



1-苯基-3-甲基-4-甲酰基-5-吡唑啉酮 Cu(II)配合物的合成及晶体结构

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Synthesis and Crystal Structure of Cu(II) Complex of 1-Phenyl-3-methyl-4-acyl-5-pyrazolone

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Abstract: A novel Cu(II) complex of 1-phenyl-3-methyl-4-acyl-5-pyrazolone was synthesized and crystallographically characterized. The single-crystal structure of the complex reveals that the crystal belongs triclinic, space group $P\bar{1}$ with cell parameters $a=0.938\ 7(4)$ nm, $b=1.124\ 4(5)$ nm, $c=1.222\ 3(5)$ nm, $\alpha=99.538(7)^\circ$, $\beta=104.049(8)^\circ$, $\gamma=113.806(6)^\circ$, and $Z=2$, $V=1.093\ 3(8)$ nm³. Cu(II) ion is coordinated by two 1-phenyl-3-methyl-4-acyl-5-pyrazolone ligands, and one methanol molecule giving a coordination number of five, the coordination polyhedron around Cu(II) ion can be described as a square pyramid. Two complex units link to each other through the hydrogen-bonding interactions to form a dimer. Meanwhile, a staircase-like layer structure was built up by offset face-to-face $\pi \cdots \pi$ stacking interactions and weak interactions between the dimers. CCDC: 625422.

Key words: 1-phenyl-3-methyl-4-acyl-5-pyrazolone; Cu(II) complex; crystal structure; hydrogen-bonding; layer structure

The design of new coordination supramolecules and polymers based on transition metal compounds and multidentate organic ligands has attracted much interest in recent years^[1-8]. Dependent on the nature of the metal and the coordination behavior of the ligand one can develop synthetic strategies to influence the one, two or three-dimensional arrangement in the crystal in a more directed way^[9]. Furthermore, it is now realized that weak intermolecular interactions that involve N-H \cdots O and/or O-H \cdots O hydrogen bonds interactions and $\pi \cdots \pi$ stack-

ing interactions also play a significant and predictable structure determining role.

4-acyl-pyrazolone derivatives are widely used in many fields in the society, especially clinical and analytical applications^[10-12], because pyrazolone, especially 4-acyl-pyrazolone, displays several different coordination modes, with respect to classical β -diketones^[13-15]. The presence of two oxygen donor atoms, they easily coordinate with metal ions and provide stable metal complexes with six-membered chelate rings^[16]. Compl-

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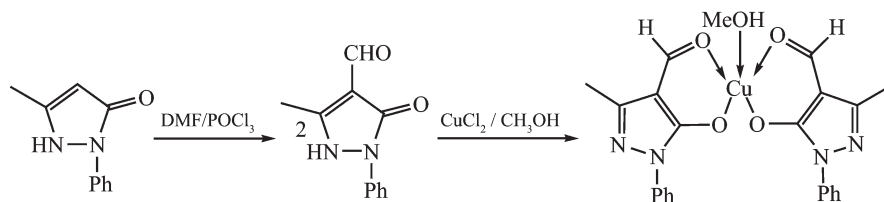
exes containing these ligands are known for almost all transition and main group metals, often showing unusual structural and chemical properties^[17,18]. In this paper we synthesized a novel Cu(II) complex of 1-phenyl-3-methyl-4-acyl-5-pyrazolone and reported the crystal structure, the hydrogen-bonding interactions and offset face-to-face $\pi \cdots \pi$ stacking interactions contribute to form the better packing format in the title complex.

1 Experimental

1.1 Synthesis of Cu(II) complex

2 mL of piperidine was added to the solution of 1-phenyl-3-methyl-4-acyl-5-pyrazolone (1.22 g) in methanol (10 mL), mixed uniformly. Then adding the solution of $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ (1.00 g) in methanol (10 mL) to above

solution. After heating and stirring for 1 hour, 10 mL solvent were lost, placed it in a refrigerator cooling for 1 hour, green flocculent precipitate was separated by filtration, washed several times with distilled water, ice methanol and ice acetone respectively. Melting point: 250 °C, Temperature uncorrected; Yield: 61.1%. The obtained green flocculent product was dissolved in dichloromethane, green solution was obtained after filtrating. Added 20 mL above dilute solution to a clean Cypriot-vitro, which was sealed with PVC film, and placed it under dark condition. Green plate crystals were obtained by slowly evaporating for a week. Anal. Calcd. for $\text{C}_{23}\text{H}_{22}\text{CuN}_4\text{O}_5$ (%): C, 55.42; H, 4.61; N, 11.25. Found (%): C, 55.12; H, 4.42; N, 11.61. The reaction equation is as follows:



1.2 X-ray crystal structure determination

A crystal of approximate dimensions of 0.15 mm × 0.12 mm × 0.10 mm was selected for the structure determination. Diffraction data were collected on a Siemens P4 four-circle diffractometer equipped with graphite crystal-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.071\ 073\ \text{nm}$) at 293(2) K. Lorentz polarization corrections and empirical absorption correction were applied to the data. The structures were solved by the direct methods with SHELXS-97 program package^[19] and

refined on F^2 by full-matrix least-squares methods using the SHELXL-97^[20]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions and refined isotropically. A summary of the crystallographic data and some structural determination parameters for the title compound is listed in Table 1. Selected bond lengths and bond angles are provided in Table 2.

CCDC: 625422.

Table 1 Crystallographic parameters of the title complex

Compound	$\text{C}_{23}\text{H}_{22}\text{CuN}_4\text{O}_5$	$\gamma / (^\circ)$	113.806(6)
Color / shape	Green / plate	Z	2
Formula weight	497.99	Absorption coefficient / mm^{-1}	1.043
Temperature / K	293(2)	$F(000)$	514
Wavelength / nm	0.071 073	Crystal size / mm	0.15×0.12×0.10
Crystal system	Triclinic	θ range for data collection / $(^\circ)$	2.549~22.412
Space group	$P\bar{1}$	Index ranges	$-11 \leq h \leq 6, -13 \leq k \leq 13, -14 \leq l \leq 13$
Volume / nm^3	1.093 3(8)	Reflections collected	3 769
a / nm	0.938 7(4)	Unique reflections	2 620
b / nm	1.124 4(5)	Observed reflections [$I > 2\sigma(I)$]	
c / nm	1.222 3(5)	Data / restraints / parameters	3 769 / 1 / 303
$\alpha / (^\circ)$	99.538(7)	Final R indices [$I > 2\sigma(I)$]	$R_1=0.042\ 7, wR_2=0.087\ 0$
$\beta / (^\circ)$	104.049(8)	R indices (all data)	$R_1=0.065\ 7, wR_2=0.093\ 2$

$$R_1 = \sum \|F_o\| - \sum \|F_c\| / \sum \|F_o\|; wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]; w^{-1} = [\sigma^2(F_o^2) + (0.034\ 9P)^2 + 0.000\ 0P]; P = (F_o^2 + 2F_c^2)/3.$$

Table 2 Select bond lengths (nm) and bond angles (°)

Cu1-O1	0.193 7(2)	Cu1-O2	0.195 9(2)	Cu1-O3	0.193 7(2)
Cu1-O4	0.194 5(2)	Cu1-O5	0.228 4(3)	O1-C1	0.126 8(3)
O2-C2	0.125 0(4)	O3-C12	0.127 3(3)	O4-C13	0.125 9(4)
N1-C4	0.130 3(4)	N1-N2	0.140 4(3)	N2-C1	0.135 7(4)
N2-C6	0.142 3(3)	N3-C15	0.130 8(4)	N3-N4	0.141 0(3)
N4-C12	0.135 5(4)	N4-C17	0.141 7(4)	C1-C3	0.142 1(4)
C2-C3	0.137 9(4)	C13-C14	0.138 7(4)	C3-C4	0.141 8(4)
O1-Cu1-O2	94.48(9)	O1-Cu1-O3	84.95(8)	O1-Cu1-O4	173.36(10)
O1-Cu1-O5	94.19(9)	O2-Cu1-O5	92.32(10)	O3-Cu1-O4	95.45(9)
O3-Cu1-O2	172.41(9)	O3-Cu1-O5	95.27(9)	O4-Cu1-O2	84.25(9)
O4-Cu1-O5	92.37(9)	C1-O1-Cu1	121.32(19)	C2-O2-Cu1	124.9(2)
C12-O3-Cu1	120.3(2)	C13-O4-Cu1	124.5(2)	C23-O5-Cu1	123.6(2)
N1-N2-C6	120.0(2)	C1-N2-N1	110.8(2)	O1-C1-C3	128.8(3)
O1-C1-N2	125.0(3)	O2-C2-C3	125.9(3)	N2-C1-C3	106.1(3)
C7-C6-N2	120.0(3)	N1-C4-C5	120.8(3)		

2 Results and discussion

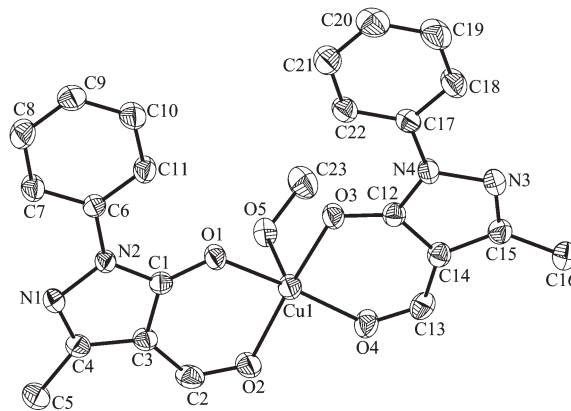
2.1 Infrared spectra

The strong bands in the ranges around 1 589 and 1 673 cm^{-1} are assigned to $\nu(\text{C}=\text{O})$ of the pyrazolone ring and $\nu(\text{C}=\text{O})$ of the lateral chain, respectively^[21]. All these suggest that structure of the ligands in the solid state are the keto form. However, in the spectra of the complex, the $\nu(\text{C}=\text{O})$ bands are both absent. Meanwhile, a new band is observed at around 1 450 cm^{-1} due to $\nu(\text{C}-\text{O})$. The weak band at 510 cm^{-1} is due to Cu-O stretching vibration. From these observations, it is concluded that the ligands react in the enol form with prototropy, then lose the enolic protons and coordinate to the central metal atoms in the complexes. The results are also confirmed by the single crystal structure of the title complex.

2.2 Description of the crystal structures

The single-crystal structure of the complex reveals that Cu(II) ion is coordinated by two 1-phenyl-3-methyl-4-acyl-5-pyrazolone ligands, and one methanol molecule giving a coordination number of five and the coordination polyhedron around Cu (II) ion can be described as a square pyramid (see Fig.1). The coordination square pyramid around Cu (II) ion is composed of O1, O2, O3, O4 and O5 atoms, the atoms O1, O2, O3 and O4 are composed of the basal plane,

and the axis of the square pyramid is held by O5. The ligand-metal-ligand bite angles differ from the ideal value of 90° , varying between $84.25(9)^\circ$ (O4-Cu1-O2) and $95.45(9)^\circ$ (O3-Cu1-O4). The bond angles of O1-Cu1-O4, O3-Cu1-O2 are $173.36(10)^\circ$ and $172.41(9)^\circ$ respectively, which are slightly deviated from the theoretical value of 180° , these information indicate that the coordination sphere of Cu is best described as a slightly distorted square pyramid. The angles of O1-Cu1-O2, O2-Cu1-O4, O4-Cu1-O3 and O3-Cu1-O1 are $94.48(9)^\circ$, $84.25(9)^\circ$, $95.45(9)^\circ$ and $84.95(8)^\circ$ respectively, which are added up to justly $359.13(25)^\circ$, the drifting distance between the Cu1 and the plane defined by O1, O2, O3 and O4 is 0.012 1 nm, all of these



Hydrogen atoms being omitted for clarity

Fig.1 Molecular structure of the title complex with thermal ellipse at the 30% probability level

indicate that the Cu1 atom is nearly in the basal plane. Because of the offset face-to-face $\pi \cdots \pi$ stacking interactions and hydrogen-bonding interactions, the distance between the layers becomes short (see Fig.3), which influences that the coordination number of Cu(II) ion, Cu(II) ion couldn't complete 6-fold coordinated complex. As far as the average bond lengths between the Cu(II) ion and the pyrazolone oxygen atom, and that between the Cu(II) ion and methanol oxygen atoms, the former is shorter than the latter, which we can confirmed from the data in Table 2. This may be result from the negative charge of the pyrazolone oxygen atom, which could be more strongly coordinated to the Cu(II) ion due to electrostatic effects^[22]. Meanwhile, it indicates that the ligand 1-phenyl-3-methyl-4-acyl-5-pyrazolone has better donating properties than the methanol molecule^[23,24], and the ligand can approach closer to the central ion. The length of Cu1-O1 and Cu1-O2 are 0.193 7(2) nm, 0.195 9(2) nm respectively, the longer Cu1-O2 bond links to the shorter C-O (C2-O2), this is because of the asymmetry of β -diketones^[25]. The C1-O1, C2-O2, C12-O3 and C13-O4 bond distances are 0.126 8(3), 0.125 0(4), 0.127 3(3) and 0.125 9(4) nm, respectively, which are shorter than 0.143 nm for a C-O single bond and longer than 0.122 nm for a C=O double bond length, which confirms that the keto form of the ligand isomerizes to the enol form and then participates in bonding^[26]. The two complex units link to each other through the hydrogen-bonding interactions between the nitrogen atoms of 1-phenyl-3-methyl-4-acyl-5-pyrazolone ligands and the oxygen atoms of methanol molecules (N1-H \cdots O5) with a distance (0.284 8(3) nm) to form a dimer (see Fig.2). The molecular packing diagram of the complex viewed along a -axis is depicted in Fig.3. The molecules are stacked into a staircase-like layer structure through the hydrogen-bonding interactions from the pyrazolone rings and methanol molecules. There are also weak intermolecular interactions C9-H9 \cdots O2(0.093 1, 0.251 0, 0.340 4 nm, 161.07°) in the complex^[27], which linked the dimers along b -axis and extended infinitely. Another important intermolecular interaction is the offset face-to-face stacking interaction between the dimmers. The shortest

$\pi \cdots \pi$ centroid-to-centroid distance between the offset face-to-face (the interior alternate angle is 73.81°) aromatic rings of neighbouring pyrazolone ring is 0.349 6 nm, hence, the $\pi \cdots \pi$ stacking interactions are very strong, and these interactions extended along c -axis infinitely.

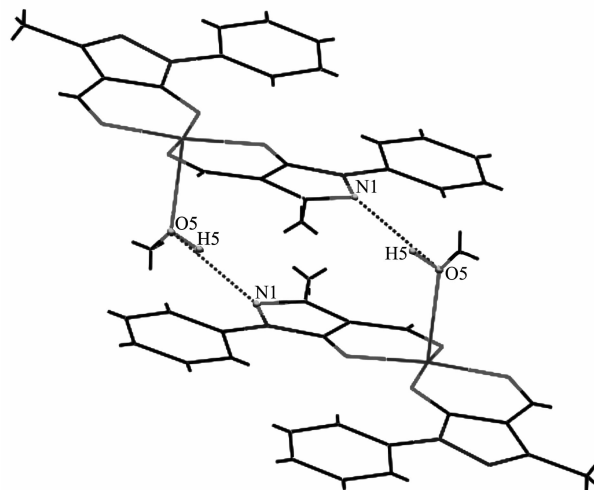


Fig.2 N \cdots O intermolecular hydrogen bond between two molecules viewed along the a -axis

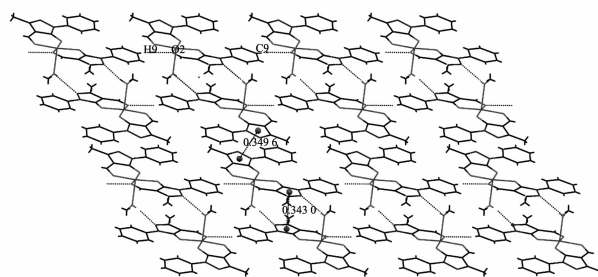


Fig.3 Staircase-like layer structure of the title complex viewed along the a -axis

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