

Preparation and Crystal Structure of a Phenoxo-Bridged Dinuclear Copper(II) Complex with *N*-Salicylidene-2-hydroxy-5-bromobenzylamine

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The title compound, phenoxo-bridged dinuclear copper(II) complex with *N*-salicylidene-2-hydroxy-5-bromobenzylamine (H₂shbb) [Cu₂(shbb)₂(dmsO)₂·2dmsO (dmsO = dimethyl sulfoxide), was synthesized and the crystal structure was determined by the single-crystal X-ray diffraction method at 90 K. It crystallizes in the monoclinic space group *P*2₁/*n* with *a* = 16.994(3) Å, *b* = 8.3932(16) Å, *c* = 15.755(3) Å, β = 111.547(3)°, *V* = 2090.2(7) Å³, *D*_x = 1.665 g/cm³, and *Z* = 2. The *R*1 and *wR*2 values are 0.0505 and 0.0649, respectively, for 4759 reflections. The molecule is a phenoxo-bridged dinuclear copper(II) complex having an elongated square-pyramidal coordination geometry with the *O*₃*N* basal atoms from the shbb²⁻ ligands and the apical *O* atom from the dmsO ligand.

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N-Salicylidene-2-hydroxybenzylamine and its substituted derivatives are unique ligands having two phenolic-oxygen and one imino-nitrogen donor atoms, forming mononuclear manganese(IV)¹ and vanadium(IV)² complexes and dinuclear vanadium(V),² iron(III),³ and copper(II)⁴ complexes with a meridional *O,N,O*-chelating. Recently, we found that one of these ligands forms a hydrogen-bonded dimer structure in the crystal.⁵ Concerning the dimer structure, we are interested in the dinuclear structure of phenoxo-bridged copper(II) complexes with these ligands. Although we reported on the crystal structure for one of these, the title compound, before (Fig. 1), the X-ray diffraction data were measured at room temperature and were not sufficient to get good-quality data, and the structural detail had not been described in the literature.⁴ We also reported preliminary magnetic susceptibility data, and interpreted the magnetic data by a dimer model based on the room-temperature structure.⁴ In order to understand the magnetic property of the complex exactly, it is desirable to

confirm the low-temperature structure. In this study, we determined the crystal structure of the title compound at 90 K.

The title compound was prepared by a previously reported procedure.⁴ A mixture of 2-hydroxy-5-bromobenzylamine (20 mg, 0.1 mmol) and salicylaldehyde (12 mg, 0.1 mmol) dissolved in 3 mL of dimethyl sulfoxide was heated gently. To this solution was added copper(II) acetate (18 mg, 0.1 mmol), and the mixture was heated with stirring for 40 min, and then filtered. The resulting green solution was allowed to stand at

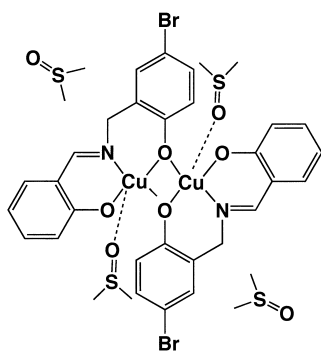


Fig. 1 Chemical structure of the title compound.

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Table 1 Crystal and experimental data

| | |
|--|---|
| Chemical formula: C ₃₆ H ₄₄ Br ₂ Cu ₂ N ₂ O ₈ S ₄ | |
| Formula weight = 1047.87 | |
| <i>T</i> = 90 K | |
| Crystal system: monoclinic | Space group: <i>P</i> 2 ₁ / <i>n</i> |
| <i>a</i> = 16.994(3) Å | |
| <i>b</i> = 8.3932(16) Å | β = 111.547(3)° |
| <i>c</i> = 15.755(3) Å | |
| <i>V</i> = 2090.2(7) Å ³ | <i>Z</i> = 2 |
| <i>D</i> _x = 1.665 g/cm ³ | |
| Radiation: Mo <i>K</i> _α (λ = 0.71073 Å) | |
| μ(Mo <i>K</i> _α) = 3.180 mm ⁻¹ | <i>F</i> (0 0 0) = 1060 |
| Crystal size = 0.41 × 0.25 × 0.04 mm ³ | |
| No. of reflections collected = 12136 | |
| No. of independent reflections = 4759 | |
| θ range for data collection: 1.51 to 28.41° | |
| Data/Restraints/Parameters = 4759/0/244 | |
| Goodness-of-fit on <i>F</i> ² = 0.949 | |
| <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]: <i>R</i> 1 = 0.0304, <i>wR</i> 2 = 0.0615 | |
| <i>R</i> indices (all data): <i>R</i> 1 = 0.0505, <i>wR</i> 2 = 0.0653 | |
| (Δσ) _{max} = 0.001 | |
| (Δρ) _{max} = 0.846 eÅ ⁻³ | (Δρ) _{min} = -0.374 eÅ ⁻³ |
| Measurement: Bruker Smart APEX CCD diffractometer | |
| Program system: SHELXTL | |
| Structure determination: Direct methods (SHELXS-97) | |
| Refinement: full matrix least-squares (SHELXL-97) | |
| CCDC deposition number: 765313 | |

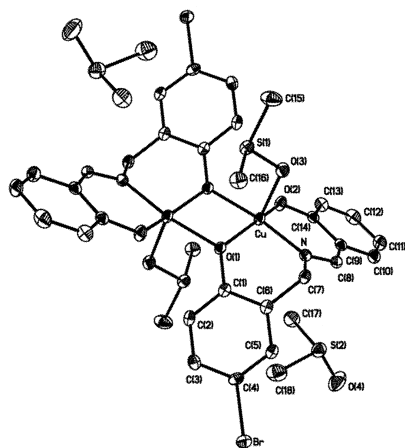


Fig. 2 ORTEP view of the title compound. The thermal ellipsoids are shown at the 50% probability level.

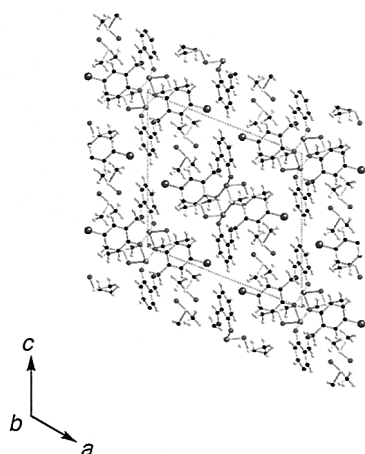


Fig. 3 Packing diagram of the title compound.

room temperature. After 2 days, deep-green crystals were deposited. These were collected by filtration, washed with methanol, and then dried under a vacuum over P_2O_5 . Yield: 84 mg (73%). *Anal.* Found: C, 41.10; H, 4.27; N, 2.66%. Calcd for $C_{32}H_{32}Br_2Cu_2N_2O_6S_2 \cdot 2C_2H_6SO$: C, 41.26; H, 4.23; N, 2.67%. IR(KBr): $\nu(\text{ArH})$ 3057, 3044, 3003, 2989, 2858, $\nu(\text{C=N})$ 1635 cm^{-1} , $\nu(\text{S=O})$ 1024 cm^{-1} . Diffuse reflectance spectrum: λ_{max} 281, 385, 644, 730 sh, 879 sh nm. Magnetic moment: $\mu_{\text{eff}}/\text{Cu} = 1.51 \mu_B$ at 300 K.

A preliminary examination was made, and data were collected on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo- K_α radiation. Crystal data and details concerning data collection are given in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares methods. The hydrogen atoms were inserted at their calculated positions and fixed there. All of the calculations were carried out on a Pentium IV Windows 2000 computer utilizing the SHELXTL software package.

The molecular structure drawn by ORTEP is shown in Fig. 2. Selected bond distances and angles are given in Table SI. The crystal structure consists of neutral centrosymmetric dinuclear entities and dmsu molecules, showing the same crystal structure

as that analyzed at room temperature.⁴ Two copper ions are bridged by phenolic-oxygen atoms of two Schiff-base ligands. The coordination geometry around the copper atom is an elongated square pyramid. One Schiff-base ligand is coordinated to the copper ion in a meridional fashion, giving a basal plane with a bridging phenolic-oxygen atom of the other Schiff-base ligand. The apical position is occupied by the dmsu ligand. The basal plane, defined by O1-N-O2-O1A, deviates from the strict planar configuration within $\pm 0.17 \text{ \AA}$, and the Cu atom is 0.20 \AA above the mean plane towards the oxygen atom of the dmsu molecule. The bond distances Cu-O1 [1.998(2) \AA], Cu-O1A [1.963(2) \AA], Cu-N [1.914(2) \AA], Cu-O2 [1.895(2) \AA], and Cu-O3 [2.387(2) \AA] are comparable to those found at room temperature [Cu-O1 2.001(8) \AA , Cu-O1A 1.970(9) \AA , Cu-N 1.912(11) \AA , Cu-O2 1.911(9) \AA , and Cu-O3 2.480(9) \AA].⁴ The difference in the bond distances between at room temperature and 90 K may come from the crystal-packing effect. The Cu...Cu distance within the dinuclear unit is 3.0862(8) \AA . The Cu-O(phenolic)-Cu bridging angle is 102.37(7) $^\circ$. These important bonding parameters are essentially the same as those found at room temperature [Cu...Cu 3.077(2) \AA , Cu-O-Cu 101.6(4) $^\circ$]. Therefore, we can suppose a dimer model without any significant structural change for the temperature dependence of the magnetic susceptibility. In the Schiff-base moiety, the N-C7 distance is 1.475(3) \AA , which is normal for a single bond, while the N-C8 bond length of 1.282(3) \AA shows a double-bond character. The C7, N, C8, and C9 moiety is essentially flat (*r. m. s.* deviation from the mean plane is 0.0008 \AA), which is consistent with the sp^2 hybrid character of the N atom. The torsion angles around C7, C6-C7-N-C8, C1-C6-C7-N, and C5-C6-C7-N (Table SI) show that this molecule twists slightly at the C7 atom, giving a dihedral angle of the aromatic rings containing C1 and C9 of 57.30(9) $^\circ$. This structural feature is also found in the ligand, itself,⁵ and may be in harmony with the coordination to metal ion in a meridional fashion of this ligand. In the crystal, each molecule is well separated, giving a good example of the dimer model. The closest contact between the dinuclear unit and the crystal dmsu is 3.300(3) \AA of O4...C7 ($-x+1/2, y-1/2, 3/2-z$) (Fig. 2). Further work on the magnetic properties is in progress in our laboratory.

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