Structure and magnetic properties of a tetranuclear Cu₄O₄ open-cubane in [Cu(L)]₄·4H₂O with L²⁻ = (E)-N'-(2-oxy-3-methoxybenzylidene)benzohydrazide

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A B S T R A C T
The in-situ formed hydrazone Schiff base ligand (E)-N’-(2-oxy-3-methoxybenzylidene)benzohydrazide (L²–) reacts with copper(II) acetate to a tetranuclear open cubane [Cu(L)]₄ complex which crystallizes as two symmetry-independent (Z = 2) S₄-symmetrical molecules in different twofold special positions with a homodromic water tetramer. The two independent (A and B) open- or pseudo-cubanes with CuO₄ cores of 4 + 2 class (Ruiz classification) each have three different magnetic exchange pathways leading to an overall antiferromagnetic coupling with J₁A = J₁B = −17.2 cm⁻¹, J₁A = −36.7 cm⁻¹, J₂A = −159 cm⁻¹, J₁B = 33.5 cm⁻¹, g = 2.40 and ρ = 0.0687. The magnetic properties have been analysed using the H = −∑j,k(SjSj) spin Hamiltonian.

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1. Introduction
The design of polynuclear transition-metal clusters with novel magnetic properties is a major goal of current research in the field of condensed matter physics and material chemistry [1–3]. Copper(II) complexes are of particular interest from both structural and functional points of view. Tetranuclear copper(II) clusters which exhibit a large diversity of structural types, e.g. cyclic [4], pin-wheel [5], square planar [6], dimeric [7], face-to-face [8], roof-shaped [9] and cubane type [10], are of permanent interest in magnetostructural research, bioinorganic modeling, catalysis and multielectron transfer.

Salicylaldehyde benzoylhydrazone (H₂sb) possesses mild bacteriostatic activity [11] and inhibits DNA synthesis and cell growth [12]. The copper(II) complex was shown to be significantly more potent than the metal-free chelate, leading to the suggestion that the metal complex was the biologically active species. Salicylaldehyde acetylhydrazone (H₂sa) displays radioprotective properties [13], and a range of acylhydrazones have been shown to be cytotoxic, the copper complexes again showing enhanced activity. Because of the biological interest in this type of chelate system, several structural studies have been carried out on copper [14–16] with H₂sb and analogues. Structurally there is a preference for planar, phenolato bridged Cu(II) dimers with these ligands which often exhibit antiferromagnetism [15,16].

This class of diprotic ligands typically acts as tridentate, planar chelate ligands coordinating through the phenolic and amide oxygen and the imine nitrogen atom. The actual ionization state is dependent upon the conditions and metal employed. With Cu(II) in basic media, both the phenolic and amide protons are ionized. In neutral and mild acidic solution the ligands are monoanionic. Strongly
acids are necessary to form compounds formulated with a neutral ligand.

A few structurally characterized multinuclear complexes containing Schiff base ligands have been reported [17,18]. Herein, we describe the structural and magnetic properties of a tetranuclear hydrazide Schiff base open-cubane copper(II) complex [Cu(L)]₄·4H₂O.

2. Experimental

Benzhydrazide, 2-hydroxy-3-methoxybenzaldehyde, copper(II) acetate monohydrate and solvents with high purity were purchased from Merck and Fluka and used as received. IR spectra were recorded as KBr disks with a Perkin Elmer 1600 FT-IR spectrophotometer in the range 4000–450 cm⁻¹. Microanalytical (CHN) data were obtained with a Carlo Erba Model EA-1108 analyzer.

2.1. Synthesis of tetrakis[(E)-N’-(2-oxy-3-methoxybenzyliden-Benzohydrazidocopper) tetrahydrate, [Cu(L)]₄·4H₂O]

Benzhydrazide (0.040, 0.33 mmol), 2-hydroxy-3-methoxybenzaldehyde (0.044 g, 0.28 mmol) and copper(II) acetate monohydrate (0.058 g, 0.28 mmol) were placed in the main arm of the branched tube (‘branched tube’ method [19]). A mixture of methanol and ethanol (50:50 v/v) was carefully filtered off and washed with methanol and air dried. After 1 week, deep green crystals were deposited in the cooler part of the tube. 

A mixture of methanol and ethanol (50:50 v/v) was carefully filtered off, and the tube was sealed and the reagents containing arm immersed in an oil bath at 60 °C while the other arm was kept at ambient temperature. Other solvents like H₂O:EtOH and EtOH were also examined but in the methanol:ethanol mixture the crystals grew fastest. After 1 week, deep green crystals were deposited in the cooler part of the tube, which were filtered off, washed with methanol and air dried. 

2.2. X-ray structure determination

A suitable single crystal was carefully selected under a polarizing microscope. Data Collection: Rigaku R-axis Spider with image plate detector, temperature 223(2) K, Mo Kα radiation (λ = 0.7073 Å), graphite monochromator, double-pass method ω-scan. Data collection with d trek [20], cell refinement and data reduction with Xsop [20], empirical absorption correction. Structure Analysis and Refinement: The structure was solved by direct methods (SHELXS-97) [21]; refinement was done by full-matrix least squares on F² using the SHELXL-97 program suite [21]. All non-hydrogen positions were refined with anisotropic temperature factors. Hydrogen atoms on the carbon atoms were placed at calculated positions with an appropriate riding model (AFIX 43 for aromatic CH, AFIX 33 for CH₃) and an isotropic temperature factor of Uiso(C) = 1.5 Ueq(C). The hydrogen atoms of the water of crystallization were refined with Uiso(O) = 1.5Ueq(O) (see Table S1 in Supporting information). Graphics were obtained with DIAMOND [22]. Computations on the supramolecular π-interactions were carried out with PLATON for Windows [23]. Crystal data and details on the structure refinement are given in Table 1.

2.3. Magnetic susceptibility measurements

Magnetic susceptibility measurements on polycrystalline samples were carried out in the temperature range 1.9–300 K by means of a Quantum Design SQUID magnetometer operating at 10 000 Oe. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants. Experimental susceptibility were also corrected for the temperature-independent paramagnetism [60 × 10⁻⁶ cm³ mol⁻¹ per Cu(II)] and the magnetization of the sample holder.

3. Results and discussion

3.1. Synthesis

The hydrazone pro-ligand H₂L was obtained by the in-situ condensation of benzhydrazide and 2-hydroxy-3-methoxybenzaldehyde. By potentiometric titration the acidity constant pK_a of the phenolic hydrazo group is about 9.00, whereas the pK_a value obtained for the second amide acidity constant is 10.92 in MeOH/H₂O (0.9/0.1 v/v) at 25.0 °C [24]. In reaction with basic copper(II) acetate, H₂L forms a dinegative ligand and occupies three Cu(II) coordination sites [25].

The ligand H₂L shows IR bands assigned to ν(OH) (3563 cm⁻¹), ν(=NH) (3377 and 3215 cm⁻¹), ν(C=O) (1654 cm⁻¹), and ν(C=N) + amide (1608–1576 cm⁻¹). On complexation the ν(C=O) and ν(C=N) + amide bands for the ligand are shifted, showing that coordination involves the carbonyl-O and imine-N atoms.

3.2. Crystal structure of [Cu(L)]₄·4H₂O

The title compound forms a tetrameric and tetratomic complex where each two-fold deprotonated Schiff base ligand coordinates to a Cu atom with its imine nitrogen atom, its phenolate and its amide carbonyl oxygen atoms thereby forming a six- and a five-membered chelate ring. At the same time each ligand bridges to a neighboring Cu atom through its phenolate group (Fig. 1). In the tetramer, four Cu(II) atoms and four oxygen atoms

Table 1

<table>
<thead>
<tr>
<th>Crystal data and structure refinement for [Cu(L)]₄·4H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula: Cu₂H₄Cu₂N₈O₁₂·4H₂O</td>
</tr>
<tr>
<td>M (g mol⁻¹): 1399.29</td>
</tr>
<tr>
<td>Crystal size: mm³</td>
</tr>
<tr>
<td>Crystal appearance: plate, green</td>
</tr>
<tr>
<td>2θ range: 6.06 – 54.96</td>
</tr>
<tr>
<td>a: 22.71, c: 31.33</td>
</tr>
<tr>
<td>Crystal system: monoclinic</td>
</tr>
<tr>
<td>Space group: P2₁/c</td>
</tr>
<tr>
<td>μ (mm⁻¹): 1.483</td>
</tr>
<tr>
<td>Max./Min. transmission: 0.9033/0.6403</td>
</tr>
<tr>
<td>Indep. reflections: 13630 (R(int) = 0.0616)</td>
</tr>
<tr>
<td>Observed reflections: 10164</td>
</tr>
<tr>
<td>Parameters refined: 827</td>
</tr>
<tr>
<td>Max./Min. Δρ(eq) e Å⁻³: 0.575/–0.438</td>
</tr>
<tr>
<td>R₁: 0.0358/0.0518</td>
</tr>
<tr>
<td>R₁ (all refl.): 0.0358/0.0518</td>
</tr>
<tr>
<td>Goodness-of-fit (GOF) on F²: 1.036</td>
</tr>
<tr>
<td>Weighting scheme: w = 1/F²</td>
</tr>
<tr>
<td>χ²: 0.0310/3.4427</td>
</tr>
</tbody>
</table>

Note: w = 1/[σ²(F²) + (bp)²] where P = (max(F²) + 0) + 2F²/3.
alternatingly occupy the vertices of a cube where four of the twelve edges are longer. Hence, the tetranuclear unit forms an open- or pseudo-cubane structure with a Cu₄O₄ core with idealized S₄-symmetry (Fig. 2, Scheme 1). The geometry of the Cu atoms is best described as square planar with additional (Jahn–Teller distorted) longer contacts to the methoxy oxygen atom and very long contacts to the already bridging phenolate along the open edge.

The crystal structure contains two independent tetranuclear molecules (Z = 2) in different twofold special positions [26], that is, only half (2 ligands + 2 Cu) of each pseudo-cubane is symmetry independent (unique).

The two independent tetramers have largely similar structural data (Fig. 1 and Table 2). There is a crystallographic pseudo mirror symmetry between the two independent molecules. Yet, the two molecules are no “enantiomeric” mirror images but superimposable through a simple rotation (e.g. Cu₃O matches with Cu₂O, O₉ with O₄ and so on in Fig. 2). One distinct difference between the two independent molecules lies in the orientation of the methoxy group – bent out of the aryl ring plane in molecule 1 and positioned in line with the aromatic plane in molecule 2 (Fig. 1). The presence of two independent molecular halves may be explained with packing frustration. Here, the aryl-group decorated molecules of [Cu(L)₂]₄ apparently cannot pack efficiently through π–π or C–H–π stacking [27–29]. Crystal water tetramers with homodromic hydrogen bonds [30] are found in cavities created by the [Cu(L)₄] molecules (Fig. 3 and Figs. S4–S6 in Supporting information). The crystal water is not lost upon air-drying. There is an ongoing discussion on the origin of so-called Z > 1 structures. Different ideas have been put forward to rationalize this phenomenon [31]: A “fossil relic” of a more stable form [32], a crystal “on the way” [33–35] or strong and special supramolecular interactions between the two (or more) symmetry-independent units [36–38]. The frustration between chirality and the formation of centrosymmetric synthons almost invariably has to lead to the presence of two independent hydrogen bonding functionalities [39]. A high Z is also obtained when the molecule has different equi-energetic conformations, with these conformations co-existing in the crystal [40].

Related open or pseudo-cubanes have been structurally described and magnetically analyzed (see Table S2 in Supporting information) [41–45].

### 3.3 Magnetic properties

The thermal dependence of χM/T of [Cu(L)₄]₄·4H₂O in the temperature range 1.9–300 K is depicted in Fig. 4 (χM being the magnetic susceptibility per mol of Cu₄). The χM/T value at room temperature is 1.56 cm³ mol⁻¹ K and the curve shows a continuous decay tending to a plateau at temperatures below 10 K. The value at 1.9 K is 0.11 cm³ mol⁻¹ K. This behaviour is indicative of a dominant antiferromagnetic coupling that leads to a 5 + 0 spin ground state together with some paramagnetic impurities that make the χM/T vs. T curve to deviate from 0 at low temperatures. As has been described in the structural part, the copper(II) ions build two different cubane-like tetramers, A and B. Both cubanes have the same pattern (4 + 2 class, Scheme 2) [46–48]. However, the Cu(II)–Cu(II) distances and the Cu–O–Cu angles have significant differences that argue for their separate analysis. Cubane A (Table 2) has Cu(II)–Cu(II) distances that range from 3.28 to 3.40 Å and three different magnetic exchange-path-ways can be defined, J₁A, J₂A and J₃A. In cubane B the distances range from 3.21 to 3.51 Å and the Cu–O–Cu angles are different from those of cubane A. Then three additional coupling constants can be defined (Scheme 3).
Table 2
Selected bond lengths [Å] and angles [°] in [Cu(L)]₄·4H₂O.

<table>
<thead>
<tr>
<th>Cubane A</th>
<th>Cubane B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1–N1</td>
<td>Cu3–N5</td>
</tr>
<tr>
<td>Cu1–O5</td>
<td>Cu3–O11</td>
</tr>
<tr>
<td>Cu1–O4</td>
<td>Cu3–O10</td>
</tr>
<tr>
<td>Cu2–N1</td>
<td>Cu4–N3</td>
</tr>
<tr>
<td>Cu2–O6</td>
<td>Cu4–O10</td>
</tr>
<tr>
<td>Cu2–O1</td>
<td>Cu4–O7</td>
</tr>
<tr>
<td>Cu1–O3</td>
<td>Cu2–O4</td>
</tr>
<tr>
<td>O3–Cu2–O4</td>
<td>Cu2–O12</td>
</tr>
<tr>
<td>Cu1–O3</td>
<td>Cu2–O4</td>
</tr>
<tr>
<td>Cu2–O4</td>
<td>Cu4–O10</td>
</tr>
</tbody>
</table>

Symmetry labels: 2/C0

O3–Cu2–O4: 88.28(6) O10–Cu4–O9: 88.59(7)

The magnetic susceptibility expression for such a system can be obtained by means of the following zero-field spin Hamiltonian (Eq. (1)).

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\[
\mathcal{H} = -J_{1A}(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_3 \cdot \hat{S}_4) - J_{2A}(\hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_3) - J_{3A}(\hat{S}_1 \cdot \hat{S}_6 + \hat{S}_2 \cdot \hat{S}_5) - J_{4A}(\hat{S}_1 \cdot \hat{S}_6 + \hat{S}_2 \cdot \hat{S}_5)
\]

The magnetic susceptibility expression for such a system can be obtained by means of the following zero-field spin Hamiltonian (Eq. (1)).

Under this approach the magnetic properties of [Cu(L)]₄·4H₂O should be analyzed by means of the following zero-field spin Hamiltonian (Eq. (1)).

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\]
between the $d_{x^2}$ and $d_{y^2}$ orbitals, that provide a very poor overlap between the orbitals bearing the unpaired electrons that usually lead to ferromagnetism [51]. $J_{1B}$ and $J_{2B}$ indicate a weak antiferromagnetic coupling among the copper(II) ions in cubane B. The values obtained also fall in the expected range [50] and in particular they are very close to those found by Walz and co-workers for a compound with very similar structural parameters [52]. $J_{1A}$ and $J_{2A}$ are antiferromagnetic as expected from their large Cu–O–Cu angles, also they are stronger in intensity than $J_{1B}$ and $J_{2B}$, following the general trend that predicts stronger antiferromagnetic couplings for larger Cu–O–Cu bridging angles [50]. The $g$ values are higher than expected; they may be contaminated by some correlations in the evaluation of $J_{2A}$ which has also a slightly higher value than expected. However, in general, the result of the magnetic analysis is in agreement with recent previous studies for this class of compounds [50].

4. Conclusions

The tetranuclear open-cubane complex [Cu(L)$_4$]$_4$ with an in-situ formed dinicotinato 2-hydroxy-3-methoxybenzylidene)benzohydrazide ligand crystallizes as the stable tetrahydrate [Cu(L)]$_4$$_4$4H$_2$O with two symmetry-independent S$_2$-symmetrical tetranuclear molecules in a $Z = 2$ structure. Both open Cu$_4$O$_4$ cubanes have significant differences that lead to a system with 6 different magnetic exchange pathways, three each between the Cu(II) atoms in cubane A and cubane B, respectively. One of these exchange pathways in each cubane is ferromagnetic, the other two are antiferromagnetic. All of them have been determined and their nature and intensity show a full agreement with the conclusions of previous previous magnetostuctural studies [50].

Acknowledgments

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Appendix A. Supplementary material


References