Synthesis and Structural Characterization of a Double Helical Dinuclear Copper(II) Complex With Tetradeutate Biacetyl Bis(benzoylhydrazone)

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Abstract

The reaction of tetradeutate hydrazone ligand H2babh with Cu(CH3COO)2 in methanol solvent leads to the formation of the mono-nuclear complex [Cu(babh)]. However, on being dissolved in dichloromethane solvent and on addition of ethanol solvent, a dinuclear complex of [Cu2(μ1,3-babh)2(C2H5OH)2] is obtained. The X-ray crystallography indicates that the dinuclear helical complex formation is caused due to the unsymmetrical twisting of the H2babh ligand. One oxygen and two nitrogen atoms from the ligand and one oxygen atom from the other ligand coordinate to each copper(II) center. Both the copper(II) centers in a dinuclear unit are penta-coordinate with a slightly distorted square pyramidal geometry. The IR spectra of mono- and dinuclear copper(II) complexes have different bands. The absorption spectra of mono- and di-nuclear complexes are quite similar in methanol solvent. However, the electronic absorption spectra of the two complexes are basically different in the solid state.

Keyword: Copper(II) complex; Hydrazone ligand; Dinuclear; Helical complex; Unsymmetrical twisting

1. Introduction

The design and construction of multinuclear transition metal complexes have attracted great interest in recent years because of the role that these metal systems play in a large number of biological processes, molecular magnetic materials, and their variety of structures and interesting properties.1–8 Among them, the synthesis and study of multinuclear copper(II) complexes has attracted considerable interest due to exploration of their structures, and also because the function of copper(II) centers in many important biological processes.8–12

There are a variety of strategies for synthesizing homo- and hetero-multinuclear complexes. The bridging ligands such as halides, pseudo-halides, oxalate, sulfate, etc. have been widely used in the synthesis of multinuclear complexes.13–16 In the self-assembly process, the constituent ligands play important roles in the synthesis of multinuclear copper(II) compounds. The most common ligands used for the construction of these complexes are especially Schiff base ligands, which contain potentially bridging phenoxo or hydroxo oxygen donor atoms.11,17,18
are helicity processes. Helical structures are often formed via a self-assembly process by ligands that connect two or more bidentate coordinating units with appropriate spacers and two or more metal ions.

Herein, we have described the synthesis and crystal structures of a dinuclear copper(II) complex double helicates with the tetradentate \( \text{N}_2\text{O}_2 \)-donor ligand biacetyl bis( benzoylhydrazone), \( \text{H}_2\text{babh} \) (Scheme 1). Also, the structure of the complex is compared with mono- and di-nuclear copper(II) complexes that have been previously reported with the \( \text{H}_2\text{babh} \) ligand.

### 2. Experimental

#### 2.1. Materials

The tetradentate hydrazone ligand, \( \text{H}_2\text{babh} \), and the mononuclear complex \([\text{Cu}(\text{babh})] \) were prepared as previously reported elsewhere by others. All chemicals were used as supplied by Merck and Fluka without further purification.

#### 2.2. Physical Measurements

Infrared spectra were taken with an Equinox 55 Bruker FT-IR spectrometer using KBr pellets in the 400–4000 cm\(^{-1} \) range. Absorption spectra were determined in the solvent methanol using a GBC UV-Visible Cintra 101 spectrophotometer in the range of 200–800 nm. Elemental analyses \( \text{(C, H, N)} \) were performed using a CHNS-O 2400II PERKIN-ELMER elemental analyzer.

#### 2.3. X-ray Crystallography

Diffraction images were measured at 150 K on a Nonius Kappa CCD diffractometer using Cu \( K\alpha \) with graphite monochromator \( (\lambda = 1.54184 \ \text{Å}) \). Data was extracted using the CrysAlis PRO Agilent Technologies. The structures were solved by direct methods with the use of SIR92 and refined on \( F^2 \) by full matrix least-squares techniques using the CRYSTALS program package. Crystallographic details are summarized in Table 1.

### 3. Results and Discussion

#### 3.1. Characterization of the Complex

A comparison of the IR spectra of the free ligand and mononuclear, \([\text{Cu}(\text{babh})] \), and dinuclear, \([\text{Cu}_2(\mu_1,3\text{-babh})_2(\text{C}_2\text{H}_5\text{OH})_2]\), complexes indicates that the ligand is coordinated to the copper(II) center. The IR spectrum of the \( \text{H}_2\text{babh} \) ligand shows bands at 1600 and 1651 cm\(^{-1} \), which are assigned as \( \nu(C=N) \) and \( \nu(C=O) \), respectively. In the IR spectra of the \( \text{H}_2\text{babh} \) ligand, shows bands at 1600 and 1651 cm\(^{-1} \), which are assigned as \( \nu(C=N) \) and \( \nu(C=O) \), respectively. In the IR spectra of the \( \text{Cu}(\text{babh}) \) complex, the strong bands at 1613 and 1619 cm\(^{-1} \) are assigned to \( \nu(C=N) \), respectively. The IR spectra of the \( \text{Cu}(\text{babh}) \) complexes have different bands at the range of 1000–1600 cm\(^{-1} \). The electronic absorption spectra were recorded for copper(II) complexes in various solvents, methanol, ethanol, dichloromethane and \( \text{N},\text{N}'\)-dimethylformamide (DMF) in the visible and UV regions. The absorption spectra of mono- and di-nuclear \( \text{Cu}(\text{II}) \) complexes are quai-

#### Table 1. Crystallographic data of \([\text{Cu}_2(\mu_1,3\text{-babh})_2(\text{C}_2\text{H}_5\text{OH})_2]\) complex

| Compound | \([\text{Cu}_2(\mu_1,3\text{-babh})_2(\text{C}_2\text{H}_5\text{OH})_2]\) |
|----------|---------------------------------------------------|
| Chemical formula | \( \text{C}_{40}\text{H}_{44}\text{Cu}_2\text{N}_8\text{O}_6 \) |
| Formula weight | 859.93 |
| Temperature (K) | 150 |
| Space group | Triclinic, \( \text{P}^\overline{1} \) |
| \( Z \) | 2 |
| Unit cell dimensions | |
| \( a (\text{Å}) \) | 8.4016(4) |
| \( b (\text{Å}) \) | 15.5626(5) |
| \( c (\text{Å}) \) | 16.3803(7) |
| \( \alpha (°) \) | 101.944(3) |
| \( \beta (°) \) | 104.296(4) |
| \( \gamma (°) \) | 102.394(3) |
| \( V(\text{Å}^3) \) | 1949.09(15) |
| \( F(000) \) | 892 |
| \( D_{\text{calc}} (\text{g cm}^{-3}) \) | 1.465 |
| \( \mu (\text{mm}^{-1}) \) | 1.82 |
| Measured reflections | 21666 |
| Independent reflections | 7466 |
| \( R(\text{int}) \) | 0.032 |
| Observed reflections | 6388 |
| \( R[F^2 > 2\sigma(F^2)] \) | 0.035 |
| \( wR(F^2) \) (all data) | 0.089* |

* \( w = 1/(\sigma^2(F^2) + (0.04P)^2 + 1.32P) \), where \( P = (\max(F^2,0) + 2F^2)/3 \)
te similar in studied solvents. The spectra exhibit one maximum at 642 nm which can be attributed to the d–d transition. Two bands at 446 and 274 nm are due to intraligand π–π* and n–π* transition, respectively. Therefore, we can conclude that the dinuclear copper(II) complex in the solvent is converted to mononuclear complex.

The electronic spectra of the complexes were recorded also in the solid state. The electronic absorption spectra of the two complexes are basically different in the solid state (Fig. 1). Both complexes exhibit a band in the region 265 nm due to intraligand transition. The broad band is centered at 410 nm for the dinuclear complex and two bands at 547 and 423 nm for the mononuclear complex are attributed to LMCT transitions. Therefore, we can conclude that the dinuclear copper(II) complex in the solvent is converted to mononuclear complex.

The single crystal X-ray diffraction data for the complex is listed in Table 1. A structural representation and selected interatomic distances and angles of the complex are presented in Fig. 2 and Table 2. The complex crystallizes in the triclinic space group P1. The asymmetric unit consists of two Cu(II) ions, two babh$^{2-}$ ligands, and two coordinated ethanol molecules (Fig. 2). There is disorder in the packing of one of the ethanol species over two positions have relative occupancies which refined to 57%:43%.

![Fig. 1. The solid state electronic spectra of [Cu(babh)] (———) and [Cu$_2$(μ$_{1,3}$-babh)$_2$(C$_2$H$_5$OH)$_2$] (- - - - -).](image)

3. 2. Description of Crystal Structure of the Complex

The single crystal X-ray diffraction data for the complex is listed in Table 1. A structural representation and selected interatomic distances and angles of the complex are presented in Fig. 2 and Table 2. The complex crystallizes in the triclinic space group P1. The asymmetric unit consists of two Cu(II) ions, two babh$^{2-}$ ligands, and two coordinated ethanol molecules (Fig. 2). There is disorder in the packing of one of the ethanol species over two positions have relative occupancies which refined to 57%:43%.

![Fig. 2. The structure of the [Cu$_2$(μ$_{1,3}$-babh)$_2$(C$_2$H$_5$OH)$_2$] complex, with labelling of selected atoms. Anisotropic displacement ellipsoids exhibit 30% probability levels. Hydrogen atoms are drawn as circles with small radii](image)

| Bond Lengths (Å) and Angles (°) in [Cu$_2$(μ$_{1,3}$-babh)$_2$(C$_2$H$_5$OH)$_2$] complex |
|---------------------------------|-----------------|-----------------|-----------------|
| Cu1–O1                          | 2.0402(15)      | O1–Cu1–O5       | 90.41(6)        |
| Cu1–O4                          | 1.9062(15)      | O1–Cu1–O4       | 92.04(6)        |
| Cu1–O5                          | 2.2883(16)      | O1–Cu1–N2       | 94.29(7)        |
| Cu1–N2                          | 1.9212(18)      | O2–Cu1–O5       | 78.78(6)        |
| Cu1–N3                          | 2.0604(18)      | O2–Cu1–N2       | 157.40(7)       |
| Cu2–O2                          | 1.9041(15)      | O3–Cu2–O6       | 87.98(6)        |
| Cu2–O3                          | 2.0568(15)      | O3–Cu2–N7       | 172.20(7)       |
| Cu2–O6                          | 2.2644(17)      | O6–Cu2–N7       | 98.26(7)        |
| Cu2–N6                          | 1.6213(18)      | O1–Cu1–N3       | 157.40(7)       |
| Cu2–N7                          | 2.0658(19)      | O3–Cu2–O6       | 93.94(7)        |
| Cu1N7                           | 2.7494(18)      | O3–Cu2–N7       | 156.91(7)       |
| Cu2N3                           | 2.7254(19)      | O2–Cu2–N6       | 172.20(7)       |
| C1–O1                           | 1.289(3)        | N2–N1–C1        | 108.21(18)      |
| C1–N1                           | 1.331(3)        | N2–N1–C1        | 113.09(19)      |
From the crystal structure and based on the bond lengths between the copper and coordinating atoms, it has been found that in the complex, two copper(II) centers are penta-coordinate with a N₂O₃ donor. Coordination geometry about each copper(II) ion is essentially a distorted square pyramid with one oxygen atom and two nitrogen atoms from the ligand, one oxygen atom from ethanol molecule and one oxygen atom from the other ligand of the dinuclear complex. The four equatorial positions are occupied by two nitrogen atoms (N2 and N3), one oxygen atom (O1) from one hydrazone ligand and the fourth position is occupied by the oxygen atom (O4) of the other ligand of the dinuclear complex. The axial position is occupied by one oxygen atom (O5) of the ethanol molecule. The axial Cu–O5 bond is 2.2883(16) Å which is longer than the equatorial Cu–O ones [1.9062(15) and 2.0402(15) Å], and consistent with analogous systems observed in the literature.²⁷–³⁰ The coordination spheres of the copper(II) ions in the complex are best described as a distorted square pyramidal according to the Addison parameter τ values of 0.27 (for Cu1) and 0.25 (for Cu2). The parameter τ is defined as 

\[ \tau = \frac{\alpha - \beta}{60}, \quad \alpha > \beta, \]  

where \( \alpha \) and \( \beta \) are the largest angles; with \( \tau = 1 \) for a regular trigonal bipyramid and \( \tau = 0 \) for a regular square pyramid.³¹ The copper(II) ion is displaced from the basal plane of N₂O₂ by 0.116 Å towards the apical oxygen atom. The Cu–Cu distance is 3.149 Å.

The comparison of C–O and C–N bond lengths of the hydrazone ligand is a useful techniques in identifying the mode of bonding of the ligand (keto or enol) to the metal ion.³² The C₁–O₁ and C₈–O₄ bond lengths of complex (1.289(3) and 1.283(3) Å, respectively) and C₁–N₁ and C₈–N₈ (1.331(3) and 1.314(3) Å, respectively) are similar and are in good agreement with analogous Cu(II) complexes observed in the literature where a hydrazone ligand coordinates to the Cu(II) center in its iminolate form.²,¹³,¹⁴,²⁵,³³

The average of Cu–O bond lengths in the dinuclear complex (1.978 Å) is very similar to the corresponding distances in previously reported mononuclear copper(II) complex (1.978 Å).²² However, the average of Cu–N bond lengths in the dinuclear complex (1.992 Å) is longer than the corresponding bonds in mononuclear copper(II) complex (1.918 Å).²² The differences are perhaps due to the difference in the coordination modes and the twisting of ligand babh²– along the –C=N–N=C– single bond for the coordination of the ligand to the copper(II) ions in the formation of [Cu₂(μ₁,₃-babh)₂(C₂H₅OH)₂].

The dinuclear helical complex formation is caused by the unsymmetrical twisting along the –C=N–N=C– single bond and two nitrogen atoms and one oxygen from each ligand are coordinated to each copper(II) center. In the dinuclear complex reported by Pal²¹ the complex was formed by symmetrical twisting around the central C–C single bond in fragment of =-(CH₃)C–C(CH₃)=. One nitrogen atom and one oxygen from each ligand of babh was coordinated to each copper(II) center.

The single crystal X-ray analyses indicate the presence of non-covalent interactions between the nitrogen atom of the imine group of the ligand and the other copper(II) center in the dinuclear complex. The distance between Cu1 and Cu2 centers and the N atoms of the imine group is 2.750(1) Å for Cu1–N7 and 2.725(1) Å for Cu2–N3, respectively, which suggests a weak non-covalent interaction.

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**Table 3.** Hydrogen bonding (Å) and angles (°) for [Cu₂(μ₁,₃-babh)₂(C₂H₅OH)₂] complex

| D–H···A | D–H | H···A | D···A | D–H···A | Symmetry code |
|--------|-----|-------|-------|--------|--------------|
| O₅–H₁···O₃ | 0.76(3) | 2.03(3) | 2.776(5) | 166(3) | x + 1, y, z |
| O₆–H₂···O₁ | 0.71(4) | 2.13(4) | 2.841(5) | 171(4) | x – 1, y, z |

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Fig. 3. Various hydrogen bonding interactions, O–H···O in [Cu₂(μ₁,₃-babh)₂(C₂H₅OH)₂] complex, other hydrogen atoms are omitted for clarity.
Dinuclear complexes are involved in intermolecular O5–H1···O3(x – 1, y, z) and O6–H2···O1(x + 1, y, z) hydrogen bonding interactions between coordinated ethanol molecules and the oxygen atoms of a neighboring babh2– ligands (Fig. 3). The details of the hydrogen bonding are given in Table 3.

4. Conclusion

The new homo-dinuclear complex [Cu2(μ1,3-babh)2(C2H5OH)2] has been synthesized and the crystal structure of the complex has been determined. Single-crystal X-ray diffraction indicate that the dinuclear helical complex formation was caused due to the unsymmetrical twisting of the ligand, N2O2 along the –C=N–N=C– single bond. Two nitrogen atoms and one oxygen from each ligand are coordinated to each copper(II) center. Two nitrogen atoms from the ligand, one oxygen atom from an ethanol molecule, and one oxygen atom from the other ligand of the dinuclear complex. The absorption spectra of mono- and di-nuclear complexes are quite similar in solvent. However, the electronic absorption spectra of two the complexes are basically different in the solid state.

5. Supplementary Material

The deposition numbers of the studied dinuclear complex is CCDC 1527221. These data can be obtained free-of-charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data-request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033.

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Povzetek

Reakcija štiriveznega hidrazonskega liganda H₂babh z Cu(CH₃COO)₂ v metanolu vodi do nastanka enojedrnega kompleksa [Cu(babh)]. Po raztapijanju v diklorometanu in ob dodatku etanola nastane dvojedrni kompleks [Cu₂(μ₁,₃-babh)₂(C₂H₅OH)₄]. Rentgenska kristalografija razkrije, da zaradi nesimetričnega zvijetja H₂babh liganda nastane dvojedrni kompleks z vijačno strukturo. En kisikov in dva dušikova atoma z liganda in en kisik z drugega liganda se koordinirajo na posamezni bakrov(II) center. Oba bakrova(II) centra v dvojedrni enoti sta pentakoordinirana z delno popaženo kvadratno-piramidalno geometrijo. IR spektra eno- in dvojedrnega bakrovega(II) kompleksa imata različne trakove. Absorpcijska spektra eno- in dvojedrnega kompleksa v metanolu sta zelo podobna, medtem ko se elektronska absorpcijska spektra obeh kompleksov v trdnem stanju delno razlikujeta.

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