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Supramolecular Chelate Copper(II) Complex with 4-[(Ethoxyimino)(phenyl)methyl]-5-methyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one: Synthesis, Crystal Structure, and Properties

W.-K. Dong, G. Wanga, Y.-X. Sun, X.-Y. Dong, J. Yao, and X.-H. Gaob

Lanzhou Jiaotong University
West Anning Road 88, Lanzhou, 730070 P. R. China
e-mail: dongwk@126.com

Lanzhou Petrochemical Research Center, PetroChina, Lanzhou

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Abstract—A supramolecular Cu(II) complex, $[Cu(L)_2(H_2O)]\cdot C_2H_5OH$ {HL = 4-[(ethoxyimino)(phenyl)methyl]-5-methyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one]} was synthesized and characterized structurally. The structure of the Cu(II) complex consists of one Cu(II) atom, two bidentate L-units, one coordinated H_2O and one crystallization ethanol molecule. The Cu(II) atom of the complex has a slightly distorted tetragonal pyramidal geometry. Moreover, every Cu(II) complex molecule links four other molecules into an infinite 2D-layer supramolecular structure via intermolecular O–H···O, O–H···N, and C–H···O hydrogen bonds.

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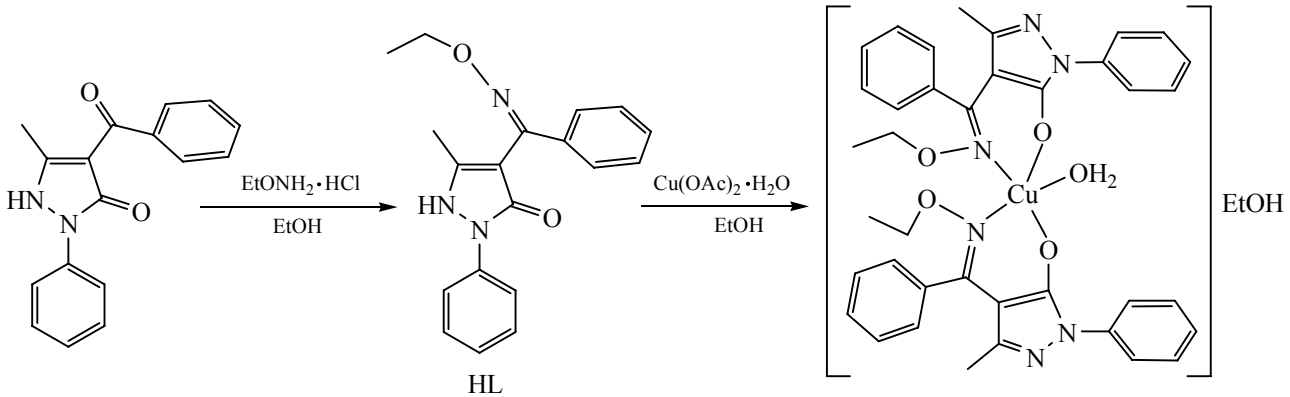
Oxime-type ligands and their complexes play an important part in the development of coordination chemistry [1]. 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone is a β-diketone compound, which is used for efficient phytoextraction of metal ions and also can form different types of coordination compound due to the keto-enol tautomerism [2]. Oxime-type compounds have recently attracted much attention because they are used extensively as disinfecting and antiviral agents, and also as reagents imitating the enzyme catalysis [3–7]. Transition metal complexes with oxime-type ligands are widely used as chelating agents [8], luminescent materials [9–11], dyes, dioxygen carriers [12] and as catalysts in the oxidation of organic molecules [13]. They also are widely applied as mimetics of cobalamin (B12) coenzymes [14].

In order to further investigate the syntheses, structures, properties of metal complexes with oxime-type ligands, we synthesized a supramolecular Cu(II) complex with the mono-oxime chelating ligand, $[Cu(L)_2(H_2O)]\cdot C_2H_5OH$ {HL = 4-[(ethoxyimino)(phenyl)-



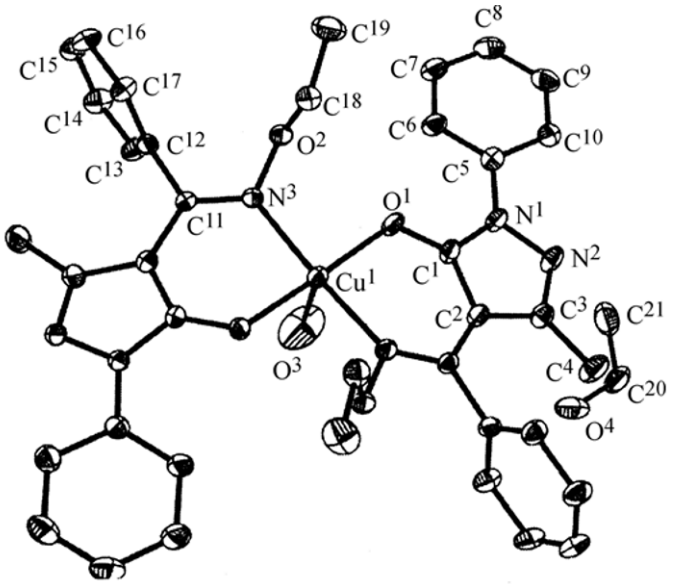


Fig. 1. Molecular structure and atom numberings of the Cu(II) complex (hydrogen atoms are omitted for clarity).

methyl]-5-methyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one} that was characterized by elemental analyses, IR and UV-Vis spectra, and by XRD analysis.

The reaction of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone with $CH_3CH_2ONH_2 \cdot HCl$ in a 1:1 molar ratio affords HL, which reacts with $Cu(OAc)_2 \cdot H_2O$ to give $Cu(L)_2(H_2O)] \cdot C_2H_5OH$.

X-ray crystallographic analysis of the Cu(II) complex reveals the formation of a mononuclear structure. The Cu(II) complex crystallizes in the trigonal system, space group $P3_221$, Z 3. The complex consists of one Cu(II) atom, two bidentate L-units, one coordinated H_2O and one crystallization ethanol molecule. The molecular structure of the Cu(II) complex is shown in Fig. 1, the main crystallographic parameters, selected bond distances and angles are listed in Tables 1, 2.

In the molecule the Cu(II) complex the central Cu(II) atom is coordinated with two oxygen atoms of keto groups, and two oxime nitrogen atoms from two

Table 1. Bonds lengths (Å) and bond angles (deg) in the structure of $Cu(L)_2(H_2O)] \cdot C_2H_5OH$[a]

Bond, angle	*d*, ω	Bond, angle	*d*, ω	Bond, angle	*d*, ω
Bonds lengths					
$Cu^1–O^1$	1.927(3)	$Cu^1–N^3$	2.025(4)	$Cu^1–O^3$	2.297(9)
$Cu^1–O^{1\#1}$	1.927(3)	$Cu^1–N^{3\#1}$	2.025(4)		
Bond angles					
$O^1Cu^1O^{1\#1}$	176.5(3)	$N^3Cu^1N^{3\#1}$	171.0(3)	$O^1Cu^1O^{3\#1}$	100.8(2)
$O^1Cu^1N^3$	89.06(2)	$O^1Cu^1O^3$	82.6(2)	$O^{1\#1}Cu^1O^{3\#1}$	82.6(2)
$O^{1\#1}Cu^1N^3$	90.67(2)	$O^{1\#1}Cu^1O^3$	100.8(2)	$N^3Cu^1O^{3\#1}$	94.0(4)
$O^1Cu^1N^{3\#1}$	90.67(2)	$N^3Cu^1O^3$	94.8(4)	$N^{3\#1}Cu^1O^{3\#1}$	94.8(4)
$O^{1\#1}Cu^1N^{3\#1}$	89.06(2)	$N^{3\#1}Cu^1O^3$	94.0(4)	$O^3Cu^1O^{3\#1}$	18.2(4)

[a] Symmetry transformations used to generate equivalent atoms: #1: x-y, -y, -z+ 1/3.

ligands, and one oxygen atom of the coordinated water molecule. The Cu(II) atom adopts a slightly distorted tetragonal pyramidal geometry with axial donors of O^{1} and $O^{1\#1}$ (τ 0.108) [15], and deviates from the mean plane of O^{1}, $O^{1\#1}$, N^{3}, and $N^{3\#1}$ atoms by 0.108(2) Å. Two ketone oxygen and two oxime nitrogen atoms are in mutual *trans*-positions. Four coordination atoms O^{1}, $O^{1\#1}$, N^{3}, and $N^{3\#1}$ form a slightly distorted tetrahedrally mean plane, the distances from the four atoms to the mean plane are equal [0.050(3) Å], while the distances of Cu(II) atom to the five donor atoms are different [1.926(4), 1.928(4), 2.025(4), 2.026(4), 2.298(4) Å, respectively]. The distance of the O^{3} atom to the mean plane is 2.377(4) Å in the Cu(H) complex. In addition, two ketone oxygen, two oxime nitrogen atoms, and their carbon chains form two six-membered chelate rings with the Cu(II) atom in the complex. The angle $O^{1\#1}Cu^{1}N^{3}$ in the six-membered ring is 90.66(4)°. The dihedral angle between the two pyrazole rings is 20.05(3)°.

The complex $[Cu(L)_2(H_2O)]\cdot C_2H_5OH$ contains one crystallization ethanol molecule, and the oxygen atom O^{4} of the crystallization ethanol molecule is hydrogen-bonded to the hydroxy group $O^{3}H^{3}$ of the disordered coordination water molecule. The methyl group $C^{20}H^{20A}$ is bonded to the oxygen atom O^{3} of the disordered coordination water molecule.

Meanwhile, the $O^{4}H^{4}$ group of ethanol is bonded to the nitrogen atoms N^{2} in the pyrazole ring of the deprotonated L-unit. In addition, this linkage is further stabilized by a couple of intermolecular $C^{17}–H^{17}\cdots N^{2}$ hydrogen bonds between the methine groups $C^{17}H^{17}$ of the benzene rings and nitrogen atoms N^{2} in the pyrazole rings of the adjacent molecules. Thus, every Cu(II) complex molecule links four other molecules into an infinite 2D-layer supramolecular structure via intermolecular O–H···O, O–H···N, and C–H···O hydrogen bonds (Fig. 2, Table 3).

The IR spectrum of ligand contains characteristic band of C=N stretching vibrations at 1618 cm^{-1}, which is shifted to 1593 cm^{-1} in the spectrum of the Cu(II) complex indicating that the nitrogen atom of C=N group is coordinated to the Cu(II) center. The C=O stretching vibrations band at 1724 cm^{-1} is observed in the spectrum of HL, while this band disappears in the spectrum of the Cu(II) complex, indicating that the Cu–O bonds are formed between the Cu(II) atom and oxygen atoms of C=O groups from ligands. The characteristic absorp-tion bands at 3395, 1641, and 571 cm^{-1} in the Cu(II) complex are assigned to the coordinated water molecule [16, 17].

Table 2. Main crystallographic data of $[Cu(L)_2(H_2O)]\cdot C_2H_5OH$ complex

Parameter	Value
Formula	$C_{40}H_{44}CuN_6O_6$
M	768.35
Temperature, K	298(2)
λ, Å	0.71073
Symmetry	Trigonal
Space group	$P3_221$
a, Å	9.553(1)
b, Å	9.553(1)
c, Å	38.289(3)
γ, deg	120
V, $Å^3$	3025.9(5)
Z	3
d_{calc}, g cm^{-3}	1.265
μ, mm^{-1}	0.593
F(000)	1209
Crystal size	0.48×0.47×0.45
Angles range, deg	1.60 to 25.01
Index range	$-11 \le h \le 8$, $-10 \le k \le 10$, $-34 \le l \le 45$
Reflections collected	12518
Independent reflections	3566
R_{int}	0.0392
$GOOF$	1.170
R_1, wR_2 [$I > 2\sigma(I)$]	0.0615, 0.1682
R_1, wR_2 (all data)	0.0680, 0.1727
Residual electronic density (min/max), $eÅ^{-3}$	0.956/–0.642

The IR spectrum of $[Cu(L)_2(H_2O)]\cdot C_2H_5OH$ also contains the absorption bands ν(Cu–O) and ν(Cu–N) at 438 and 478 cm^{-1}, respectively. These assignments are consistent with the literature data [16–18]. The main parameters of the IR spectra (cm^{-1}) of the ligand and its Cu(II) complex are presented further.

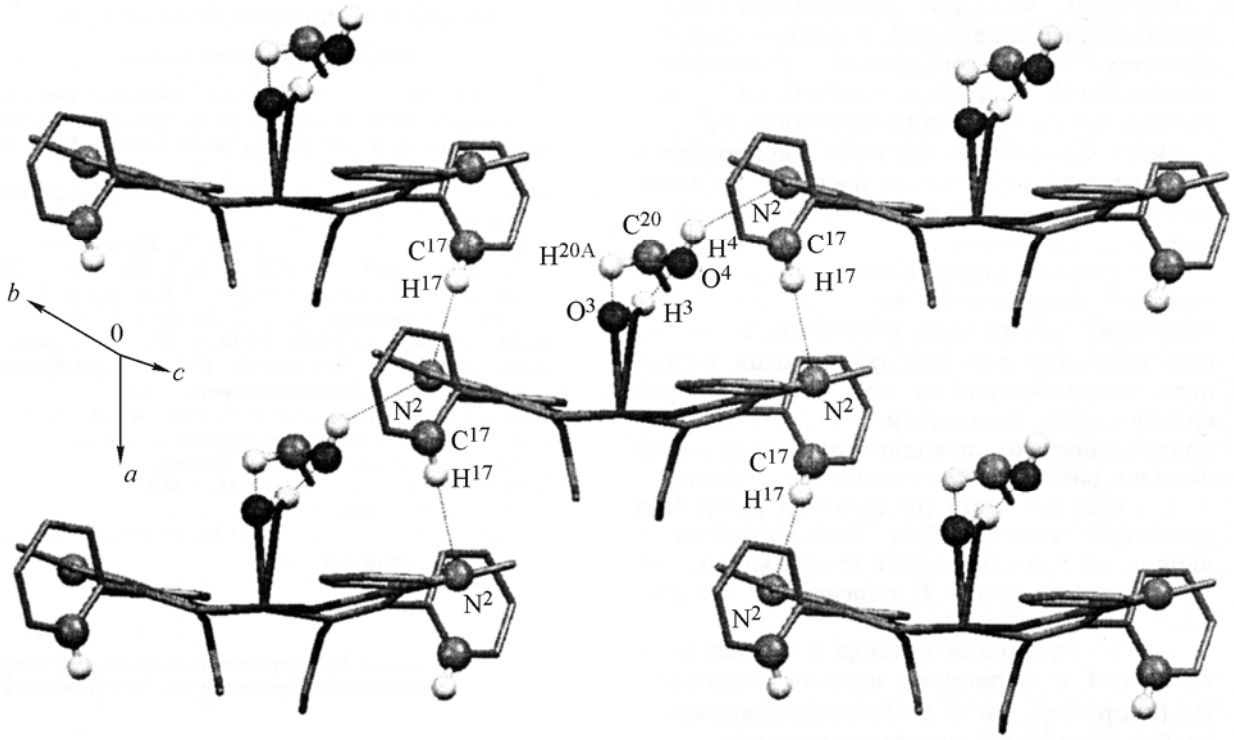


Fig. 2. Fragment of 2D-layer supramolecular structure of $[Cu(L)_2(H_2O)]\cdot C_2H_5OH$ complex.

Compound	ν(C=N)	ν(C=O)	ν(C–O)	ν(Cu–N)	ν(Cu–O)	ν(H_2O)	δ(H_2O)	ρ(H_2O)
HL	1618	1724	1053	–	–	–	–	–
Complex	1593	–	1016	478	438	3397	1641	571

The UV absorption spectra of 4-[(ethoxyimino)-(phenyl)methyl]-5-methyl-2-phenyl-1*H*-pyrazol-3-(2*H*)-one and its Cu(II) complex were registered from 5×10^{-5} mol l^{-1} $CHCl_3$ solution. The UV spectrum of the ligand contains two absorption bands at 242 (ε 42.8 l mol^{-1} cm^{-1}) and 271 nm (ε 8.4 l mol^{-1} cm^{-1}). The former absorption peak at 242 nm can be assigned to the π–π*-transition in the benzene ring, which is shifted to 250 nm in the Cu(II) complex (ε 1074.0 l mol^{-1} cm^{-1}) indicating the coordination of the Cu(II) atom with the deprotonated ligand. The latter peak can be attributed to the intra-ligand π–π*-transition of the C=N bonds, which is observed at 278 nm (ε 479.7 l mol^{-1} cm^{-1}) in the Cu(II) complex.

Table 3. Length of intermolecular hydrogen bonds in $[Cu(L)_2(H_2O)]\cdot C_2H_5OH$ complex

D–H···A	*d*(D–H), Å	*d*(H···A), Å	*d*(D···A), Å	∠DHA, deg
O^4–H^4···N^2	0.82	2.47	3.122(3)	138
O^3–H^3···O^4	0.98	1.68	2.579(2)	151
C^{20}–H^{20A}···O^3	0.97	2.71	3.104(1)	105
C^{17}–H^{17}···N^2	0.93	2.64	3.567(2)	177

EXPERIMENTAL

Elemental analysis for Cu was performed on an IRIS ER/S' WP-l ICP atomic emission spectrometer. The C, H, and N analyses were carried out on a GmbH VariuoEL V3.00 automatic elemental analyzer. The IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer from KBr (400–4000 cm^{-1}) or CsI pellets (100–500 cm^{-1}). The UV-Vis absorption spectra were taken on a Shimadzu UV-2550 spectrometer. The ^{1}H NMR spectra were obtained on a Mercury-400BB spectrometer at room temperature

using $CDCl_3$ as solvent. Melting points were measured on a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company. The X-ray single crystal structure was determined on a Bruker Smart 1000 CCD area detector. The diffraction data were collected using a graphite monochromated MoK_α-irradiation (λ 0.71073 Å) at 298(2) K. The structure was solved by using the program SHELXS-97 [19] and difference Fourier techniques, and refined by full-matrix least-squares method with respect to F^2 using SHELXL-97 program [19]. The non-hydrogen atoms were refined anisotropically. Both oxygen atoms O^3 and O^4 from one coordinated water molecule and one crystallization ethanol molecule are disordered between two positions with equal population (0.50:0.50 and 0.50:0.50).

4-[(Ethoxyimino)(phenyl)methyl]-5-methyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one (HL). A solution of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (556.6 mg, 2 mmol) in hot ethanol (7 ml) was added dropwise to a solution of ethoxyamine (189.1 mg, 2 mmol) in ethanol (5 ml). After stirring the solution at 338 K for 6 h, the solvent was removed under a reduced pressure and the residue was recrystallized from ethanol to give white needle-like crystals. Yield 71.8%, mp 171–172°C. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 7.24–7.85 m (10H, H-Ar), 4.08 q (2H, OCH_2, *J* 6.8 Hz), 2.16 s (3H, CH_3), 1.23 t (3H, CH_3, *J* 6.8 Hz), 8.84 br. s (1H, NH). Found, %: C 71.32; H 5.81; N 13.15. $C_{19}H_{19}N_3O_2$. Calculated, %: C 71.01; H 5.96; N 13.08.

Complex $[Cu(L)_2(H_2O)]\cdot C_2H_5OH$. A solution of copper(II) acetate monohydrate (2.01 mg, 0.01 mmol) in ethanol (6 ml) was added dropwise to a solution of HL (6.43 mg, 0.02 mmol) in ethanol (6 ml) at room temperature. The color of the mixed solution turned to dark-brown immediately. The obtained transparent mixed solution was allowed to stand at room temperature for about one month. The solvent was partially evaporated and several black single crystals which suitable for X-ray crystallographic analysis were obtained. Found, %: C 62.78; H 5.52; Cu 8.54; N 10.76. $C_{40}H_{44}CuN_6O_6$. Calculated, %: C 62.53; H 5.77; Cu 8.27; N 10.94.

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