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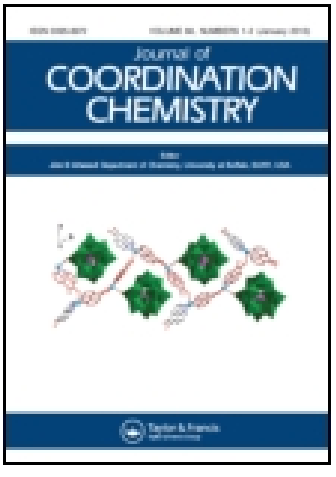

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Synthesis, crystal structure, and antimicrobial activity of bis((2-(2-aminoethyl)imino-3-butanone oxime)copper(II) perchlorate

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Synthesis, crystal structure, and antimicrobial activity of bis ((2-(2-aminoethyl)imino-3-butanone oxime)copper(II) perchlorate

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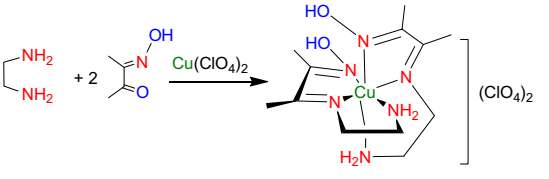

Copper(II) complex of an unsymmetrical tridentate ligand containing oxime, imine, and amine donors was synthesized with a condensation between diacetylmonoxime and ethylenediamine in the presence of copper(II) perchlorate. The complex is characterized by elemental analysis, IR, UV–vis, molar conductance, thermogravimetry, and single-crystal X-ray diffraction. The cation consists of two tridentate 2-(2-aminoethyl)imino-3-butanone oxime with coordination sphere of CuN_6 type. The geometry around copper(II) is distorted octahedral with two amine donors, two imine, and two nitrogens of the oxime. Photoluminescence reveals that the complex exhibits strong fluorescent emission in acetonitrile at room temperature. The antibacterial activity of the complex was also studied.

Keywords: Copper(II) complex; Crystal structure; Tridentate ligand; Synthesis; Imine oxime; Antibacterial activity

1. Introduction

Many Schiff bases, containing substituted oxime, have been synthesized, characterized, and used in coordination with transition metal ions because of their biological and structural importance arising from specific and selective reactions with metal ions [1, 2]. A number of articles have appeared dealing with synthesis, structure, and magnetic properties of oxime-containing complexes [3–6]. One reason for current interest in oxime metal complexes is

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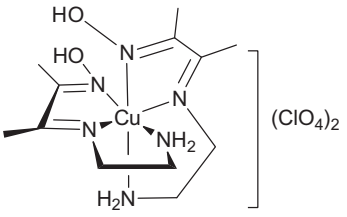

Scheme 1. The complex under study.

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the ability of oximes to coordinate in different modalities to metals as well as the easy tunability of their properties by alteration of the substituents [7, 8]. Due to biological activity of oxime metal complexes [9], copper(II) complexes with oxime-containing ligands have been used as models for many important biological processes [10–13], as well as semiconducting properties [14]. In this article, we report synthesis and structure, physical properties, and antibacterial activity of a copper(II) complex of an unsymmetrical tridentate imino-oxime ligand, $[Cu(L)_2](ClO_4)_2$, as shown in scheme 1.

2. Experimental

2.1. *Reagents and apparatus*

Ethylenediamine (Merck), diacetylmonoxime (Aldrich), and $Cu(ClO_4)_2{\cdot}6H_2O$ (Fluka) were used as received. Infrared spectrum (potassium bromide disk) was recorded using a Bruker FT-IR instrument. The electronic absorption spectrum was measured using a Cecil 5000 model UV–vis spectrophotometer. Emission spectra were obtained on a Spex Flurolog Fl 221 with a cooled photomultiplier R928 using DM 3000 version 3.3 SPEX Inc. software. Elemental analyses were performed on a LECU 600 CHN elemental analyzer. Absolute metal percentage was determined by an atomic absorption-flame spectrometer. Crystallographic analysis of complex: a single crystal was mounted on a Nonius Kappa-CCD area detector diffractometer (Mo Kα $\lambda = 0.71073$ Å). Data reduction, including the absorption correction, was performed with the Denzo software package [15]. The structure was solved using direct methods (SHELXS97) and refined on F^2 using the SHELXS97 software [16]. Hydrogens of NH_2 and OH were found in difference Fourier synthesis. Crystal, data collection, and refinement parameters are given in table 1. *Caution! Perchlorate salts are potentially explosive and should be handled with appropriate care*.

2.2. *Synthesis of complex*

To a mixture of diacetylmonoxime (2.2 g, 2.0 mM) and ethylenediamine (0.06 mL, 1.0 mM) in ethanol (50%, 10 mL), $Cu(ClO_4)_2{\cdot}6H_2O$ (370 mg, 1.0 mM) was added. The reaction mixture was refluxed for 2 h. During the heating, a dark green solid precipitated. After cooling the reaction mixture to room temperature, the solid was separated by filtration and then crystallized from hot methanol, followed by slow cooling to room temperature which yielded 390 mg (71%) of the desired compound as green needles. Anal. Calcd for

Table 1. Crystal data and refinement parameters for the complex.

Empirical formula; (formula weight)	$C_{12}H_{26}Cl_2CuN_6O_{10}$; (548.83)
Color	Needle, green
Temperature	150(1) K
Wavelength	0.71073 Å
Crystal system; space group	Monoclinic; *C*2/*c*
Unit cell dimensions	0.10 × 0.06 × 0.06 mm
a = 21.3440(2) Å; b = 7.1470(3) Å; c = 14.8200(5) Å; β = 111.9640(10)°	
Volume; Z	2096.64(11) Å^3; 4
Calcd density	1.739 g/cm$^{3\geq}$
Absorption coefficient	1.361 mm^{-1}
F (0 0 0)	1132
θ Range for data collection	3.0–27.5°
Index ranges	$-27 \leq h \leq 27$; $-9 \leq k \leq 8$; $-18 \leq l \leq 19$
μ (mm^{-1})	1.36
Reflections collected/unique	7344/1824 [R(int) = 0.077]
Completeness to 2θ = 27.53	99.9%
Data/restraints/parameters	2410/0/144
Final R indices[a] [$I > 2\sigma(I)$][b]	$R_1 = 0.049$, $wR_2 = 0.097$
Goodness-of-fit on F^2[c]	1.06
R indices (all data)	$R_1 = 0.076$, $wR_2 = 0.106$
Extinction coefficient	none
Largest diff. peak and hole	0.42 and −0.71 e Å^{-3}
(Δ/σ)max	<0.001

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR = [(\Sigma[F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.
[c] $S = \sum[w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$.

$C_{12}H_{26}Cl_2CuN_6O_{10}$ (M_W = 548.82 g M^{-1}) (%): C, 26.26; H, 4.78; N, 15.31; Cu, 11.58%. Found: C, 26.06; H, 4.82; N, 15.65; Cu, 11.42. FT-IR: (KBr, cm^{-1}): 3339 (m) N–OH, 3292, 3277 (m) N-H_2, 1674 C=N(imine), 1602(s) C=N(oxime), 1427(s) C=C, 1382 (m), 1308 (s), 1113 (s) ClO_4, 928 (w) N–O, 622 (m) ClO_4.

2.3. *Antimicrobial activity*

The antibacterial activities of the synthesized compound were assayed onto LB medium containing (Merck): bacto™ tryptone, 10.0 g L^{-1}; yeast extract, 5.0 g L^{-1}; NaCl, 5.0 g L^{-1}; and glucose, 1.0 g L^{-1} [17]. The medium was dispensed into universal bottles and sterilized at 121 °C for 15 min. The complex was dissolved into DMSO and filter sterilized using a 0.22 μm Ministart (Sartorius). The sterile stock solutions were added into LB medium to give a final concentration of 1–300 μg mL^{-1} as required. The antibacterial activity of the compound was compared with the known antibiotic tetracycline at the same concentration.

Minimum inhibitory concentration (MIC) of the compounds was assayed using a standard method against some bacteria including *Escherichia coli* PTCC 1330, *Pseudomonas aeruginosa* PTCC 1074, *Staphylococcus aureus* ATCC 35923, and *Bacillus subtilis* PTCC 1023. Late exponential phase of the bacteria was prepared by inoculating 1% (*v*/*v*) of the cultures into fresh LB medium and incubating on an orbital shaker at 37 °C and 100 rpm overnight. Before using the cultures, they were standardized with a final cell density of approximately 108 cfu mL^{-1}. A 1% (*v*/*v*) inoculum of each culture was inoculated into the LB medium containing different concentration of the synthesized compounds and incubated on the orbital shaker at 37 °C and 100 rpm. The compound sensitivity of the strains was assayed for positive or negative growth after 24–48 h.

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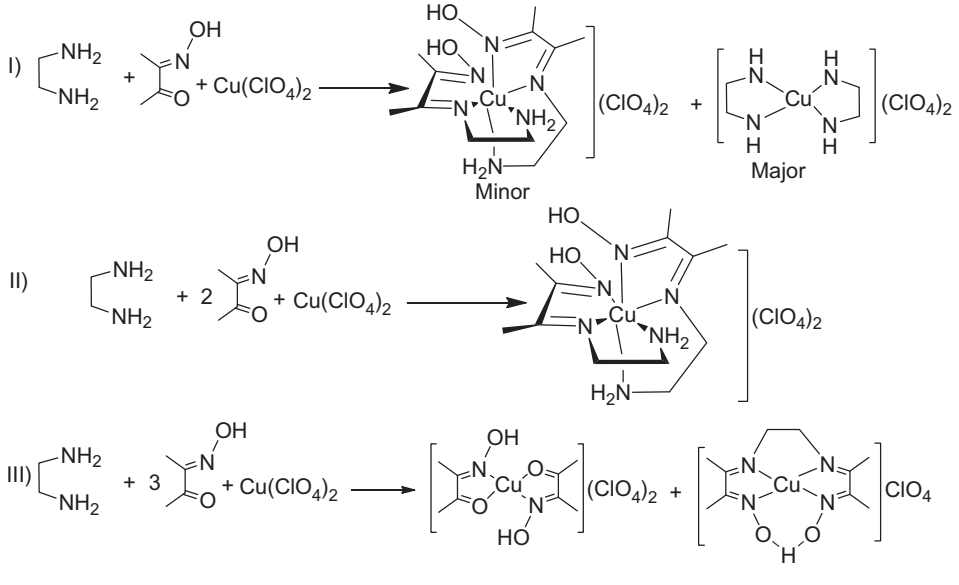
3. Results and discussion

3.1. *Synthesis*

Initial studies revealed that the reaction of an equimolar amount of diacetylmonoxime, ethylenediamine, and copper(II) perchlorate resulted in a mixture of bis(ethylenediamine)copper (II) perchlorate as a major product along with the desired singly condensed monoxime complex (route I in scheme 2). Subsequently, it was found that utilizing an equivalent amount of ethylenediamine and copper(II) as well as two equivalents of diacetylmonoxime, the desired singly condensed product was produced as the major component (route II in scheme 2). However, using more than two equivalents of the diacetylmonoxime with the same reaction conditions and reaction period decreased the yield of the desired product and resulted in the formation of bis-diacetylmonoxime copper(II) complex along with copper(II) complex from ligand generated by condensation of a part of ethylenediamine with two parts of acetylmonoxime (route III in scheme 2). However, in the optimized procedure (route II in scheme 2) only one of the amine groups of ethylenediamine is involved in the *in situ* condensation reaction and another amine group remained intact. Although the primary amine group of the ligand is engaged in coordination to copper(II), it can be subsequently condensed with various carbonyl compounds to study the variation and fine tuning of stability, reactivity, and electronic properties of such complexes.

3.2. *Crystal structure of the compound*

Selected bond distances and angles are listed in table 2 and a view of the complex cation with the atom numbering scheme is depicted in figure 1. Copper(II) lies at the center of a distorted octahedron that is coordinated by two ligands and has a N_6 coordination sphere. The ligand coordinates tridentate through oxime, imine, and amine nitrogens, and the



Scheme 2. Products based on different ratios of diacetylmonoxime, ethylenediamine, and copper(II) perchlorate.

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

Bond	Dist.	Bond	Dist.	Bond	Dist.
Cu(1)–N(1)	2.124(3)	Cu(1)–N(1)a	2.124(3)	N(3)–O(1)	1.396(3)
Cu(1)–N(2)	2.006(3)	Cu(1)–N(2)a	2.006(3)	N(2)–C(3)	1.275(4)
Cu(1)–N(3)	2.128(2)	Cu(1)–N(3)a	2.128(2)	N(3)–C(4)	1.280(4)
Angle	(°)	Angle	(°)	Angle	(°)
N(1)–Cu(1)–N(2)	81.74(10)	N(1)–Cu(1)–N(3)	156.44(10)	N(2)–Cu(1)–N(3)	75.63(10)
N(1)–Cu(1)–N(2)a	95.39(10)	N(1)–Cu(1)–N(1)a	94.08(15)	N(1)–Cu(1)–N(3)a	94.46(10)
N(2)–Cu(1)–N(1)a	95.39(10)	N(2)–Cu(1)–N(2)a	175.83(14)	N(2)–Cu(1)–N(3)a	107.54(10)
N(3)–Cu(1)–N(1)a	94.46(10)	N(3)–Cu(1)–N(2)a	107.54(10)	N(3)–Cu(1)–N(3)a	86.29(13)

Note: Symmetry transformation of a: $-x, y, -z+3/2$.

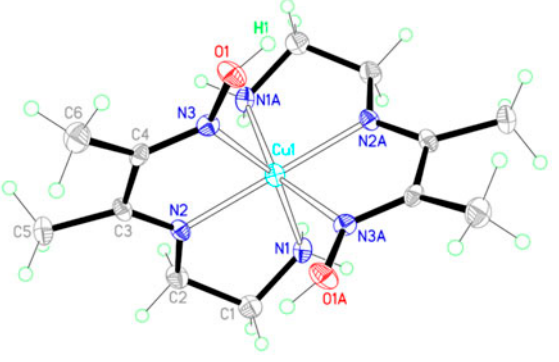


Figure 1. Crystal structure of the cationic part of copper complex.

shortest copper ligand contact in the complex is 2.006(3) Å for the N(2) imine nitrogen and the longest is 2.128(2) Å for N(3), the oxime nitrogen. The required bite angle from imine and oxime coordination [75.63(10)°] causes the greatest deviation from regular octahedral, with N(1)–Cu(1)–N(3) being 156.44(10)°. The oxime groups are located in *cis* positions but the primary amine groups are *trans*. The complex has a doubly charged complex cation in which both oxime oxygens are protonated.

In the crystal structure of the complex, the protonated oximes and the protons of amines (the protons were located crystallographically) are involved in long-range interactions in the lattice with oxygen of the perchlorates. O(1) has close contact of 2.704 Å to O(3) of ClO_4^-. The O(3) is also close to N(1) of the other complex (3.099 Å). Amine N(1) lies 3.198 Å from O(4), one of the four oxygens of perchlorate. A packing diagram of the complex is illustrated in figure S1 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.913135).

3.3. *Physical characterization of the compound*

The molar conductance value at room temperature of the copper(II) complex in 1×10^{-3} M solution in acetonitrile indicates a 2 : 1 electrolyte.

The thermal stability of the complex was evaluated by thermogravimetric analysis (TGA) at 20–600 °C in N_2 (10 °C min^{-1}) (figure 2). Decomposition occurred at 259 °C corresponding to 31.17% of the weight loss (Calcd 31.01%) which can be attributed to loss of two

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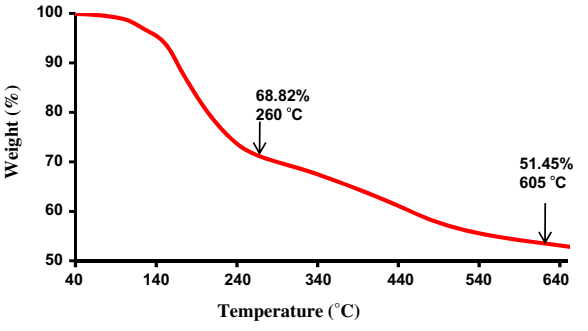

Figure 2. TGA curve of the complex.

acetylmonoxime moieties. The next weight loss at 604 °C can be associated to the loss of four oxygens caused by decomposition of perchlorate and followed by oxidation of organic species equivalent to 17.38% (Calcd 17.59%).

Electronic absorption spectral data of the complex in acetonitrile at room temperature were investigated (figure S2 in Supplementary material). The ligand showed imine $n\rightarrow\pi^*$ transitions at 287 nm ($\varepsilon = 2790\ M^{-1}\ cm^{-1}$). However, this transition appeared at 325 nm ($\varepsilon = 2150\ M^{-1}\ cm^{-1}$) in the complex along with a less intense band at 581 nm ($\varepsilon = 50\ M^{-1}\ cm^{-1}$) assigned to $d\rightarrow d$ transitions of the copper(II). In the complex, imine $n\rightarrow\pi^*$ transition shifted to longer wavelength as a consequence of coordination to the copper(II).

The photoluminescence of the complex in acetonitrile at room temperature was investigated. It shows a blue photoluminescence emission at 442 nm upon excitation at 366 nm, which is probably attributable to the $\pi^*\rightarrow\pi$ transitions. The luminescence decay is a single exponential function, suggesting the presence of one emissive center in solution (figure S3 in Supplementary material).

3.4. *Antimicrobial activity*

To screen antibacterial activity of synthesized compound, MIC was evaluated against Gram-positive, *S. aureus* and *B. subtilis*; and Gram-negative, *E. coli* and *P. aeruginosa*. The inhibition of micro-organisms was correlated with a standard antibiotic tetracycline (table 3). The results revealed that the complex has moderate to good inhibitory effect against some micro-organisms. Among the bacteria tested, the complex exhibited highest activity against *B. subtilis* and *S. aureus*. However, the MIC values for the synthesized compound against bacteria were high compared to the standard antibiotic tetracycline; these results suggest that the compound exhibited good antibacterial activities and can be further developed for application as effective antimicrobial agent.

Table 3. MIC of the compound (μg mL^{-1}) against some bacteria.

	Minimum inhibitory concentration (μg mL^{-1})		
Strain	Complex	$Cu(ClO_4)_2{\cdot}6H_2O$	Tetracycline
E. coli PTCC 1533	200	200	25
P. aeruginosa PTCC 1707	150	150	50
S. aureus ATCC 25923	100	200	10
B. subtilis PTCC 1156	100	200	25

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4. Conclusion

A copper(II) complex of an unsymmetrical tridentate ligand containing oxime, imine, and amine donors was synthesized by template intramolecular condensation and characterized. In this reaction, only one of the two NH_2 groups of ethylenediamine participated in condensation and the other NH_2 is intact. The complex exhibits very good photoluminescence in solution at room temperature. In addition to the synthetic and structural investigations, this study helps to evaluate the effectiveness of Schiff-base complexes of copper(II) as antibacterial agents. Compared to standard tetracycline, the present compound is much less active against some bacteria. However, a comparison of the data with those of oxime derivative copper(II) complexes [18–20] shows that the antibacterial activity is significantly enhanced on addition of a bulky group to the oxime. The bulky group reduces the polarity of the compounds [21] due to delocalization of positive charge over the whole molecule, which in turn increases the hydrophobic character of the copper(II) complexes and thus facilitate diffusion of the complexes through cell membrane of micro-organism.

Supplementary material

CCDC 735410 contains the supplementary crystallographic data for the complex. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax:+ 44 1223 336033 or E-mail: deposit@ccdc.cam.uk.

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