

Synthesis and Characterization of Copper(II) and Zinc(II) Complexes Containing 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone

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The synthesis, structure, and physical properties of a series of mononuclear complexes *viz.* [Cu(L)₂] **1**, [CuL₂(CH₃O)₂] **2** and [Zn(L)₂] **3** (where L = 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP)) are presented. The complexes were characterized by elemental analysis, IR and electronic spectroscopy (**1** and **2**), magnetic measurements at room temperature (**1** and **2**) and thermogravimetric analysis. The structures of all the three complexes were determined by single crystal X-ray diffraction studies. The coordination geometry around complexes CuL₂ (**1**) and ZnL₂ (**3**) is slightly distorted square planar while the geometry around Cu(II) of [Cu(L)₂(CH₃O)₂] (**2**) is distorted octahedral with four oxygen atoms of two PMBP ligand occupying the equatorial positions and two methanol molecules occupying the two axial positions.

Key words: PMBP Complex, Crystal Structure, Copper and Zinc Ions

Introduction

It has been noticed that copper(II) complexes as anti-inflammatory drugs are often more active than the parent ligands themselves [1]. In recent years, several works have appeared concerning models of copper enzymes [2–4]. This growing interest in mimicking the active sites of metalloproteins has a major contribution to the development of new ideas and trends in coordination chemistry. The coordination chemistry of pyrazole derived ligands has received much attention, primarily due to their biological implications. Several studies have centered around synthesis and structural studies of metal complexes of pyrazole containing bidentate ligands (N, O donors) due to the reported anticarcinogenic and antiviral activity of these donor ligands and complexes obtained from them. It has been reported that substituted pyrazolones, pyrazolines and pyrazoles have potential biological activity [5, 6]. Derivatives of 2-pyrazolines-5-ones have been studied for their importance as antipyretics and analgetics [7]. 2-Pyrazolones and their nitroso derivatives have been found to be effective germicides and fungicides [8].

The coordination chemistry of zinc is of considerable interest [9]. The active binding sites of zinc could be applied in highly efficient and catalytic reactions by using a variety of coordination possibilities such as the variability and flexibility of ligands in biologically relevant coordination spheres [10]. Since changes in coordination geometry due to the flexibility of the binding ability of ligands can lead to an open position at the metal ion site, these may be beneficial for catalytic reactions to occur [11]. The ligands containing imidazole or substituted imidazole groups, similar to pyrazole or substituted pyrazole groups are known to occur in metalloproteins [12].

In this paper we describe the synthesis, physical properties and crystal structures of three neutral complexes of copper(II) and zinc(II) ions containing 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP).

Experimental Section

Materials

All chemicals were of reagent grade. Copper acetate, zinc acetate and methanol were used as received. 1-Phenyl-3-

Table 1. Crystal data and structure refinement for **1**, **2** and **3**.

	1	2	3
Empirical formula	C ₃₄ H ₂₆ N ₄ Cu O ₄	C ₃₆ H ₃₂ N ₄ Cu O ₆	C ₃₄ H ₂₆ N ₄ Zn O ₄
Formula weight	618.13	680.20	619.96
Temperature	296(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	1.54178 Å	1.54178 Å
Crystal system, space group	monoclinic, <i>P</i> 2 ₁ / <i>c</i>	monoclinic, <i>P</i> 2 ₁ / <i>c</i>	monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 6.8347(6) Å <i>b</i> = 23.857(2) Å <i>c</i> = 9.1596(8) Å α = 90° β = 108.993(2)° γ = 90°	<i>a</i> = 11.08(2) Å <i>b</i> = 15.91(2) Å <i>c</i> = 9.438(8) Å α = 90° β = 103.92(10)° γ = 90°	<i>a</i> = 6.843(6) Å <i>b</i> = 23.868(13) Å <i>c</i> = 9.172(5) Å α = 90° β = 108.92(5)° γ = 90°
Z, Volume	2, 1412.2(2) Å ³	2, 1615(3) Å ³	2, 1417(2) Å ³
Density (calculated)	1.454 g cm ⁻³ ,	1.398 g cm ⁻³ ,	1.453 g cm ⁻³
Absorption coefficient	0.821 mm ⁻¹	1.392 mm ⁻¹	1.591 mm ⁻¹
Crystal size	0.25 × 0.20 × 0.10 mm	0.10 × 0.08 × 0.06 mm	0.10 × 0.07 × 0.04 mm
Theta range for data collection	2.50 to 33.48°	4.11 to 50.00°	3.70 to 49.98°
Index ranges	-10 ≤ <i>h</i> ≤ 10, -37 ≤ <i>k</i> ≤ 34, -9 ≤ <i>l</i> ≤ 13	0 ≤ <i>h</i> ≤ 11, -15 ≤ <i>k</i> ≤ 0, -9 ≤ <i>l</i> ≤ 9	-6 ≤ <i>h</i> ≤ 6, 0 ≤ <i>k</i> ≤ 23, 0 ≤ <i>l</i> ≤ 9
Reflections collected / unique	13429 / 5238 [<i>R</i> (int) = 0.0621]	1642 / 1642 [<i>R</i> (int) = 0.0000]	1455 / 1455 [<i>R</i> (int) = 0.0000]
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / parameters	5238 / 248	1642 / 217	1455 / 197
Goodness-of-fit on <i>F</i> ²	0.954	1.057	1.018
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0623, <i>wR</i> 2 = 0.1230	<i>R</i> 1 = 0.0486, <i>wR</i> 2 = 0.1293	<i>R</i> 1 = 0.0460, <i>wR</i> 2 = 0.1190
<i>R</i> Indices (all data)	<i>R</i> 1 = 0.1365, <i>wR</i> 2 = 0.1505	<i>R</i> 1 = 0.0569, <i>wR</i> 2 = 0.1382	<i>R</i> 1 = 0.0618, <i>wR</i> 2 = 0.1309
Largest diff. peak and hole	0.399 and -0.256 e / Å ³	0.643 and -0.342 e / Å ³	0.401 and -0.408 e / Å ³

methyl-5-pyrazolone was received from Lancaster and used without any purification.

Physical measurements

Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer. Infrared spectra of the complexes were recorded on a Perkin-Elmer 883-IR spectrophotometer using KBr pellets, the UV-vis spectra with a Perkin Elmer λ-40 (UV-VIS) spectrophotometer in acetonitrile solution and in solid state using nujol. The magnetic susceptibility was measured for the solid samples at room temperature using a vibrating sample magnetometer using mercury (tetrathiocyanato) cobaltate as a standard. TGA analyses were carried out on a Shimadzu TGA – 50 thermal analyzer under a dynamic nitrogen environment.

X-ray crystallography

X-ray intensity data for the complexes **1**, **2** and **3** were collected on a CAD 4 diffractometer using graphite - monochromatized Mo-K α radiation for **1** and Cu-K α for **2** and **3** (λ = 0.71073 Å for **1** and 1.54178 Å for **2** and **3** respectively). The lattice constants were determined by least squares refinements of the setting angle for 25 reflections ($33.48 \geq \theta \geq 2.50$) for **1**, ($50.00 \geq \theta \geq 4.11$) for **2** and ($49.98 \geq \theta \geq 3.70$) for **3**, respectively. The structures were solved by direct

methods (SHELXS-97) [13] and refined on *F*² by full-matrix least-squares using all unique data (SHELXL-97) [14]. For **1**, **2** and **3**, all non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in calculated positions (riding model). The structures were finally refined to the conventional *R*-values of 0.0623, 0.0486 and 0.0460 for **1**, **2** and **3**, respectively. The crystal data, the conditions for the intensity data collection, and important features of the structural refinements for the compounds are listed in Table 1. Selected bond lengths and angles are presented in Table 2. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center with deposition numbers 208954 – 208956. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1233 336033; E-mail: deposit@ccdc.cam.ac.uk).

Synthesis of the ligand

1-Phenyl-3-methyl-5-pyrazolone (7.5 g) was dissolved in 80 ml of 1,4-dioxane by heating. Calcium hydroxide (12 g) was added followed by addition of benzoyl chloride (5 ml) dropwise within 1 min. The temperature increased during the first few minutes and the reaction mixture became a thick paste. The reaction mixture was refluxed for 30 min. Calcium complex of the desired ligand formed in the flask was decomposed by pouring the mixture into dilute hydrochloro-

Table 2. Bond lengths [Å] and angles [deg] for **1**, **2** and **3**.

1:			
Cu(1)-O(1)	1.9068(17)	Cu(1)-O(2)	1.9189(17)
O(1)-Cu(1)-O(1)#1	180.0	O(1)-Cu(1)-O(2)#1	86.53(7)
O(1)-Cu(1)-O(2)	93.47(7)	O(2)#1-Cu(1)-O(2)	180
2:			
Cu(1)-O(1)	2.033(3)	Cu(1)-O(2)	2.108(4)
Cu(1)-O	2.152(4)		
O(1)-Cu(1)-O(1)#1	180	O(1)-Cu(1)-O(2)#1	90.63(13)
O(1)-Cu(1)-O(2)	89.37(13)	O(2)#1-Cu(1)-O(2)	180
O(1)-Cu(1)-O#1	88.37(12)	O(1)-Cu(1)-O	91.63(12)
O(2)-Cu(1)-O	87.5(2)	O(2)#1-Cu(1)-O(1)	92.5(2)
O#1-Cu(1)-O	180		
3			
Zn(1)-O(1)	1.909(3)	Zn(1)-O(2)	1.922(3)
O(1)-Zn(1)-O(1)#1	180	O(1)-Zn(1)-O(2)#1	86.59(13)
O(1)-Zn(1)-O(2)	93.41(13)	O(2)#1-Zn(1)-O(2)	180

ric acid (100 ml). An orange precipitate was formed slowly. It was filtered under suction, washed with a little water and 1,4-dioxane, and recrystallised from a slightly acidified methanol-water mixture to destroy any undecomposed calcium complex.

Synthesis of the complexes

The complex [Cu(PMBP)₂] **1** was prepared by the addition of the ligand (PMBP) to a methanolic solution of copper acetate in 2:1 ratio. The resulting mixture was stirred for 25 min. and then it was kept at r.t. Green rectangular shaped crystals appeared after 10 d, from which crystals suitable for X-ray analysis were separated. Yield: 85%.

Analysis for [Cu(PMBP)₂]: calcd. C 66.01, H 4.20, N 9.05, Cu 10.27; found C 65.99, H 4.11, N 9.01, Cu 10.31.

The complex [Cu(PMBP)₂(CH₃O)₂] **2** was prepared by the addition of the ligand (PMBP) to an aqueous-methanolic solution of copper acetate in 2:1 ratio. The resulting mixture was kept at r.t. from which shiny green rectangular shaped crystals appeared after 7 d. Yield: 77%.

Analysis for [Cu(PMBP)(CH₃O)₂]: calcd. C 66.51, H 4.70, N 8.23, Cu 9.34; found C 66.53, H 4.73, N 8.27, Cu 9.36.

The complex [Zn(PMBP)₂] **3** was prepared by the addition of a methanolic solution of zinc acetate to a methanolic solution of PMBP ligand in 2:1 ratio. Light yellow square shaped crystals appeared after 8 d from which crystals suitable for X-ray analysis were separated. Yield: 75%.

Analysis for [Zn(PMBP)₂]: calcd. C 65.82, H 4.20, N 9.07, Zn 10.57; found C 65.81, H 4.19, N 9.03, Zn 10.55.

Result and Discussion

Infrared studies

The IR spectra of the complexes show several strong bands in the range of 2844–3345 cm⁻¹, which are due

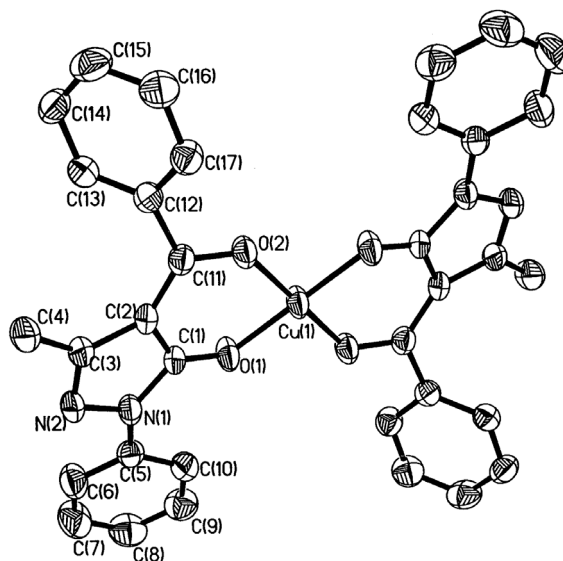


Fig. 1. Ortep plot of complex **1** with atom numbering scheme.

to $\nu(\text{NH})$ stretching and may also be due to the presence of methanol which is also confirmed by the crystal structure analysis for the complex **2**. For the other two complexes several bands appeared in the range 2885, 2954, 2988, 3000 cm⁻¹, assigned to aliphatic C-H stretching vibrations. It is reasonable to assign the two bands at 425 and 495 cm⁻¹ as $\nu(\text{Cu}-\text{O})$ stretching mode [15].

Electronic studies

The electronic spectrum of complex **1** in dichloromethane exhibited the metal-to-ligand charge transfer band at 460 nm, which is comparable to those of previously reported complexes [16]. The electronic spectrum of complex **2** in methanol showed a weak absorption at 675 nm followed by several intense absorptions in the range 600–670 nm which for copper(II) complexes of Schiff bases and related ligands are assigned to *d-d* transitions [17–19]. The intense absorptions are most probably due to the ligand-to-metal charge transfer and intraligand transitions.

Thermal studies

It is observed from the TGA curve that on heating under non-isothermal condition, complex **2** loses two molecules of methanol in the temperature range 75–85 °C. Then it underwent decomposition at higher temperature resulting in the formation of

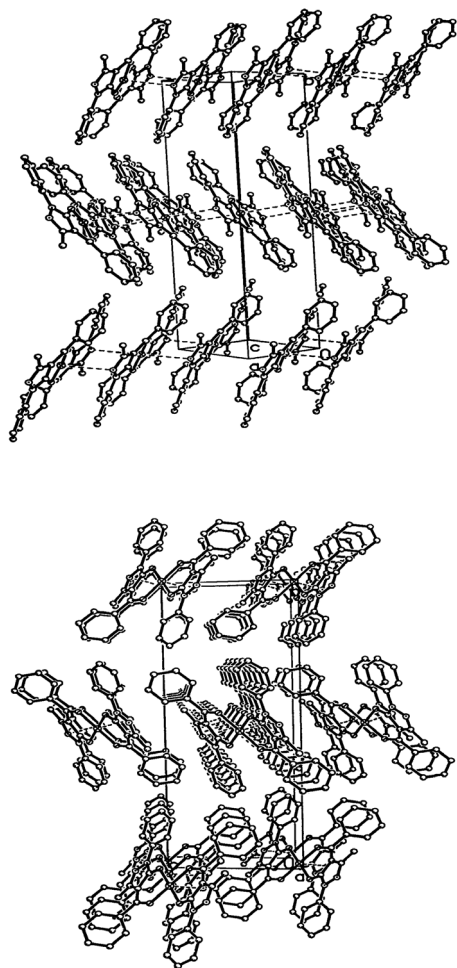


Fig. 2. The packing diagrams of complex **1**.

copper oxide, which was confirmed by qualitative test.

Magnetic susceptibility

The room temperature magnetic moments ($1.72 \mu_B$ for **1** and $1.74 \mu_B$ for **2**) of the complexes are very close to the spin only values for copper(II) systems.

Structural discussion

The X-ray structural investigation of $[\text{Cu}(\text{PMBP})_2]$ **1** shows that in this compound copper(II) ions have a four coordinate square planar structure with slight distortion. An ORTEP plot along with the atom numbering scheme of $[\text{Cu}(\text{PMBP})_2]$ is given in Fig. 1 and the packing arrangement of the molecules in the unit cell

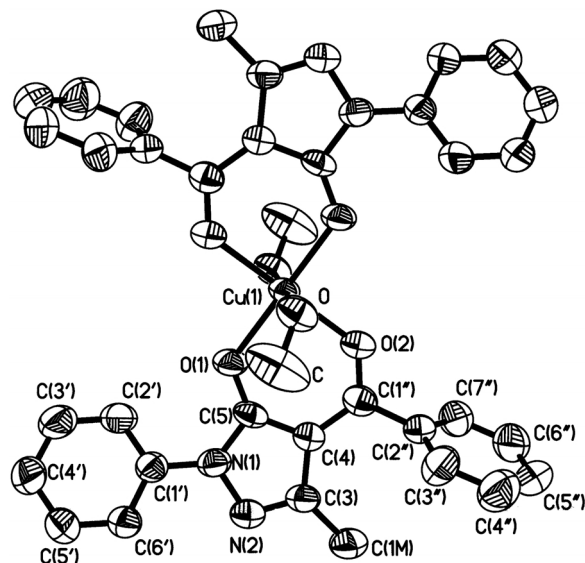


Fig. 3. Ortep plot of complex **2** with atom numbering scheme.

with intermolecular contacts through nitrogen atoms of the pyrazole ring with copper is given in Fig. 2. The bond lengths and angles for complex **1** are listed in Table 2. In the discrete molecule the central copper ion is attached to four oxygen atoms of deprotonated 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone ligands at the four equatorial positions. In the equatorial plane the *trans* angles $[\text{O}(1)\text{-Cu}(1)\text{-O}(3)]$ and $[\text{O}(2)\text{-Cu}(1)\text{-O}(4)]$ are exactly 180° while the bite angles deviate slightly from 90° $[\text{O}(1)\text{-Cu}(1)\text{-O}(2)] = 93.47^\circ$; $[\text{O}(2)\text{-Cu}(1)\text{-O}(3)] = 86.53^\circ$. Each ligand molecule forms a six-membered ring with the metal ion. The distortion of the structure from square planar to tetrahedral can be evaluated through the parameter Δ introduced by Galy *et al.* [20] and applied by Ribas and Kahn [21]. Cu-O bond lengths 1.9086(17) and 1.9189(17) Å are well comparable with the Cu-O bond lengths found in other Cu(II) complexes. Comparable distances between Cu(1)-O(1) and Cu(1)-O(2) indicate that delocalization of the negative charge occurs between O(1) and O(2) of the ligand.

The crystals of complex $[\text{Cu}(\text{PMBP})_2(\text{CH}_3\text{O})_2]$ **2** contain discrete molecules. Here also four oxygen atoms of two deprotonated 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone ligand occupy the four equatorial positions of a distorted octahedron around Cu(II) like the square planar coordination in $\text{Cu}(\text{PMBP})_2$ **1**. The two CH_3OH molecules are coordinated to cop-

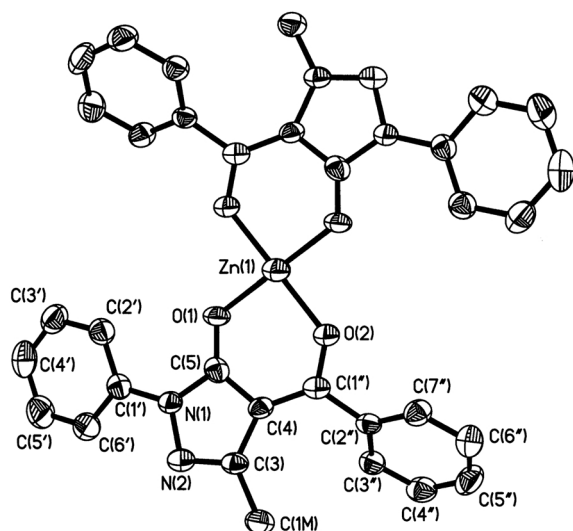


Fig. 4. Ortep plot of complex **3** with atom numbering scheme.

per(II) by their oxygen atoms and occupy the *trans* axial positions.

An ORTEP plot of complex $[\text{Cu}(\text{PMBP})_2(\text{CH}_3\text{O})_2]$ **2** along with the atom numbering scheme is given in Fig. 3. The bond distances and angles are listed in Table 2. The central Cu(II) center in $[\text{Cu}(\text{PMBP})_2(\text{CH}_3\text{O})_2]$ possesses a slightly distorted octahedral geometry with *trans* angles at 180° . The *cis* angles $[\text{O}(1)\text{-Cu}(1)\text{-O}(2), 89.37(13)^\circ; \text{O}(1)\text{-Cu}(1)\text{-O}(2)\#1, 90.63(13)^\circ]$ deviates slightly from 90° . In the compound $[\text{Cu}(\text{PMBP})_2(\text{CH}_3\text{O})_2]$ **2**, the distortion of *cis* angles from 90° are small in comparison to that of

the square planar $[\text{Cu}(\text{PMBP})_2]$ **1**. The negative charge of the ligand is also delocalized over the two oxygen atoms as evidenced from the O-C bond distances $[\text{O}(2)\text{-C}(1''), 1.258(5) \text{ \AA}; \text{O}(1)\text{-C}(5), 1.273(5) \text{ \AA}]$. The copper atom is located at a center of inversion. In $[\text{Cu}(\text{PMBP})_2(\text{CH}_3\text{O})_2]$, the two independent Cu-O bond lengths $[\text{Cu}(1)\text{-O}(1) = 2.033(3), \text{Cu}(1)\text{-O}(2) = 2.108(4) \text{ \AA}]$ are comparable with the Cu-O distances of other reported copper complexes but longer than those found in square planar $[\text{Cu}(\text{PMBP})_2]$ **1**. A methanol molecule is coordinated to Cu(II) from a more distant position $[\text{Cu}(1)\text{-O} = 2.152(4) \text{ \AA}]$.

X-ray structural investigation of $[\text{Zn}(\text{PMBP})_2]$ **3** indicates that the Zn(II) ion is surrounded by four oxygen atoms of two deprotonated 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone ligands in a square planar geometry. An ORTEP plot along with the atom numbering scheme is given in Fig. 4. The bond lengths and angles are listed in Table 2. The discrete molecule of $[\text{Zn}(\text{PMBP})_2]$ **3** possesses a slightly distorted square planar geometry. Here also *trans* angles $[\text{O}(1)\#1\text{-Zn}(1)\text{-O}(1), \text{O}(2)\text{-Zn}(1)\text{-O}(2)\#1]$ are 180° by symmetry and the *cis* angles $(\text{O}(1)\#1\text{-Zn}(1)\text{-O}(2) = 86.59(13)^\circ; \text{O}(1)\text{-Zn}(1)\text{-O}(2) = 93.41(13)^\circ)$ deviate slightly from 90° , but are similar to $[\text{Cu}(\text{PMBP})_2]$ **1**. The Zn-O bond distances $[\text{Zn}(1)\text{-O}(1) = 1.909(3); \text{Zn}(1)\text{-O}(2) = 1.922(3) \text{ \AA}]$ are comparable with the Zn-O bond distances found in similar compounds.

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