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Synthesis, characterization and crystal structure of Cu(II) complex with a diimine-dioxime ligand, [Cu₂(LH)₂](ClO₄)₂. Influence of the weak Cu···O(perchlorate) interaction on the structure of the Cu₂N₂O₂ metallocycle

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Abstract: The diimine–dioxime ligand, 3,3'-(1,4-butanediyl-dinitrilo)bis-2-pentanone, 2,2'-dioxime (LH₂), containing a N₄ donor set was prepared by the Schiff base condensation of 2-hydroxyimino-3-pentanone and 1,4-diaminobutane in two ways: in a protic and in an aprotic solvent. A higher yield of the (LH₂) imine was obtained when the synthesis was performed using a protic solvent (C₂H₅OH) instead of aprotic benzene (78 and 30 %, respectively). The Cu(II) metal complex of diimine–dioxime was synthesized in CH₃OH from the perchlorate salt of LH₂ in a 1:1 mole ratio. The isolated complex was characterized by the elemental analysis, IR spectroscopy and cyclic voltammetry. The structure of [Cu₂(LH)₂](ClO₄)₂ was determined by single-crystal X-ray diffraction analysis. Comparison with structurally related diimine–dioxime Cu(II) complexes revealed the influence of a weak Cu···O(perchlorate) interaction on the geometry of the metallocycle.

Keywords: Cu(II) complex; weak interactions; supramolecular aggregates; diimine–dioxime ligand.

INTRODUCTION

Schiff bases are typically formed by the condensation of primary amines and aldehydes.^{1,2} Schiff base ligands containing strong donor sites, such as phenoxo oxygen atoms or imine nitrogen atoms, have been shown to exhibit a broad range of biological properties, including antifungal,^{3,4} antibacterial⁵ and antitumor^{6,7}

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activities. They are used as pigments and dyes, catalysts, polymer stabilizers, intermediates in organic synthesis⁸ and extractants for metal ions in solvent extractions.⁹ Schiff bases represent an important class of chelating agents with the capability of forming stable complexes with most transition metals.¹⁰

Transition metal complexes of polydentate Schiff base ligands, especially tetradentate Schiff bases, are applicable in catalysis and material chemistry,^{11,12} and played a significant role in various reactions for the enhancement of the yield and product selectivity.¹³ The Schiff base ligands readily form complexes with the transition metals.^{14–16} Recent studies have focused particularly on the development of new Schiff bases containing the diimine–dioxime functionality, a potential ligand for ⁶⁴Cu radiopharmaceuticals.¹⁷ These studies also included investigations of lipophilic, cationic copper(II) complexes of diimino–dioxime as potential positron emission tomography (PET) radiopharmaceuticals for imaging myocardial perfusion and multi-drug resistance in cancer.¹⁸ Of particular interest is the capability of the deprotonated diimine–dioximes to form bridges between metal ions giving rise to complexes of different nuclearity.¹⁹ These complexes are of current interest in connection with the ability of oximate bridges to mediate strong antiferromagnetic interaction between metal centers.²⁰ During complex formation, one of the oxime groups loses a proton and a hydrogen bond is formed between the two oxime groups. The strength of the hydrogen bond is dependent on the size of the metal ion, the length of the methylene linkage and chemical environment around the metal ion.²¹ A number of these studies were based on the analysis of the crystal structures and subsequent identification of the bonding and non-bonding interactions relevant for the explanation of the molecular and crystal properties.²²

A particular problem arises concerning the use of copper in the synthesis of metal complexes. Copper is known for its flexible coordination behavior associated with the capability to form weak bonds, a property termed “plasticity”.²³ This problem becomes more pronounced in the studies of weaker non-bonding interactions.²⁴ Detailed analysis of the copper environment followed by computational or database studies²⁵ may provide additional insight into the non-bonding contacts relevant for the properties of copper complexes. One of the ligands frequently used in the synthesis of copper complexes is the perchlorato group. As a ligand, the ClO₄[−] group may appear in various bonding arrangements, however its steric properties limit its coordinating ability in the presence of smaller potential ligands.²⁶ Recently the coordinating properties of ClO₄[−] bonded to Cu were studied.^{27,28} However, in most of the crystal structures, ClO₄[−] is present as a non-coordinated ion.

In the present study, the copper(II) complex of the 3,3′-(1,4-butanediyl-dinitrilo)bis-2-pentanone, 2,2′-dioxime ligand was chosen for study to enable comparison with the previously studied copper(II) complex^{29,30} of the closely related ligand with two methyl groups in place of the present two ethyl groups.

EXPERIMENTAL

General

All reagents obtained from commercial sources were of analytical grade and used without further purification. The infrared spectra were obtained using a FTIR BOMEM MB 100 Hartmann Braun Fourier transform infrared spectrometer. The samples were analyzed in the form of KBr pellets after removal of the liquid under high vacuum at a low temperature. Elemental analysis (C, H, N) of the samples were performed using a VARIO EL III elemental analyzer. The melting points (uncorrected) were determined on Mel-Temp melting point apparatus (Laboratory Devices Inc., USA).

The electrochemical experiments were performed using standard equipment for cyclic voltammetry measurements and a three electrode electrochemical cell, as described in detail previously, was used.^{31,32} Glassy carbon (Pine rotating disc electrode) served as the working electrode (only for the stationary measurements) and a gold wire was used as the counter electrode while a saturated calomel electrode (SCE) was the reference electrode. The glassy carbon electrode (surface area 0.500 cm²) was polished with diamond paste, cleaned with a mixture of 18 M Ω -water and sulfuric acid and further cleaned with 18 M Ω -water in an ultrasonic bath. The Cu(II) complex and the diimine–dioxime ligand containing a donor set of N₄ were examined in 0.05 M NaHCO₃. The complex is soluble in 0.05 M NaHCO₃ while ligand was dissolved in 1 mL of methanol before addition into the electrolyte. The methanol was electrochemically inactive under the described experimental conditions. Prior to the addition of the Cu(II) complex and ligand, the electrolyte was deoxygenated by purging with nitrogen. Cyclic voltammetry was performed at a sweep rate of 50 mV s⁻¹. The potential range applied was between -0.5 and 0.8 V. All the potentials are given vs. SCE. All the experiments were performed at room temperature.

Synthesis

2-Hydroxyimino-3-pentanone (KO) was synthesized as described earlier³³ in 75 % yield. The diimine–dioxime ligand, 3,3'-(1,4-butanediyl-dinitrilo)bis-2-pentanone, 2,2'-dioxime (LH₂), was prepared in two ways: in aprotic (benzene) and in protic (ethanol) solvents. The synthesis in benzene was realized using a previously described method³⁴ in 30 % yield. The synthesis and characterization of the ligand LH₂ in ethanol was described elsewhere³⁵ (78 % yield).

Synthesis of [Cu₂(LH)₂](ClO₄)₂. Copper(II) acetate monohydrate (110 mg, 0.625 mmol), suspended in 10 mL of CH₃OH was added to a hot CH₃OH suspension of the ligand LH₂ (175 mg, 0.625 mmol). The reaction mixture was then refluxed for 3 h. The reddish-brown product was isolated as the perchlorate salt by the addition of a saturated aqueous solution of NaClO₄. The reaction mixture was allowed to stand at room temperature for 3 days, when brown crystals were formed. The crystals were collected and dried in a desiccator. Crystals suitable for X-ray diffraction were grown by slow diffusion of a saturated aqueous solution of NaClO₄ into a methanolic solution of the product. Yield 68 %; mp: >225 °C explosive. Anal. Calcd. for C₂₈H₅₀Cl₂Cu₂N₈O₁₂: C, 37.84; H, 5.67; N, 12.61 %. Found: C, 37.67; H, 5.99; N, 12.38 %. Selected IR data (KBr, cm⁻¹): $\nu_{C=N}$ 1521.92 *m*, 1624.97 *w* (*m*, medium; *w*, weak).

Crystallography

Single-crystal X-ray diffraction data were collected on an Oxford Diffraction Gemini S four-circle diffractometer equipped with a Sapphire CCD detector, using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å) at room temperature. The data reduction was realized using the Oxford Diffraction program CRYCALISPRO.³⁶ Empirical absorption

corrections were applied using spherical harmonics implemented in the SCALE3 ABSPACK³⁶ scaling algorithm. The structure was solved by direct methods using the SIR92 program³⁷ as implemented in the WinGX program system.³⁸ One of the O atoms from the ClO₄ is disordered over two positions at 70 % and 30 % occupancy. All non-hydrogen atoms were refined anisotropically using SHELXL-97³⁹ by applying a full-matrix least-squares method based on F^2 , including all reflections. The hydrogen atoms were placed in the idealized positions and refined riding on their parent atoms. The geometrical calculations were performed using the programs PARST⁴⁰ and PLATON.⁴¹ The programs CAMERON,⁴² Mercury⁴³ and ORTEP⁴⁴ were employed for graphical presentations of the structure. The crystal data and refinement parameters are summarized in Table I.

TABLE I. Crystal data and structure refinement for [Cu₂(LH)₂](ClO₄)₂

Formula	C ₂₈ H ₅₀ Cl ₂ Cu ₂ N ₈ O ₁₂
Formula weight	888.74
Crystal system	Monoclinic
Space group	P21/n
<i>a</i> , <i>b</i> , <i>c</i> / Å	7.6214(2), 20.2174(6), 12.4894(3)
α , β , γ / °	90, 94.204(3), 90
<i>V</i> / Å ³	1919.25(9)
<i>Z</i>	2
<i>D</i> _{calc} / g cm ⁻³	1.538
μ (MoK α) / mm ⁻¹	1.315
Crystal size, mm	0.20 × 0.22 × 0.26
Temperature, K	293
λ (MoK α) / Å	0.71073
θ Range, °	3.4–29.1
Reflections collected	8595
Unique reflections	4399
Reflections observed, (<i>I</i> > 2 σ (<i>I</i>))	3013
<i>R</i> _{int}	0.024
Data / restraints / parameters	4399 / 0 / 246
Goodness-of-fit on F^2	0.940
Final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> 1 = 0.0371, <i>wR</i> 2 = 0.0870
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0620, <i>wR</i> 2 = 0.0918
Largest diff. peak and hole, e Å ⁻³	0.431 and –0.322

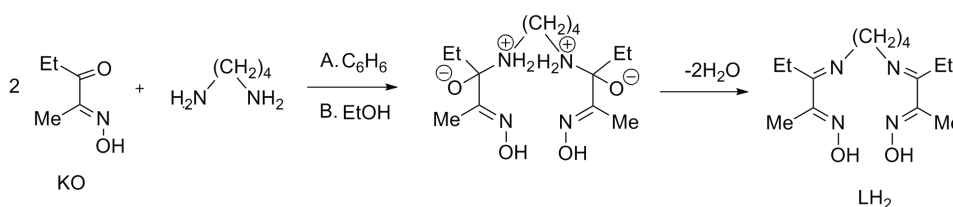
RESULTS AND DISCUSSION

Syntheses

The diimine–dioxime ligand (LH₂) and its Cu(II) complex were synthesized and characterized. In the present study, synthesis of a linear alkyl derivative of the diimine–dioxime ligand system was performed according to published procedures^{34,35} in two ways: in aprotic (A) and in protic (B) solvents (Scheme 1).

A higher yield of imine (78 %) was obtained when the synthesis was performed using the protic solvent (C₂H₅OH). In the case of the aprotic benzene, a poor yield of imine (30 %) was achieved. The synthesis of a Schiff base (imine)

is accomplished *via* the condensation reaction of a carbonyl compound with a primary amine.⁴⁵ In this addition–elimination reaction, a fast nucleophilic attack of the amine nitrogen on the carbonyl carbon is followed by the slow elimination of water. The synthesis of the Cu(II) complex was readily accomplished when the reaction was performed in CH₃OH. The IR spectrum of the ligand showed a $\nu(\text{C}=\text{N})$ peak at 1622 cm⁻¹ and the absence of a $\nu(\text{C}=\text{O})$ peak at around 1700 cm⁻¹, which is indicative of a Schiff base condensation. After formation of the complex, two C=N bonds are discernable. The two $\nu(\text{C}=\text{N})$ were observed at lower frequencies than that in the free ligand, in accordance with coordination at the oxime and imine nitrogens.



Scheme 1. Synthetic route for the ligand LH₂ in aprotic (A) and protic (B) solvents.

Electrochemical behavior of [Cu₂(LH)₂](ClO₄)₂

The cyclic voltammogram of glassy carbon electrode in 0.05 M NaHCO₃ (dashed line) and after the addition of Cu(II) complex (full line) are presented in Fig. 1.

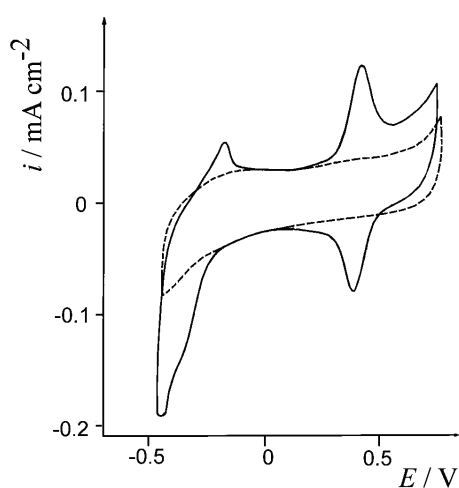


Fig. 1. Cyclic voltammogram of a glassy carbon electrode in 0.05 M NaHCO₃ (dashed line) and after the addition of the Cu(II) complex, concentration 2.0×10^{-3} mg·cm⁻³ (full line), sweep rate: 50 mV·s⁻¹. Only the first sweep was recorded.

In Fig. 1, the reversible oxido-reduction processes of the Cu(II) complex can be observed at 0.45 V, while the reduction reaction occurred between -0.3 V and

–0.5 V. It could be supposed that the observed electrochemical processes should be attributed to reactions on the reactive groups of the ligand. In order to check this assumption, under the same experimental conditions, the LH₂ ligand containing a donor set of N₄ was investigated. It was shown that the diimine–dioxime ligand exhibits the same reversible oxido reduction processes at 0.45 V. Thus, the Cu(II) complex is electrochemically characterized by the reversible oxido reduction processes at 0.45 V, which proceeds on the ligand. Additionally, the Cu(II) complex exhibits the beginning of an additional oxidation reaction at 0.7 V, which could be attributed to the central copper atom.^{46,47} Moreover, a very apparent reduction reaction was observed between –0.3 and –0.5 V and small anodic peak at –0.30 V, which could be attributed to the interaction of central copper atom with the ligand. In Fig. 1, only the first sweep is shown because the decreases in the peak current values during sweeping were negligible.

Crystal structure analyses

In the complex, Cu(II) is five coordinated by the four imine nitrogen atoms of LH[–] and the oximate oxygen from the neighboring cationic complex. Selected bond lengths and angles are given in Table II.

TABLE II. Selected bond lengths (Å) and angles (°); symmetry code: $i = 1-x, -y, 1-z$

Cu1–O1 ^{<i>i</i>} 2.318(2)	N1–C1 1.288(3)	N1–Cu1–N2 80.54(8)	O1 ^{<i>i</i>} –Cu1–N3 92.23(7)
Cu1–N1 1.954(2)	N4–C4 1.281(3)	N1–Cu1–N3 174.26(9)	O1 ^{<i>i</i>} –Cu1–N4 96.21(7)
Cu1–N2 1.970(2)	N2–C2 1.277(3)	N1–Cu1–N4 94.52(9)	O1 ^{<i>i</i>} –Cu1–O4 174.71(8)
Cu1–N3 1.992(2)	N2–C5 1.464(3)	N2–Cu1–N3 103.13(8)	O4–Cu1–N1 90.23(8)
Cu1–N4 1.977(2)	N3–C8 1.473(4)	N2–Cu1–N4 153.98(9)	O4–Cu1–N2 75.98(9)
Cu1–O4 2.947(3)	N3–C3 1.275(4)	N3–Cu1–N4 80.25(9)	O4–Cu1–N3 86.43(9)
O1–N1 1.341(2)		O1 ^{<i>i</i>} –Cu1–N2 109.31(7)	O4–Cu1–N4 78.53(8)
O2–N4 1.378(3)		O1 ^{<i>i</i>} –Cu1–N1 90.68(7)	Cu1–O1–Cu1 ^{<i>i</i>} 97.76(5)

Two cationic fragments related by a center of inversion are assembled into binuclear units with the Cu(II) centers bridged by deprotonated oxime fragments (Fig. 2).

Similar features were previously observed in structurally related oximate-bridged dinuclear copper(II) complexes.²⁰ The pentacoordinate geometry can be described using the distortion parameter τ ,⁴⁸ where $\tau = 1$ corresponds to an ideal trigonal bipyramid and $\tau = 0$ to an ideal square pyramid. According to the trigonality index $\tau = 0.34$ for the title compound, the coordination geometry around a Cu(II) ion could be described as a severely distorted square pyramid. The basal plane is formed by N1, N2, N3 and N4 atoms, and the metal ion deviates by 0.24 Å from this plane, towards the apical positions occupied by oxime oxygen O1. The intra-molecular Cu⋯Cu separation is 3.9424(4). In order to gain more insight into the structural features of the title compound **I**, the obtained results

were compared with those for similar crystal structures of Cu complex cations containing a diimine–dioxime ligand and $(\text{ClO}_4)^-$ as the counter ion, *i.e.*, the two polymorphs of the Cu(II) complex of the deprotonated anion of 3,3'-(1,4-butanediyl-dinitrilo)bis-2-pentanone, 2,2'-dioxime (**II**),^{29,30} and the Cu(II) complex with a thio-oxime ligand (**III**)⁴⁹ (Scheme 2).

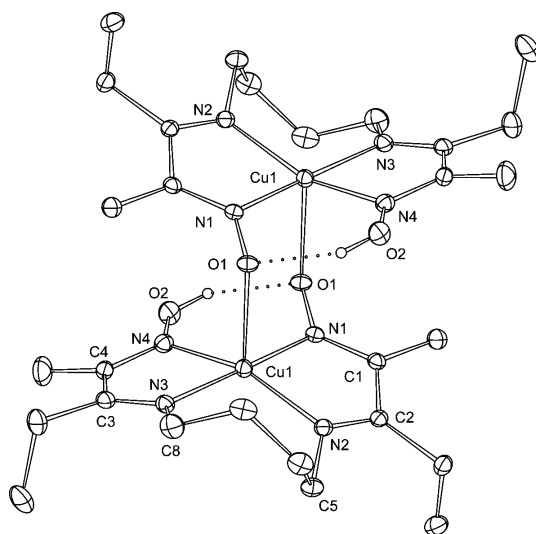
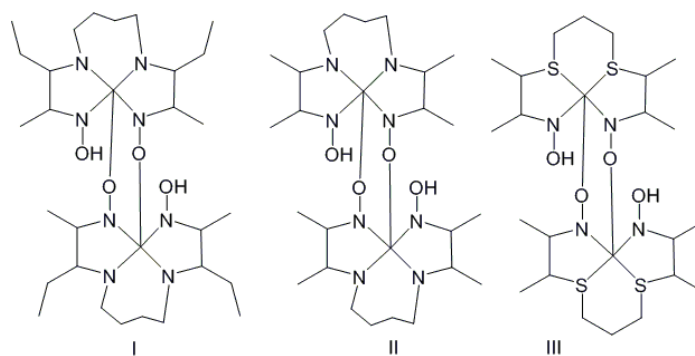


Fig. 2. Molecular diagram and atom numbering scheme of $[\text{Cu}_2(\text{LH})_2]^{2+}$. Methyl and methylene hydrogens are excluded for clarity. Intramolecular O–H...O hydrogen bonds are depicted by dotted lines.



Scheme 2. Structural formulas of the cationic complexes used for comparison.

The three complexes differ in the presence of an ethyl instead of a methyl substituent at the five-membered chelate ring in **I**, and the presence of a six-membered chelate ring and sulfur instead of nitrogen in the diimine–dioxime ligand in **III**. Comparison of geometric parameters of **I**, **II** and **III** indicate similarity of the $\text{Cu}_2\text{O}_2\text{N}_2$ ring conformation and the shape of the coordination polyhedron in all three complexes. The overlay of the three solid state structures presented in Fig. 3 illustrates their similarity.

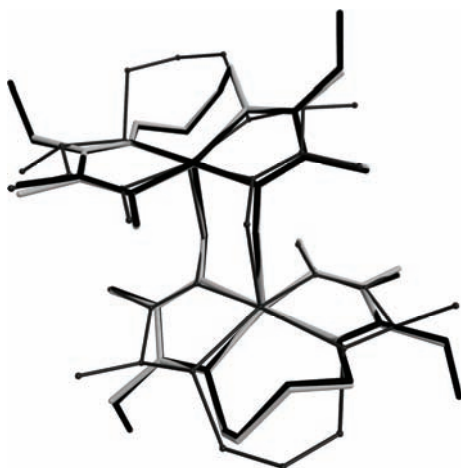


Fig. 3. Overlay of the solid-state structures of **I** (black), **II** (light grey) and **III** (dark grey, thin line).

Although the overall structures of **I**, **II** and **III** are similar, subtle differences in the geometry of the metallocycle were observed. These differences are caused mainly by differences in the Cu–O1 bond (Fig. 2). In **I** and **III**, these Cu–O bonds are 2.318(2) and 2.293 Å, respectively, which is longer than 2.266/2.262 Å found in the two polymorphs of **II**. While these differences in the axial Cu–O bonds could be attributed to the “plasticity”²³ of the copper coordination sphere, it is interesting to examine the possible influence of the closest perchlorato fragment on these bonds. In the crystal structures of **I** and **III**, the closest perchlorato oxygen is at Cu–O distances of 2.947(3) and 2.907 Å, respectively. These are on the borderline of values that have been reported for a semi-coordinated perchlorato group.^{50,51} In the crystal structure of **II** however, the closest perchlorato oxygen is at a rather larger distance of 3.767/3.766 Å and cannot be considered as semi-coordinated to Cu. If the presence of the semicoordinative bond Cu–O(perchlorate) *trans* to the Cu–O(oximate) bond is taken into account, the elongation of the Cu–O bonds in **I** and **III** relative to **II** could be attributed to the *trans* influence of the weakly coordinated perchlorato oxygen. The nearest intermolecular Cu···Cu separation in **I** is 7.621(5) Å. This is longer than the corresponding values of 6.484/6.480 and 6.016 Å found in **II** and **III**, respectively. Bearing in mind the overall similarity of these compounds (Fig. 3), this difference could be attributed to the difference in the molecular volume, caused mainly by the presence of the additional methyl groups in the molecule of the title compound. This complex exhibits an intramolecular hydrogen bond (Fig. 2) between *cis* oxime groups with an O···O distance of 2.593(3) Å, H···O = 1.83 Å and O–H···O angle of 154°. The role of O1 as an acceptor of a hydrogen bond is associated with the different geometry of two N–O bonds. Both the N1–O1 and N1–Cu1 bonds are shorter than the N4–O2, and N4–Cu1 bonds, respectively. This finding implies more multiple bond character in the fragment O1–N1–Cu1,

relative to O2–N4–Cu1. Bearing in mind the association of molecules in the solid state, it is interesting to note the lack of strong hydrogen bonding donors. There is only one strong donor O2–H, which is involved in the intradimer hydrogen bond to O1 (Fig. 2). Due to steric requirements, it is highly unlikely that the O2–H bond could be involved in additional, intermolecular, contacts. Hence, it was anticipated that intermolecular contacts between the C–H donors and perchlorate oxygens would govern the association of molecules in the crystal. Inspection of the intermolecular geometry confirms that the ClO₄[−] anions participate in weak hydrogen bonds in the cationic complex through C–H⋯O interactions. Fig. 4 illustrates the role of the weak Cu–O(perchlorate) interaction and the C–H⋯O contacts (Table III) in the packing of molecules in the crystal structure.

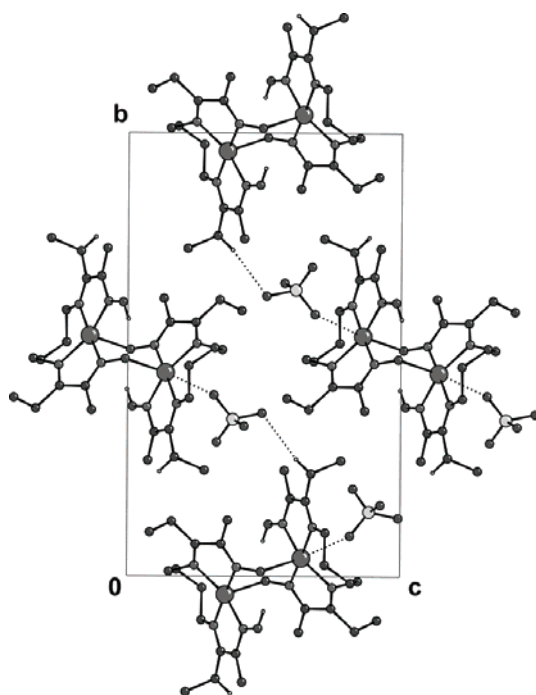


Fig. 4. Part of the crystal structure showing the contacts relevant for the association of molecules in the crystal structure of [Cu₂(LH)₂](ClO₄)₂. Hydrogen atoms not involved in the non-bonding contacts have been excluded for clarity.

TABLE III. Geometry of the hydrogen bonds; symmetry code: $i = x-1/2, -y+1/2, +z-1/2$

D–H⋯A	H⋯A / Å	D–H⋯A / °
O2–H1⋯O1	1.83	154
C13–H5⋯O61 ⁱ	2.67	171
C12–H36⋯O6 ⁱ	2.67	145

CONCLUSIONS

The complex [Cu₂(LH)₂](ClO₄)₂ was prepared by reaction of copper(II) acetate monohydrate and 3,3'-(1,4-butanediyl-dinitilo)bis-2-pentanone, 2,2'-dioxime

(LH₂) in CH₃OH, followed by the addition of NaClO₄. The compound was characterized by elemental analysis, IR spectroscopy, cyclic voltammetry and single-crystal X-ray crystallography. The crystal structure consists of centrosymmetric [Cu₂(LH)₂]²⁺ and perchlorato anions. The copper(II) atom is in a distorted square-pyramidal coordination with four imine-nitrogen atoms comprising the basal plane and the bridging oximate-oxygen from the other half of the dimer in the axial position. During complex formation, one oxime proton is lost, and a hydrogen bond between the two oxime groups of the same ligand is formed. Comparison with structurally related diimine–dioxime complexes indicates that the geometry of the metallocycle could be influenced by the presence of a weakly coordinated perchlorato anion.

SUPPORTING INFORMATION

CCDC 881203 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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ИЗВОД

СИНТЕЗА, КАРАКТЕРИЗАЦИЈА И КРИСТАЛНА СТРУКТУРА [Cu₂(LH)₂](ClO₄)₂. УТИЦАЈ СЛАБЕ Cu···O(ПЕРХЛОРАТО) ИНТЕРАКЦИЈЕ НА СТРУКТУРУ Cu₂N₂O₂ МЕТАЛОЦИКЛА

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Лиганд 3,3'-(1,4-бутандиил-динитрило)бис-2-пентанон, 2,2'-диоксим (LH₂), синтетисан је у реакцији 2-хидроксиимино-3-пентанона и 1,4-диаминобутана. Утврђено је да постоји разлика у приносу у зависности од поларности растварача. Када се реакција одиграва у етанолу принос је 78 %, а уколико се користи бензен принос је 30 %. Реакцијом бакар(II)-ацетата и лиганда LH₂ добијен је бинуклеарни центросиметрични комплекс чија је формула [Cu₂(LH)₂](ClO₄)₂. Једињење је окарактерисано елементалном анализом, инфрацрвеном спектроскопијом и цикличном волтаметријом. Структура комплекса у чврстом стању је одређена применом метода рендгенско–структурне анализе на монокристалу. Поређење кристалне структуре добивеног једињења са структурно сличним бакар(II) комплексима указује на утицај слабе Cu···O(перхлорато) интеракције на структурна својства Cu₂O₂N₂ металоцикла.

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