Crystal Structure and Magnetic Exchange Interaction in
Binuclear Copper(II) Schiff Base Complex Bridging $m$-phenylenediamine Ligand

C. T. Zeyrek$^{a,b}$, A. Elmali$^b$, Y. Elerman$^b$ and I. Svoboda$^c$

$^a$Ankara Nuclear Research and Training Centre, Turkish Atomic Energy Authority,
06100 Besevler-Ankara, Turkey

$^b$Department of Engineering Physics, Faculty of Engineering, University of Ankara,
06100 Besevler-Ankara, Turkey

$^c$Institut for Materials Science, Darmstadt University of Technology, Petersenstrasse 23,
D-64287 Darmstadt, Germany

Reprint requests to A. Elmali, e-mail: elmali@eng.ankara.edu.tr
Condensation of 2-hydroxy-3-methoxybenzaldehyde with \textit{m-phenylenediamine} (1,3-diaminobenzene) \((m\text{-pda})\) gives ligand \([N,N'\text{-bis(2-hydroxy-3-methoxybenzylidene)-1,3-diaminobenzene}]\) which reacts with cupric ion to give the complex \([\text{Cu}_2(L-m\text{-pda})_2\cdot2\text{H}_2\text{O}, [L = 2-hydroxy-3-methoxybenzaldehyde}]\), respectively. The molecular structure of the complex \([\text{Cu}_2(L-m\text{-pda})_2\cdot2\text{H}_2\text{O}]\) has been determined by single-crystal X-ray analysis.

\((C_{44}H_{40}Cu_2N_4O_8)\cdot2\text{H}_2\text{O}\), triclinic, space group \(P\bar{1}\), \(a = 8.953(2), b = 11.264(5), c = 11.318(2)\) \(\text{Å}\), \(\alpha = 100.74(2), \beta = 105.23(10), \gamma = 103.47(3)^{\circ}\), \(V = 1033.1(5)\) \(\text{Å}^3\), \(Z = 1\). Two identical \([\text{Cu}(L-m\text{-pda})]\) fragments, related by an inversion center, are connected by \textit{m-phenylene} groups to form a binuclear unit. The coordination geometry around each copper(II) can be described as a distorted tetrahedron formed by the \(N_2O_2\) donor set of the Schiff base ligands, respectively. The intramolecular Cu\textsuperscript{2+}Cu separation is 7.401(6) \(\text{Å}\). There are also two non-coordinating water molecules in the crystal structure. The magnetic susceptibility of the complex was measured in the range 5–301 K temperature range. The values of the interaction parameters are \(J = -0.4\) \(\text{cm}^{-1}\) and \(g = 2.17\). This indicates a weak intramolecular antiferromagnetic interaction between copper(II) ions. Extended Hückel molecular orbital (EHMO) calculations on the copper(II) ions with \textit{m-phenylenediamine} bridging fragment have been performed in order to gain insight into the molecular orbitals that participate in the super-exchange pathway.

\textit{Key words:} Dinuclear Copper(II) Complex, Antiferromagnetic Interactions, Super-exchange Interactions, Schiff Base, Molecular Orbital Calculation.
Introduction

Series of binuclear transition-metal complexes which display different physical properties have been investigated extensively in recent years. This is partly because of the use of such complexes to mimic aspects of bimetallic bio-sites in various proteins and enzymes [1, 2], and partly because of attempts to understand the structural and electronic factors that govern magnetic exchange phenomena [3-6]. The previous papers in this series have sought to establish various criteria for judging the viability of a particular single-atom or polyatomic bridging unit to support magnetic exchange interactions between two paramagnetic metal ions [7-9]. Much of papers have been concerned with exchange interactions in binuclear or dimeric copper(II) complexes and have indicated that the strength of the exchange interaction depends primarily upon the symmetry and energy of the copper(II) ion ground state relative to the highest occupied molecular orbitals of the bridging moiety. These complexes exhibit ferromagnetic or antiferromagnetic character depending on their geometry.

Recently, we have studied the crystal structure and magnetic properties of \(\mu\)-acetate-\(N,N^\prime\) bridged dicopper(II) complexes of 1,3-bis((5-bromo-2-hydroxybenzylidene)amino)-propan-2-ol, 1,3-bis((2-hydroxy-1-naphthylidene)amino)-propan-2-ol [7,9] and \(\mu\)-pyrazol-\(N,N^\prime\)bridged dicopper(II) complexes of 1,3-bis((3,5-dichlorosalicylidene)amino)-propan-2-ol and 1,3-bis((3,5-dibromosalicylidene)amino)-propan-2-ol [10]. In this study, we present the synthesis, crystal structure and magnetic properties of a binuclear copper(II) complex, \([\text{Cu}_2(L-m-pda)_2]_2\cdot2\text{H}_2\text{O}\), \(L = 2\)-hydroxy-3-methoxybenzaldehyde)] of Schiff base derived from \(m\)-phenylenediamine. We have measured magnetic susceptibilities in the temperature range 5 – 301 K using the SQUID magnetometer to investigate the relationship between the magnetic properties and the molecular structure. We also performed extended Hückel molecular orbital (EHMO) calculations to determine the nature of the frontier orbitals and to
clarify the influence of the bridging ligand the \textit{m}-phenylenediamine on the super-exchange interaction in the investigated complex.

\begin{center}
\includegraphics[width=0.8\textwidth]{Scheme1.png}
\end{center}

\textbf{Experimental Section}

\textit{Preparation}

The 2-hydroxy-3-methoxybenzaldehyde and 1,3-diaminobenzene were purchased from Aldrich. The Schiff base ligand ($N,N'$-bis(2-hydroxy-3-methoxybenzylidene)-1,3-diaminobenzene) was synthesized by reaction of 1,3-diaminobenzene and 2-hydroxy-3-methoxybenzaldehyde 1:2 molar ratio at room temperature. The yellow Schiff base ligand was obtained from the solution on cooling. For the preparation of the binuclear Cu(II) complex, the Schiff base ligand (1mmol, 0.35 gr) in a hot acetonitrile (50 ml) and a solution of Cu(CH$_3$COO)$_2$$\cdot$H$_2$O (1mmol, 0.20 gr) in hot methanol (40 ml) were added. The resulting mixture was set aside for 3 d and the prismatic dark blue crystals which formed were filtered off and washed with cold ethanol (Scheme 1). [Found: C, 55.97; H, 4.87; N, 6.11%; C$_{44}$H$_{44}$N$_4$O$_{10}$Cu$_2$ Calcd: C, 55.75; H, 4.68; N, 5.91%].
**X-ray structure determination**

A crystal of dimension 0.30×0.20×0.05 mm was mounted on an Enraf-Nonius CAD-4 diffractometer [11] equipped with a graphite monochromatized MoKα radiation (λ=0.71073 Å). Experimental conditions are summarized in Table 1. Precise unit cell dimensions were determined by least-squares refinement on the setting angles of 25 reflections (2.32° ≤ θ ≤ 29.20°) carefully centred on the diffractometer. The standard reflections (1 0 3, 1 0 3, 2 2 2) were measured every 7200 s and the orientation of the crystal was checked after every 600 reflections. A total of 6257 reflections were recorded, with Miller indices $h_{\text{min}} = -11$, $h_{\text{max}} = 4$, $k_{\text{min}} = -13$, $k_{\text{max}} = 13$, $l_{\text{min}} = -13$, $l_{\text{max}} = 13$. Data reduction and corrections for absorption and decomposition were achieved using the Nonius Diffractometer Control Software [11]. The structure was solved by SHELXS-97 [12] and refined with SHELXL-97 [13]. The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.96 Å), and refined using a riding model. H atom displacement parameters were restricted to be 1.2Ueq of the parent atom. The hydrogen atoms of the water molecule were located in the difference Fourier maps calculated at the end of the refinement process as a small positive electron density and were not refined. The final positional parameters are presented in Table 2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 220656 [14].

**Susceptibility measurements**

Variable-temperature magnetic susceptibility measurements of a powdered sample were performed with a QUANTUM design SQUID magnetometer in the temperature range 5 – 301 K. The applied field was about 2 T. Diamagnetic corrections of the molar magnetic susceptibility of the compound were applied using Pascal’s constant [15]. The effective
magnetic moments were calculated by the equation \( \mu_{\text{eff}} = 2.828(\chi T)^{1/2} \), where \( \chi \) is the magnetic susceptibility per Cu(II) ions.

**Molecular orbital calculations**

Extended Hückel molecular orbital calculations (EHMO) have been performed in order to gain insight into the molecular orbitals that participate in the super-exchange pathway by using the Computer Aided Composition of Atomic Orbitals (CACAO) package programs [16]. The interatomic distances were taken from the x-ray results. Molecular orbital representations were plotted using CACAO software [16].

**Results and Discussion**

**X-ray crystal structure**

A perspective drawing of the molecule is shown in Fig. 1 [17]. Selected bond lengths, angles and hydrogen-bonding interactions are summarized in Table 3. The molecule is dimeric and centrosymmetric, with each coordination centre being bridged by two \( m \)-phenylene groups. The distance between the Cu1 and Cu1\( ^a \) [symmetry transformation used to generate equivalent atoms: \( ^a(-x, -y+1, -z) \)] centres in the dimer is 7.401(6) Å. Also, the closest separation between Cu(II) ions belonging to neighbouring molecules in the unit cell is large (8.953(6) Å) and preclude significant intermolecular magnetic interaction. The coordination about each copper atom can be described as distorted tetrahedral since the angle between the two 2-hydroxy-3-methoxybenzaldehyde residues is 51.5(1)°, also the dihedral angle between the corresponding [CuN\(_2\)O\(_2\)] coordination plane is 27.6(2)°. Each copper(II) ion is coordinated by two N\(_{\text{imine}}\) atoms and two O\(_{\text{phenol}}\) atoms form the imine-phenol ligand in the distorted tetrahedral coordination geometry. The atom with the greatest deviation from the [CuN\(_2\)O\(_2\)] coordination plane Cu1, N1, O2, N2 and O1 is O1 atom at -0.613(3) Å. The average Cu–O
and Cu–N distances are 1.896(4) and 1.961(4) Å, respectively. The N1–Cu1–N2 and O1–
Cu1–O2 angles are 100.4(2) and 91.2(1)°, respectively. Those distances and angles are in the
range of those of conventional Schiff base copper(II) complexes of the similar coordination
[18-20].

In the complex each bridging phenylene ring makes dihedral angles of 45.5(3) and
61.4(2)° with the two chelate residues to which it is attached and are themselves parallel, the
interplanar separation being 3.433 Å. This distance is larger than the corresponding value of
3.05 Å for the similar copper(II) complex [19], but smaller than corresponding value of 3.717
Å for the similar cobalt(II) complex [21], testifying that the steric repulsion between the two
bridging groups is smaller than cobalt(II) complex, and therefore the title copper(II) complex
is larger distorted than the cobalt(II) complex [21].

There are two non-coordinating water molecules in the crystal structure. The water
molecules which consist of O5 and O6 atoms are linked via intermolecular six hydrogen
bonds between the O atoms of the water molecules and O atoms of the ligand, O5–Ha′ · O4
[2.37(1) Å], O5–Hb′ · O3 [2.42(1) Å], O5–Hb′ · O1 [2.77(1) Å], O5–Hb′ · O2 [2.19(1) Å], O5–
Ha′ · O1 [2.44(1) Å] and O6–Hb′ · O3 [2.99(1) Å]. Also, two water molecules are linked via
intermolecular hydrogen bonds between the O atoms of the two water molecules, O6–Hb′ · O5
[1.89(1) Å] and O6–Ha′ · O5 [2.12(1) Å] (Table 3).

Magnetic properties

Magnetic susceptibility measurement for a powdered sample of the binuclear
copper(II) complex were measured by the SQUID based magnetometer in the temperature
range 5–301 K. The magnetic susceptibilities of the complex are shown as a function of
temperature in Fig. 2, and the magnetic moments are shown as a function of temperature in
Fig. 3. The magnetic susceptibility data were fitted by using the Curie-Weiss law,
\( \chi = C/(T + \theta) \). Least squares fitting of the data leads to 
\[
C = \frac{N\mu_B^2}{3k} = 0.125
\]
and Curie-Weiss constant \( \theta = -0.4 \) K. In addition, the data were fitted using the Bleaney-Bowers equation \[22\]
\[
\chi = \frac{N_k g^2 \mu_B^2}{3kT} \left[ 1 + \frac{1}{3} \exp \left( -\frac{2J}{kT} \right) \right]^{-1} + N_a
\]
and the isotropic (Heisenberg) exchange Hamiltonian \( H = -2J S_1 S_2 \) where \(-2J\) corresponds to the energy separation between spin-singlet and -triplet states, for two interacting \( S = 1/2 \) centres. \( N_a \) is the temperature-independent paramagnetism and its value is \( 6.10^{-5} \) cm\(^3\)/mol for each copper atom. Least squares fitting of the data leads to \( J = -0.4 \) cm\(^{-1}\), \( g = 2.17 \). Magnetic moments were obtained from the relation \( \mu_{\text{eff}} = 2.828 (\chi T)^{1/2} \). The magnetic moment at 301 K is about 2.75 B. M. and 2.56 B. M. at 5 K.

**Extended Hückel molecular orbital calculations (EHMO)**

We have carried out extended Hückel molecular orbital calculations (EHMO). EHMO calculations have been performed in order to gain insight into the molecular orbitals that participate in the super-exchange pathway. An energy difference of 0.140 eV is obtained between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). A graph of HOMO and LUMO orbitals for the investigated complex is depicted in Fig. 4. The LUMO orbital is a symmetrical orbital combination, whereas the HOMO orbital is an asymmetrical combination. As can be observed, the Cu metal centres use \( d_{x^2-y^2} \) type orbitals for an \( \pi \) interaction with \( p_N \) orbitals of \( m \)-phenylenediamine bridging fragment.
A qualitative relationship

A qualitative relationship between the magnitude of ground-state magnetic exchange interaction and separation between the two one-electron reduction waves can be set out for binuclear copper(II) complexes. A molecular orbital approach can be used to assess the antiferromagnetic contribution to a magnetic exchange interaction. In a copper(II) dimer, each copper(II) ion has one unpaired electron in an essentially $d$-type orbital and, to first order, the antiferromagnetic interaction reflects the level of interaction of the two unpaired-electron orbitals, one located at each copper(II) centre. The interaction between the two copper(II) $d$ orbitals is effected by an interaction with the appropriate molecular orbitals of the bridging group. If the two copper(II) ion coordination geometries in a binuclear complex are square planar, then two molecular orbitals, $\phi_1$ and $\phi_2$, will form as linear combinations of the two $d_{x^2-y^2}$ orbitals.

$$\phi_1 \approx d_{x^2-y^2}^a + d_{x^2-y^2}^b$$

$$\phi_2 \approx d_{x^2-y^2}^a - d_{x^2-y^2}^b$$

As the antiferromagnetic interaction increases, the two molecular orbitals $\phi_1$ and $\phi_2$ will separate energy. The energy separation between these two new molecular orbitals is expected to determine the super-exchange coupling constant. According to the theoretical analysis by Hoffmann and co-workers [23, 24], the coupling constant is expressed as

$$2J = 2K_{ab} - \frac{(\varepsilon_1 - \varepsilon_2)^2}{J_{aa} - J_{ab}}$$

(2)

where, $K_{ab}$, $J_{aa}$ and $J_{ab}$ are the exchange integral and one-centre and two-centre Coulomb repulsion integrals, respectively, and $\varepsilon_1$ and $\varepsilon_2$ are the energies of the two orbitals $\phi_1$ (HOMO) and $\phi_2$ (LUMO), respectively. The value of $K_{ab}$ is always positive, so the first term in (2) contributes to the ferromagnetic interaction, while the second term, which is always positive, contributes to the antiferromagnetic interaction. The energy difference between the two
molecular orbitals \((\varepsilon_1 - \varepsilon_2)\) which corresponds to the HOMO – LUMO energy gap, determines the magnitude of the antiferromagnetic interaction. From the above expression (2) for the exchange parameter, it is seen that the binuclear complex with the greater antiferromagnetic interaction has the larger \((\varepsilon_1 - \varepsilon_2)\) energy difference. The extended Hückel molecular orbital (EHMO) calculations for the investigated compound have shown that the \(\phi_1\) and \(\phi_2\) orbitals are separated by 0.140 eV, respectively. Very recently, we have studied the crystal structures and magnetic properties of \((\mu\text{-hydroxo})(\mu\text{-acetato})\) and \((\mu\text{-hydroxo})(\mu\text{-pyrazolate})\) bridged dicopper(II) complexes [9,10]. For these binuclear copper complexes \((\varepsilon_1 - \varepsilon_2)\) energy differences are found to be 0.605, 0.645 [9] and 1.11 eV [10]. These results indicate the stronger antiferromagnetic interaction than the investigated compound. These results also indicate that a large energy separation of \(\phi_1\) (HOMO) and \(\phi_2\) (LUMO) leads to a strong antiferromagnetic interaction.

**Conclusion**

In general, several structural features of binuclear copper(II) complexes are thought to regulate the strength of exchange coupling interactions: (i) the dihedral angle between the two coordination planes, (ii) planarity of the bonds around the bridging atom, and (iii) the bridging atom(s) and bridging angles [25, 26]. But, the variation of the strength of the super-exchange interaction cannot be explained completely by the structural features of binuclear copper(II) complexes. A different approach must be discussed to clarify the origin of the super-exchange mechanism of this system.

In the light of the value of exchange constant \(J\), two points deserve to be discussed: (i) the exchange pathway between the two paramagnetic copper(II) ions and (ii) the variation of the antiferromagnetic coupling with the nature of the copper(II) ions. Dealing with the first point, studies of magnetic exchange between paramagnetic metal ions exhibiting a tetrahedral
environment are very scarce [27, 28]. Tetrahedral Cu(II) complexes present magnetic orbitals of $t_2$ symmetry and, as such, the $\pi$ interaction with ligands can be very important. In addition, it has been suggested that the magnetic interaction through extended bridging ligands having a $\pi$-conjugated system is mediated via the delocalized $\pi$ framework [28-30]. In fact, the extended Hückel molecular orbital calculation [16] on the $m$-phenylenediamine bridging fragment shows that the highest occupied molecular orbitals HOMOs are of $\pi$ symmetry. Scheme 2 can be used to describe the magnetic interaction therein. One can see that the overlap between the $3d_{xy}$ type magnetic orbital of the metal ion and the $p$ orbital of the bridging ligand is greater than that involving the $3d_{xz}$ and $3d_{yz}$, whereas the overlap with the phenolato-oxygens ($p_x$, $p_y$ and $p_z$) is identical for the three $3d$ orbitals. In this respect, the trend of the orbital energy will be $\varepsilon_{d_{xy}} > \varepsilon_{d_{xz}} \approx \varepsilon_{d_{yz}}$ and due to the larger overlap between the $d_{xy}$ orbital and the bridging ligand this $3d_{xy}$ orbital will be mainly responsible for the magnetic interaction [31, 32]. In the investigated copper(II) complex, a distortion of the tetrahedron occurs, consisting of a shift of the phenolato oxygens in such a way that they are occupying the middle point of the edge as shown in Scheme 2. Such a distortion in the copper(II) family causes a larger interaction between the $d_{xz}$ orbital and the phenolato oxygens, and raise the energy of this orbital placing it above that of $d_{xy}$. However, this distortion does not modify significantly the overlap between the $d_{xz}$ orbital and the bridging ligand. So, the electronic configuration for the copper(II) complex exhibiting the above-mentioned distortion is $(d_{z^2})^2 (d_{x^2-y^2})^2 (d_{yz})^2 (d_{xy})^2 (d_{xz})^1$. 

![Diagram of a tetrahedral copper(II) complex with magnetic orbitals and ligands highlighted.]
These simple considerations allow us to analyse the second key point which is the variation of the value of $J$ parameter as a function of metal ion for a given ligand. This analyse is explained by mentioned *a qualitative relationship*.

The binuclear copper(II) complex involving weak antiferromagnetic interaction was studied in this work. Consequently, above results strongly suggest that the antiferromagnetic interaction in the dimeric must be mediated *via* the delocalized $\pi$ framework of the $m$-phenylenediamine fragment.

**Acknowledgment**

This work was supported by the Scientific Research Project Fund of the University of Ankara under grant number 2002-07-45-004.


[14] Further information may be obtained from: Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB21EZ, UK, by quoting the depository number CCDC 220656 E-mail: deposit@ccdc.cam.ac.uk.


Table 1. Crystallographic data for the investigated complex

<table>
<thead>
<tr>
<th>Sum formula</th>
<th>(C_{44}H_{40}Cu_{4}N_{4}O_{8})-2H_{2}O</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_w ) (g.mol(^{-1}))</td>
<td>947.94</td>
</tr>
<tr>
<td>Space group</td>
<td>P ( \overline{1} )</td>
</tr>
<tr>
<td>( a = 8.953(2) ) Å</td>
<td>( \alpha = 100.74(2)^\circ )</td>
</tr>
<tr>
<td>( b = 11.264(1) ) Å</td>
<td>( \beta = 105.23(10)^\circ )</td>
</tr>
<tr>
<td>( c = 11.318(2) ) Å</td>
<td>( \gamma = 103.47(3)^\circ )</td>
</tr>
</tbody>
</table>
Vol [Å³] 1033(1)
Z 1
D_{calc}(g.cm^{-3}) 1.524
µ [cm^{-1}] 1.039
F(000) 490

Index ranges
-11 ≤ h ≤ 4, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13

Reflections collected 6257
Independent reflections 4038 [R(int) = 0.016]
Data / restraints / parameters 4038 / 0 / 313
Goodness-of-fit on F² 0.972

Final R indices [I>2σ(I)]
R = 0.0445, wR = 0.0769

Largest diff. peak and hole 0.471 and -0.787 e. Å^{-3}

Table 2. Atomic coordinates and equivalent isotropic displacement parameters.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1</td>
<td>0.15254(8)</td>
<td>0.28253(6)</td>
<td>0.17413(6)</td>
<td>0.0338(2)</td>
</tr>
<tr>
<td>N1</td>
<td>-0.0032(5)</td>
<td>0.2450(3)</td>
<td>0.0043(3)</td>
<td>0.0314(10)</td>
</tr>
<tr>
<td>N2</td>
<td>0.2081(5)</td>
<td>0.4680(3)</td>
<td>0.2247(3)</td>
<td>0.0290(10)</td>
</tr>
<tr>
<td>O1</td>
<td>0.0487(4)</td>
<td>0.1326(3)</td>
<td>0.2091(3)</td>
<td>0.0408(9)</td>
</tr>
<tr>
<td>O2</td>
<td>0.3586(4)</td>
<td>0.2801(3)</td>
<td>0.2726(3)</td>
<td>0.0362(9)</td>
</tr>
<tr>
<td>O3</td>
<td>0.6179(4)</td>
<td>0.2238(3)</td>
<td>0.3674(3)</td>
<td>0.0506(11)</td>
</tr>
<tr>
<td>O4</td>
<td>-0.0590(4)</td>
<td>-0.0389(3)</td>
<td>0.3122(3)</td>
<td>0.0478(10)</td>
</tr>
</tbody>
</table>
Table 3. Selected bond lengths [Å], angles [°] characterizing the inner coordination sphere of the copper(II) centre and hydrogen – bonding interactions (see Fig. 1 for labelling scheme adopted.)

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1–O1</td>
<td>1.893(3)</td>
</tr>
<tr>
<td>Cu1–O2</td>
<td>1.898(4)</td>
</tr>
<tr>
<td>Cu1–N1</td>
<td>1.958(4)</td>
</tr>
<tr>
<td>C1–N1</td>
<td>1.306(6)</td>
</tr>
<tr>
<td>C14–N2</td>
<td>1.300(6)</td>
</tr>
<tr>
<td>C7–O1</td>
<td>1.298(5)</td>
</tr>
</tbody>
</table>
Cu1–N2 1.964(4)  C8–O2 1.288(5)

Angles

O1–Cu1–O2  91.2(1)  O1–Cu1–N1  94.5(2)  O2–Cu1–N2  93.8(2)  N1–Cu1–N2  100.4(2)  O1–Cu1–N2  143.8(2)  N1–Cu1–O2  146.9(2)

Hydrogen bonds

\[
\begin{array}{cccccc}
D & A & H & D^{AA} [\text{Å}] & D - H^{AA} [^\circ] \\
O5 & O4 & H5a & 2.37(1) & 160.8(1) \\
O5 & O3 & H5b & 2.42(1) & 133.2(1) \\
O5 & O1 & H5b & 2.77(1) & 95.7(1) \\
O5 & O2 & H5b & 2.19(1) & 156.6(1) \\
O5 & O1 & H5a & 2.44(1) & 129.8(1) \\
O6 & O3 & H6b & 2.99(1) & 113.3(1) \\
O6 & O5 & H6b & 1.89(1) & 173.3(1) \\
O6 & O5 & H6a & 2.12(1) & 161.9(1) \\
\end{array}
\]

\(^{a}(A=\text{acceptor, } D=\text{donor atom})\)

Figure Captions

**Fig. 1.** View of the molecule (numbering of atoms corresponds to Table 2). Displacement ellipsoids are plotted at the 50% probability level and H atoms are presented as spheres of arbitrary radii.
**Fig. 2.** Molar susceptibility per copper(II) vs. temperature curve.

**Fig. 3.** Magnetic moment per copper(II) vs. temperature curve.

**Fig. 4.** Drawing of HOMO and LUMO frontier orbitals (for orbitals contributing more than 1%) obtained for the complex.
LUMO orbital
$\varepsilon_i = -11.837 \text{ eV}$

HOMO orbital
$\varepsilon_i = -11.977 \text{ eV}$