. Additionally, two O3 atoms of the ligands also build an eight-membered ring [O3...H52—O5—H51]₂ to form finally a two-dimensional network of {[pzn(CuTSB)₂].4H₂O}_∞.

† Alternative name: poly[μ -pyrazine-*N: N'*-bis[μ -(*N*-salicylidene-*R, S*-alaninato-*O*¹, *N, O*²:*O*¹)copper(II)]] tetrahydrate.

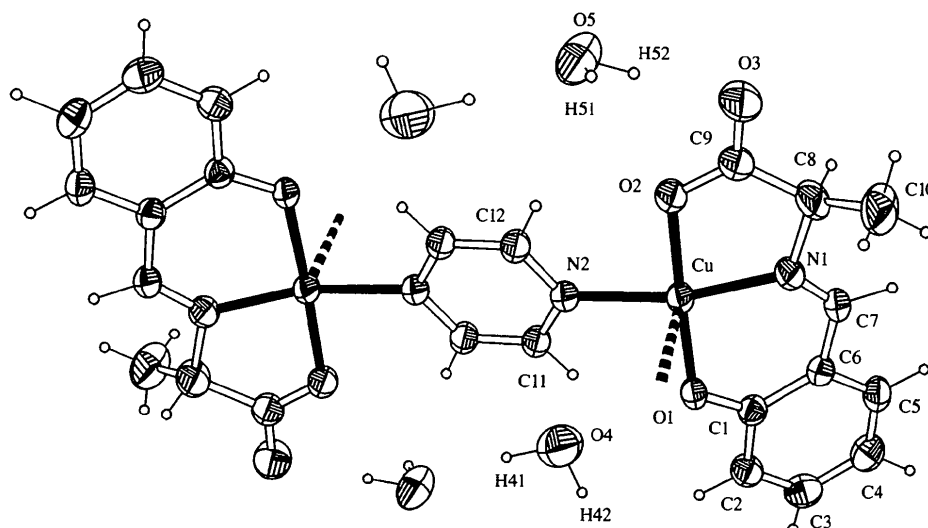


Fig. 1. The title binuclear copper(II) unit with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level. Axial ligands are represented by dashed lines (see text).

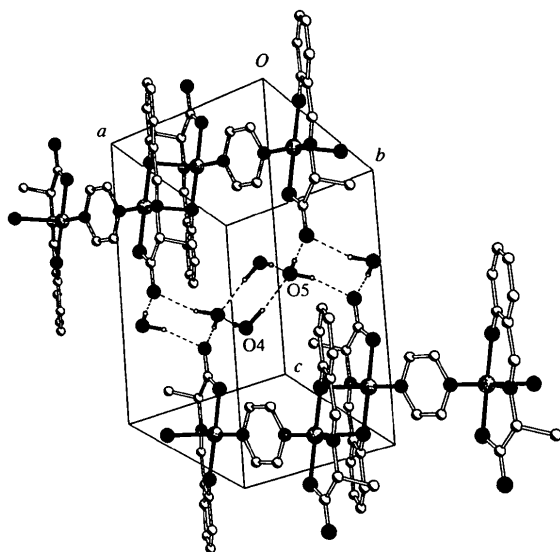


Fig. 2. Packing diagram of the title compound showing the hydrogen bonds (narrow lines).

Experimental

The title compound, (I), was synthesised from aqua(*N*-salicylidene-*R,S*-alaninato)copper(II) dihydrate according to the methods of Ueki *et al.* (1967) and Warda (1994) with pyrazine in a 1:2 dioxane–water mixture at 333 K. Transparent green plates grew within a few days.

Crystal data

$[\text{Cu}_2(\text{C}_{10}\text{H}_9\text{NO}_3)_2\text{-(C}_4\text{H}_4\text{N}_2)] \cdot 4\text{H}_2\text{O}$
 $M_r = 330.80$
 Triclinic
 $P\bar{1}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 5000 reflections
 $\theta = 2.67\text{--}28.00^\circ$

$a = 7.7750 (5) \text{ \AA}$
 $b = 8.1044 (7) \text{ \AA}$
 $c = 11.6240 (9) \text{ \AA}$
 $\alpha = 70.474 (8)^\circ$
 $\beta = 81.000 (8)^\circ$
 $\gamma = 89.478 (8)^\circ$
 $V = 681.09 (9) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.613 \text{ Mg m}^{-3}$
 D_m not measured

$\mu = 1.624 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Plate
 $0.30 \times 0.20 \times 0.04 \text{ mm}$
 Clear green

Data collection

Stoe IPDS diffractometer
 Image plate scans
 Absorption correction:
 integration (XPREP in
 SHELXTL; Siemens,
 1996a)
 $T_{\min} = 0.652$, $T_{\max} = 0.940$
 8132 measured reflections

3033 independent reflections
 2186 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 28^\circ$
 $h = -10 \rightarrow 10$
 $k = -10 \rightarrow 10$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.082$
 $S = 1.02$
 3033 reflections
 193 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0386P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.859 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.363 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Cu—O1	1.9113 (17)	Cu—N2	2.053 (2)
Cu—N1	1.927 (2)	Cu—O1 ¹	2.3961 (17)
Cu—O2	1.9277 (18)		

O1—Cu—N1	94.19 (8)	O2—Cu—N2	89.79 (8)
O1—Cu—O2	177.67 (8)	O1—Cu—O1 ⁱ	82.79 (7)
N1—Cu—O2	83.50 (9)	N1—Cu—O1 ⁱ	105.32 (8)
O1—Cu—N2	92.51 (8)	O2—Cu—O1 ⁱ	97.56 (7)
N1—Cu—N2	162.91 (8)	N2—Cu—O1 ⁱ	91.10 (7)

Symmetry code: (i) 1 - x, 1 - y, -z.

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O4—H41...O5 ⁱ	0.90 (4)	2.19 (4)	2.997 (4)	150 (4)
O4—H42...O5 ⁱⁱ	0.90 (4)	2.02 (4)	2.895 (4)	165 (4)
O5—H51...O3 ⁱⁱⁱ	0.90 (4)	2.04 (4)	2.914 (4)	165 (4)
O5—H52...O3	0.90 (4)	2.02 (4)	2.877 (5)	160 (4)

Symmetry codes: (i) 2 - x, 1 - y, -z; (ii) x, y, z - 1; (iii) 1 - x, 1 - y, 1 - z.

All H atoms, except the water H atoms, were included at calculated positions using *SHELXL97* (Sheldrick, 1997) and refined using a riding model. The U_{iso} of H atoms of CH and CH₂ groups, and the methyl group were taken as 1.2 U_{eq} and 1.5 U_{eq} of the parent atoms, respectively. The H41, H42, H51 and H52 atoms were found from difference Fourier syntheses and refined with $U_{iso} = 1.2U_{eq}$ of the water oxygen; O—H distances were restrained as equal. Atom C10 may be slightly disordered; the residual electron density of 0.86 e Å⁻³ at a distance of 1 Å from H8 is unusually high. However, no disorder model proved satisfactory. An analytical absorption correction based on face indexing was carried out with the following faces and distances (mm): 02 $\bar{1}$ 0.0924, 021 0.0924, 20 $\bar{1}$ 0.0962, $\bar{2}$ 01 0.1925, 001 0.0192 and 00 $\bar{1}$ 0.0192.

Data collection: *IPDS* (Stoe & Cie, 1997). Cell refinement: *IPDS*. Data reduction: *IPDS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97*. Molecular graphics: *XP* in *SHELXTL* (Siemens, 1996b). Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1252). Services for accessing these data are described at the back of the journal.

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Dimeric (Imidazole-*N*³)(*N*-salicylidene-*rac*-alaninato-*O,N,O'*)copper(II)†

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Abstract

The title compound, [Cu(C₁₀H₉NO₃)(C₃H₄N₂)]₂, adopts a square-pyramidal copper(II) coordination with three donor atoms of the *N*-salicylidene-*rac*-alaninato Schiff base dianion and the imidazole ligand bound in the basal plane. The axial position is occupied by an oxygen ligand from an adjacent chelate at an apical distance of 2.500 (3) Å, forming a centrosymmetric dimer. These dimers are connected through hydrogen bonding to form chains parallel to [010]. All copper polyhedra belonging to one chain are oriented parallel to each other, whereas between the two types of chains they are tilted at an angle 2γ of 38.9(2)°.

Comment

Copper(II) complexes with tridentate Schiff base dianions of the *N*-salicylideneaminoacidato type (TSB²⁻) represent a suitable model for the elucidation of structural and spectroscopic correlations. We are interested in the behaviour of the electron paramagnetic resonance (EPR) signal of Jahn–Teller ions with respect to the local geometry and the dipolar interaction between differently oriented polyhedra. For unambiguous interpretation of EPR results, X-ray structure determinations of a range of substances were undertaken.

Recently, we reported the structures of two imidazole–(TSB–Cu^{II}) complexes. In the case of imidazole(*N*-salicylidene- α -amino-2-methylpropanato)copper(II), (Warda, 1997a), the molecules are arranged in dimeric units connected by the phenolic O atom of a neighbouring monomer at an apical distance of 2.623 (2) Å. The tilting angle between the copper(II) polyhedra is 66.7 (2)°. The second imidazole compound, imidazole(*N*-salicylidene-glycinato)copper(II) (Warda, 1997b), polymerizes via carboxylic bridging at an apical distance of 2.563 (2) Å and has a tilting angle of 88.8 (2)°. In both cases, the C8 atom is achiral.

In the title compound, (I), the monomeric unit of which is shown in the formula scheme, the C8 atom is chiral; the compound crystallizes as a racemate. The

† Dedicated to Professor Jörg Lorberth on his 60th birthday.