Crystal Structure and Magnetic Properties of an Oxygen-Bridged Trinuclear Copper(II) Complex

Y. Elerman, E. Kavlakoglu, A. Elmali, and E. Kendi

a Department of Engineering Physics, Faculty of Engineering, Ankara University, 06100 Besevler-Ankara, Turkey
b Department of Engineering Physics, Faculty of Engineering, University of Hacettepe, Beytepe, Ankara, Turkey

Reprint requests to Dr. Y. Elerman. E-mail: elerman@science.ankara.edu.tr

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Trinuclear Copper(II) Complex, Super-Exchange Interactions, Antiferromagnetic Coupling

[\text{Cu}_3 (\text{L})_3].3(\text{ClO}_4) \text{ was synthesized and its crystal structure determined. It crystallizes in the triclinic space group } \text{P1 with } \alpha = 10.504(2), \beta = 10.856(2), c = 12.519(2) \text{ Å, } \alpha = 74.41(1), \beta = 70.60(1), \gamma = 63.60(1)^\circ, V = 1193.6(3) \text{ Å}^3, Z = 2. The structure consists of trimeric } [\text{Cu}_3(\text{L})_3]^3 \text{ units and three perchlorate anions in the asymmetric unit. In the compound three copper(II) ions are linked by 1,3-diamino-2-propanol molecules in such a way that an almost equilateral triangle is formed. The coordination spheres of the three copper(II) ions are slightly different from each other. The coordination geometry of Cu1 is a distorted square pyramid, and that of Cu2 is almost square planar while that of Cu3 is tetrahedrally distorted square planar. The copper(II) centers are separated by average 3.481(2) Å and antiferromagnetically coupled (J = 100 cm\(^{-1}\)), which follows from temperature-dependent magnetic susceptibility measurements in the temperature range 4.4 to 299 K. The average Cu-O-Cu angle is 128.1(1)\(^\circ\) in the super-exchange pathway. As the temperature is increased, the magnetic moment rises from 1.41 \(\mu_B\) at 4.4 K to 2.22 \(\mu_B\) at 299 K. In the \(\chi(T)\) curve no characteristic maximum was observed. The magnetic super-exchange interaction for the title compound is due to the effective overlap of the magnetic orbitals (d\(_x^2-y^2\)) with orbitals of bridging alkoxide oxygen atoms.

Introduction

Polynuclear copper(II) complexes have been investigated actively in the last two decades in order to understand the relationship between the structure and the magnetic properties [1 - 6]. In addition, copper(II) complexes are of interest because of their relevance to active site structures of metalloproteins [7, 8].

Different kinds of trinuclear copper(II) complexes have been extensively studied. In these complexes, the coordination sphere of three copper atoms may be different from each other or all three copper coordinations may be identical, or one of them may have a unique and a pair of them may have equal environments. Those of the triangular type have generated great interest because of their role in the active site of multicopper oxidases, in homogeneous catalysis and because of their structural and magnetic characteristics. Trinuclear copper(II) complexes containing a central hydroxide OH\(^-\) and oxide O\(^{2-}\) unit with three equal or unequal copper atoms have been reported [9 - 13]. The trinuclear copper(II) complexes having a nearly linear arrangement of three copper atoms were also reported [4, 14 - 16].

In this study, we have synthesized a tri-\(\mu\)-1,3-diamino-2-propanolato tricopper(II) perchlorate and determined its crystal structure by X-ray diffraction. We have measured magnetic susceptibilities in the temperature range 4.4 - 299 K using the Faraday method to investigate the relationship between the magnetic properties and the molecular structure.

\[ \begin{align*}
\text{H}_2\text{N} & \quad \text{Cu} \quad \text{NH}_2 \\
\text{H}_2\text{N} & \quad \text{O} \quad \text{O} \\
\text{H}_2\text{N} & \quad \text{NH}_2
\end{align*} \]

\[ \text{Cu}_3 (\text{L})_3].3(\text{ClO}_4) \]
Table 1. Crystallographic data for the investigated compound.

<table>
<thead>
<tr>
<th>Sum formula</th>
<th>C₂H₂₇N₆O₂Cu₃ · 3 (ClO₄)</th>
<th>f₀ (g·mol⁻¹)</th>
<th>756.34</th>
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<tbody>
<tr>
<td>Space group</td>
<td>P1</td>
<td></td>
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</tr>
<tr>
<td>a = 10.503(2) Å</td>
<td>α = 74.41(1)°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b = 10.856(2) Å</td>
<td>β = 70.60(1)°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c = 12.519(2) Å</td>
<td>γ = 63.60(1)°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vol. [Å³]</td>
<td>1193.6(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D_cal (g·cm⁻³)</td>
<td>2.104</td>
<td></td>
<td></td>
</tr>
<tr>
<td>μ [cm⁻¹]</td>
<td>69.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(000)</td>
<td>762</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Index ranges</td>
<td>-12 ≤ h ≤ 13, -12 ≤ k ≤ 13, 0 ≤ l ≤ 15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reflections collected</td>
<td>4842</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data / restraints / params.</td>
<td>4842 / 0 / 266</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.072</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R Indices for all data</td>
<td>R = 0.0412, wR = 0.0523</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R = 0.0384, wR = 0.0459</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.281 and -1.122 e·Å⁻³</td>
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</tr>
</tbody>
</table>

Experimental

Preparation

The copper(II) complex was synthesized by mixing Cu(ClO₄)₂·6 H₂O (2 mmol) with 1,3-diamino-2-propanol (2 mmol) in methanol at room temperature, followed by the addition of triethylamine (3 mmol). The product formed dark blue crystals. Analysis for (C₉₁₁N₆O₂Cu₃·3 (ClO₄)): calcld. C 15.76, H 3.97; found C 15.7, H 3.8.

X-ray structure determination

X-ray data collection was carried out on an Enraf-Nonius CAD-4 diffractometer [17] using a single crystal with dimensions 0.05×0.10×0.15 mm³ with graphite monochromatized Cu-Kα radiation (λ = 1.54180 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 (2θ ≤ 13.15°) carefully centered on the diffractometer. The standard reflections (206, 412, 042) were measured every 7200 s and the orientation of the crystal was checked after every 600 reflections. These measurements (298 K) did not indicate any variations in the experimental conditions. Data reduction and corrections for absorption and decomposition were achieved using the Nonius Diffractometer Control Software [17]. The structure was solved by SHELXS-97 [18] and refined with SHELXL-97 [19]. The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.96 Å) and refined using a riding model, and H atom displacement parameters were restricted to be 1.2 Ueq of the parent atom. The final positional parameters are presented in Table 2. A perspective drawing of the molecule is shown in Fig. 1 [20]. Selected bond lengths and angles are summarized in Table 3. 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-166214 [21].

Susceptibility measurements

Magnetic susceptibility measurements of the powdered sample were performed on a Faraday-type magnetometer consisting of a CAHN D-200 microbalance, a Leybold Heraeus VNK 300 helium flux cryostat and a Bruker BE
Table 3. Selected bond lengths [Å] and angles [°] characterizing the inner coordination sphere of the copper(II) centre (see Fig. 1 for labelling scheme adopted).

<table>
<thead>
<tr>
<th></th>
<th>Bond Lengths</th>
<th>Bond Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1-O3</td>
<td>1.932(1) Å</td>
<td>Cu1-O1 1.951(1)</td>
</tr>
<tr>
<td>Cu1-N2</td>
<td>1.980(2) Å</td>
<td>Cu1-N3 1.998(1)</td>
</tr>
<tr>
<td>Cu2-O3</td>
<td>1.928(1) Å</td>
<td>Cu2-O2 1.937(1)</td>
</tr>
<tr>
<td>Cu2-N1</td>
<td>1.999(1) Å</td>
<td>Cu2-N6 2.008(2)</td>
</tr>
<tr>
<td>Cu3-O1</td>
<td>1.940(1) Å</td>
<td>Cu3-O2 1.961(1)</td>
</tr>
<tr>
<td>Cu3-N5</td>
<td>1.971(2) Å</td>
<td>Cu3-N4 2.002(1)</td>
</tr>
<tr>
<td>O3-Cu1-O1</td>
<td>91.6(1) °</td>
<td>O3-Cu1-N2 85.7(1)°</td>
</tr>
<tr>
<td>O1-Cu1-N2</td>
<td>172.2(1) °</td>
<td>O1-Cu1-N3 169.4(1)°</td>
</tr>
<tr>
<td>Cu1-N3</td>
<td>95.0(1) °</td>
<td>N2-Cu1-N3 93.0(1) °</td>
</tr>
<tr>
<td>O3-Cu2-O2</td>
<td>97.8(1) °</td>
<td>O3-Cu2-N1 84.3(1) °</td>
</tr>
<tr>
<td>O2-Cu2-N1</td>
<td>176.0(1) °</td>
<td>O2-Cu2-N6 172.4(1)°</td>
</tr>
<tr>
<td>O2-Cu2-N6</td>
<td>85.3(1) °</td>
<td>N1-Cu2-N6 93.0(1) °</td>
</tr>
<tr>
<td>O1-Cu3-O2</td>
<td>95.1(1) °</td>
<td>O1-Cu3-N5 175.9(1)°</td>
</tr>
<tr>
<td>O2-Cu3-N5</td>
<td>86.6(1) °</td>
<td>O1-Cu3-N4 175.9(1)°</td>
</tr>
<tr>
<td>O2-Cu3-N4</td>
<td>162.4(1) °</td>
<td>N5-Cu3-N4 94.1(1) °</td>
</tr>
</tbody>
</table>

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.

Discussion

X-ray crystal structure

The title compound consists of trinuclear copper(II) complex units and perchlorate anions which are bound to the trimeric unit via hydrogen bonds. The three Cu atoms of the complex are located at the apexes of a nearly equilateral triangle and bridged by three μ-alkoxo oxygen atoms of the 1,3-diamino-2-propanolate anions to form a Cu3O3 core. Structures of triangular Cu3 complexes have been previously reported [9 - 16, 24 - 27]. Most of them have an equilateral triangle of three Cu(II) ions bridged by mono-μ3-OH or a mono-μ3-O. The title compound does have neither a μ3-OH nor a μ3-O bridge, and the Cu(II) ions are stabilized by the three μ-alkoxide bridges only. This kind of trimeric copper arrangement is quite uncommon.

In the title compound each of the copper atoms are coordinated by two oxygen and two nitrogen atoms from two separate 1,3-diamino-2-propanolate anions. The coordination spheres of the three copper(II) ions are slightly different from each other. The coordination around the Cu(1) centre can be described as a distorted square pyramid formed by a plane described by O(1), O(3), N(2) and N(3). The deviations of the atoms from the least-squares plane are as follows: O(1) = -0.005(1), O(3) = -0.057(1), N(2) = -0.007(1), N(3) = -0.055(1) Å while the Cu(1) deviates 0.124(1) Å. The geometry around the Cu(2) centre can be described as a square-planar environment formed by O(2), O(3), N(1) and N(6) with the atoms 0.084(1), -0.098(1), 0.086(1) and -0.096(1) Å from this plane, while Cu(2) deviates 0.024(1) Å, respectively. The coordination geometry of the Cu(3) centre is tetrahedrally distorted square planar. The Cu(3) atom is coordinated by O(1), O(2), N(4) and N(5). The tetrahedral distortion is reflected by the distances of the five atoms from the least-squares plane through the atoms: O(1) = -0.163(1), O(2) = 0.210(1), N(4) = 0.208(1) and N(5) = -0.160(1), Cu(3) = -0.095(1) Å.

Cu-N and Cu-O bond distances are in good agreement with data of similar compounds [12, 24]. The Cu-O-Cu bridging angles are as follows: Cu(1)-O(1)-Cu(3) = 116.2(1), Cu(1)-O(3)-Cu(2) = 129.3(1), Cu(2)-O(2)-Cu(3) = 138.9(1)° in good agreement with data of similar compounds [12, 24].

The title compound contains intermolecular (N-H...O) hydrogen bonds N2-H...O7 [3.005(3) Å], N2-H...O9 [2.995(2) Å], N3-H...O14 [3.240(2) Å], N3-H...O9 [3.239(3) Å], N4-H...O5 [2.971(3) Å], and N4-H...O14 [2.882(2) Å]. In addition, each ligand contains intramolecular hydrogen bond N1-H...O1 [2.967(2) Å].
Magnetic properties

Magnetic susceptibility measurements for a powdered sample of the complex were performed by the Faraday method in the temperature range 4.4 - 299 K. The magnetic susceptibility and the magnetic moment of the complex are shown as a function of temperature in Fig. 2. The observed and calculated magnetic moment (\( \mu_{\text{eff}} = 2.828 (\chi T)^{1/2} \)) decreases from 2.22 \( \mu_B \) at 299 K to 1.41 \( \mu_B \) at 4.4 K indicating that an antiferromagnetic interaction operates among the three Cu(II) ions. However, the curve of magnetic susceptibility as a function of temperature does not show a characteristic maximum. The molar magnetic susceptibility is calculated by using the isotropic (Heisenberg) exchange Hamiltonian first used by Kambe for this purpose [28] (eq. (1)).

\[
H = -2 \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j
\]  

When three paramagnetic ions of \( S = 1/2 \) are equivalent and form an equilateral triangle, the spin Hamiltonian in eq. (2) describes the interaction of the spins.

\[
H = -2J(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_1 \cdot \vec{S}_3)
\]  

The magnetic exchange interactions have been described by a single parameter \( J \). The resulting expression for the temperature dependence of the magnetic susceptibility is given in eq. (3).

\[
\chi(T) = (1 - x_p) \frac{\chi_{\text{Tri}}}{3} + x_p \chi_{\text{Mono}} + N_\alpha
\]

\[
\chi_{\text{Mono}} = \frac{Ng^2 \mu_B^2}{3kT} S(S+1) \text{ with } S = \frac{1}{2}
\]
\[
\chi_{\text{Tri}} = \frac{Ng^2\mu_B^2}{4kT}\frac{1 + 5\exp(3J/kT)}{1 + \exp(3J/kT)}
\]

\(N_o\) is the temperature-indepenent paramagnetism and its value is \(6 \cdot 10^{-5}\) cm\(^3\)/mol for each copper atom. \(x_p\) is the molar fraction of a monomeric impurity. The best fit parameters which were obtained by using a standard least-squares program were \(g = 2.02, J = -100\) cm\(^{-1}\), \(x_p = 0.6\%\).

The isotropic exchange interaction among the three ions of \(S = 1/2\) placed at the apexes of an equilateral triangle splits the three degenerate energy levels into one quartet state with a total spin \(S_T = 3/2\) and two degenerate doublet states with a total spin \(S_T = 1/2\). The energy separation between the quartet (\(S_T = 3/2\)) and the doublet (\(S_T = 1/2\)) states is \(-3J = 300\) cm\(^{-1}\) for the title compound.

It is instructive to compare the structural and magnetic properties of the title compound with those of other trinuclear copper(II) complexes. In general, polynuclear copper(II) complexes have several structural features to affect the strength of exchange coupling interactions, such as the Cu-O-Cu bridging angle, the dihedral angle between the two coordination planes, the planarity of the bonds around the bridging oxygen atom in certain dinuclear copper(II) complexes [29, 30], the length of the bridging bond [31], the coplanarity of the coordination plane [32], and the planar-tetrahedral distortion [33]. In mono-\(\mu_3\)-OH (or -O) bridged trinuclear copper complexes with oximate ligands, the magnitude of the \(J\) values are in the range from -120 to -1000 cm\(^{-1}\) [12, 13, 16, 17], but in the mono-\(\mu_3\)-OH bridged trinuclear copper(II) complexes with \(\mu\)-carbonyl oxygen bridges the value of the coupling constant is out of this range (-12 and -15 cm\(^{-1}\)) [18, 19]. The magnetic interaction of these complexes depends on the degree of coplanarity of the Cu coordination planes. High planarity in oxime-bridged dimers has been shown to provide strong coupling.

In the case of oxygen-bridged trimeric copper(II) complexes which have no central \(\text{OH}^-\) or \(\text{O}^-\) bridge, the magnitude of the \(J\) values is in the range -79 to -318 cm\(^{-1}\) [24, 34]. In the title compound, the magnitude of the coupling constant is in this range. The three copper(II) ions are magnetically coupled to each other by a super-exchange interaction through the oxygen atoms of the 1,3-diamino-2-propanol ligands. The magnetic interaction is due to the effective overlap of the magnetic orbitals \((d_{x^2-y^2})\) because of the almost coplanarity of the coordination planes of the three subunits. This leads to a strong magnetic interaction between the Cu(II) ions in the title compound.

Acknowledgments

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[21] Further information may be obtained from: Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB21EZ, UK, by quoting the depository number CCDC-166214. E-mail: deposit@ccdc.cam.ac.uk