# Synthesis, Structure, Antibacterial and Spectroscopic Properties of a Zinc(II) Complex with the Ligand 4-Heptanoyl-pyrazol-5-one

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**Abstract.** The long-chain ligand, 1-phenyl-3-methyl-4-heptanoyl-pyrazol-5-one (HL) and its zinc(II) complex  $ZnL_2$  were synthesized. The structure and the properties of  $ZnL_2$  were characterized by elemental analysis, IR spectroscopy, X-ray diffraction, and thermogravimetric analysis. The zinc ion is five-coordinated in a square-pyramidal environment by four oxygen atoms of the HL ligands in the equatorial plane and one water molecule in the axial position. The water molecule

# **1** Introduction

Acylpyrazolones have attracted considerable interest in the chemistry of chelate systems due to the fact that they are widely used as solvent extractions of metal ions, laser materials, and NMR shift-reagents.<sup>[1–3]</sup> Their metal complexes were found to display catalytic performance, biological activity,<sup>[4,5]</sup> and enhanced luminescence. Previously, 4-acylpyrazolone derivatives and their transition metal complexes were reported.<sup>[6–8]</sup> However, the long-chain ligand, 1-phenyl-3-methyl-4-heptanoyl-5-pyrazolone, and its zinc(II) complex has not been reported to date. In order to fill the gap of pyrazole-containing 4-h-eptanoyl ligands, this paper focused on the synthesis and characterization of a novel acylpyrazolone and its zinc complexes. Furthermore, the antibacterial properties of the complex were investigated.

## 2. Experimental Section

## 2.1 Reactants and Physical Measurements

All chemical were commercially available and used without further purification. Element analyses(C, H, and N) were performed with a Vario ELIII elementar. Infrared spectra were recorded with a Perkin-Elmer FTIR-1730 spectrophotometer (4000–400cm<sup>-1</sup>) with a crystal-line sample in KBr pellets. Thermal analysis was performed with a

is directly bonded to  $Zn^{2+}$  and involved in intermolecular hydrogen bonding network. The complex and its corresponding ligand were screened in vitro against some strains of the human pathogenic bacteria. The metal complex exhibits higher antibacterial activity than its corresponding ligand. The complex exhibits purple effect emission as the result of fluorescence from the intraligand emission excited state.

Perkin-Elmer Diamond TG-DTG thermal analyzer (6 mg sample was placed in a platinum pan Ø 5 mm and heated from 28 to 776 °C at a rate of 10 °C·min<sup>-1</sup> in a nitrogen atmosphere). Fluorescence spectra were obtained with a Perkin-Elmer LS55 luminescence spectrophotometer using a 150W xenon lamp as excitation source. UV/Vis spectra were recorded with a HitachiU-3010 UV/Vis spectrophotometer made in Japan.

#### 2.2 Synthesis

The complex was prepared as translucent crystalline material by reaction of HL (synthesized according to the method reported by *Marchetti*,<sup>[9]</sup> yield 71 %) and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in ethanol solution. The mixture was stirred and refluxed at 78 °C for 6 h. The reaction procedure is shown in Scheme 1. Single crystals for X-ray diffraction analysis were obtained by evaporating slowly the solvent from a solution of DMF at room temperature. Yield:69 %. C<sub>32</sub>H<sub>42</sub>N<sub>4</sub>O<sub>5</sub> Zn: calcd Zn 9.96; C 58.89; H 6.44; N 8.58 %; found: Zn 9.95; C 58.88; H 6.43; N 8.57 %.



Scheme 1. Reaction leading to the complex.

#### 2.3 Crystallography

Diffraction data were measured with a Bruker SMART APEX CCD diffractometer. The data were collected with graphite-monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å) at 296 K. The structure was solved by direct method and refined by full-matrix least-squares procedures using the SHELXL-97 software package. Crystallographic data are summarized in the literature.<sup>[10]</sup>

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#### 2.4 Biological Studies

The complex and the ligand were individually tested against pathogenic bacteria (Gram negative and Gram positive), namely Escherichia coli (ATCC 8739), Staphylococcus aureus (ATCC 6538), Bacillus subtilis, and Staphylococcus epidermidis. The organisms were obtained from the Department of Microbiology, Harbin University, China. Antibacterial activities of the ligand and metal complex were carried out using the disc diffusion method described by Bauer et al.[11] Bacteria were maintained on Mueller-Hinton nutrient agar at 4 °C. Molten Mueller Hinton agar was inoculated with a broth culture of the respective bacterial strains and poured over sterile 90 mm Petri dishes. Both metal complex and ligand were dissolved in DMF to a final concentration of 10 mg·mL<sup>-1</sup>. Sterile Whatman No. 1 (6 mm) disc were separately impregnated with each sample to be tested at 5.0 mg·mL<sup>-1</sup> and placed on the inoculated agar. The plates were incubated at 37 °C for 24 h and zones of inhibition were measured at the end of the incubation period. The standard antibiotic reference drug used is chloramphenicol.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-803939 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

### **3** Results and Discussion

#### 3.1 Crystal Structure

In the zinc complex, the central atom displays square-pyramidal coordination, which is strongly distorted towards trigonal-bipyramidal coordination (Figure 1 and Figure 2). Characteristic of the distortion are the angles about the zinc atom: 98.08(11)° 104.14(9)° (O1–Zn1–O5), (O5-Zn1-O3),89.97(8)° (O1-Zn1-O3), and 151.27(10)° O1-Zn1-O2. The Zn-O bond lengths were found in the range of 1.9723(18)-2.070(2) Å. The C–O and C–C bond lengths within the chelate rings are nearly equal, indicating delocalized 7r electrons. Both chelate rings are folded about the oxygen donor atoms, by angles of  $1.276(3)^{\circ}$  and  $1.252(3)^{\circ}$ . The planes formed by the chelate and pyrazolone rings are nearly parallel to each other. The double bonds N2=C9 1.316(4) Å and N4=C26 1.308(4) Å are characteristic for the pyrazolone ring. The planes of the phenyl rings are slightly twisted with respect to the pyrazolone planes (characterized by torsion angles of 11.26°). The complex shows pseudo twofold symmetry, with the Zn and O5 atoms positioned on the non-crystallographic twofold axis. Intermolecular hydrogen bonds were found between atoms O5 and N2 via H2w, as well as between atoms O5 and N4 via H1w. Thus, each molecule is linked to two others, forming infinite chains. The H1w N4 bonds are located nearly parallel to the b axis, but the H2w···N2 bonds are oriented parallel to the *ab* plane. The structure is closely related to that of aqua bis(acetylacetonato)zinc, which was also described as trigonal bipyramidal, whereas bis(benzoylacetonato)(ethanol)zinc was observed to be more square-pyramidal. However, any similar zinc chelates including the pyrazolone moiety are not known.



Figure 1. Molecular structure of the complex showing 50% probability displacement ellipsoids and hydrogen atoms as spheres of arbitrary radii.



**Figure 2.** Crystal packing of the complex, viewed along the c axis. Hydrogen atoms were omitted for clarity.

#### 3.2 IR and UV/Vis Spectroscopy

There are conspicuous differences between the complex and free ligand in the IR spectra.<sup>[12]</sup> The medium-intensity band at  $3210 \text{ cm}^{-1}$ , assigned to v(OH) of diketone tautomer, and one strong band around 1631 cm<sup>-1</sup>, assigned to (C=O) of the lateral chain, are absent in the complex.<sup>[13]</sup> In the complex, there are three new bands at 1077 cm<sup>-1</sup>, 2950 cm<sup>-1</sup>, and 432 cm<sup>-1</sup>, assigned to v(C–O<sup>-</sup>), water molecules, and v<sub>s</sub>(Zn–O), respectively.<sup>[14]</sup> From these observations, it is concluded that the enolic proton of the ligand is replaced by zinc(II) in the complex.

UV/Vis absorption spectra of the title ligand and complex in ethanol solution were tested in the wavelength range of 190– 500 nm. Three absorptions of the ligand at 205, 230, and 267 nm are attributed to  $\pi$ - $\pi$ \* transitions of the aryl ring, carbonyl, and n- $\pi$ \* transition of carbonyl, respectively.<sup>[15]</sup> Compared with the free ligand, the absorption at 205 and 230 nm disappeared in the complex. Moreover, the band at 267 nm of HL emerged blue shifting to 263 nm in the complex. The result of the shifting is that the coordination reaction reduced the auxochromic effect of the ligand.

#### 3.3 Fluorescence Spectroscopy

The fluorescence spectra of the title complex and the ligand in ethanol solution at room temperature were investigated. As shown in Figure 3, the complex emits an intense purple fluorescence centered at 406 nm upon an excitation wavelength of 338 nm. The emission of the complex is assigned to the fluorescence from the intraligand emission excited state. Compared with the ligand (440 nm), the emission wavelength of the complex is blue-shifted by 34 nm. Generally, multiple  $\pi$ -- $\pi^*$  stacking interactions and protonated ligands contribute to blue shift of emission band and enhancement of fluorescence efficiency.<sup>[16]</sup> The complex could be anticipated as potential fluorescent materials in visible light.



Figure 3. Excitation and emission spectra for the complex at room temperature. Inset shows the excitation and emission spectra of the ligand.

#### 3.4 Thermogravimetric Analysis

The TG and DTG curves of  $Zn(L)_2$ ·(H<sub>2</sub>O) show the decomposition of the complex in three regions. The first region at 176 °C with mass loss of 2.8% (weight loss of calcd. 2.76%) is the evolution of one water molecule. Meanwhile, in this temperature range, the DTA curve shows an endothermic peak. This behavior is typical of the energy absorption and the consequent energy release due to the structural rearrangement of the complex undergoing the loss of a chain involved in the coordination. The second decomposition at 317 °C with a mass loss of 65.16% is close to the theoretical mass loss of the complex stepwise decomposed to gas production. The final products are ZnO and carbon, the experimental value (12.53%) is in good agreement with the theoretical mass (12. 2%).

#### 3.5 Biological Properties

Antibacterial activity of the ligand and complex were tested in vitro against 4 human pathogenic bacteria. The activities were compared with that of chloramphenicol, a standard broad-spectrum antibiotic for bacterial strains. Zones of inhibition against the growth of various microorganisms are listed in Table 1. It was found that the inhibitory effects of the HL and the complex differed with the species of bacteria. HL and the complex were active against all the bacterial strains tested, with inhibitory zones of 10-13 and 13-19 mm, respectively. The results show that the complex exhibited higher zones on inhibition than its corresponding ligand against all the bacterial strains tested. ZnL<sub>2</sub> showed the highest zone of inhibition of 19 mm against E. coli, The increased activity of the zinc complex can be explained on the basis of Overtones concept<sup>[17]</sup> and *Tweedy*'s chelation theory.<sup>[17,18]</sup> The complex disturbs the respiration process of the cell and thus blocks the synthesis of proteins, which restricts further growth of the organism.

 Table 1. Antibacterial activities of the ligand HL and its zinc(II) complex.

| Diameter of inhibitior<br>Bacterial strains | n zone o<br>HL | f bacteria in different<br>ZnL <sub>2</sub> | compounds /mm<br>Chloramphenicol |
|---|----------------|---|----------------------------------|
| B. subtilis                                 | 11             | 13  | 21                               |
| E. coli                                     | 10             | 19  | 20                               |
| S. epidermidis                              | 13             | 17  | 22                               |
| S. aureus                                   | 10             | 18  | 20                               |

# **4** Conclusions

An 4-acylpyrazolone derivative ligand and its zinc(II) complex were synthesized and characterized. Experimental data showed that the zinc ion is coordinated by four oxygen atoms of HL ligands in the equatorial plane and one water molecule in axial positions. The solid-state structure is stabilized by hydrogen bonding involving hydrogen atoms of water and nitrogen atoms of the pyrazole ring. A comparative study of the HL and its complex showed that the complex exhibited higher antibacterial activity than the ligand.

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1.302 Mg·m<sup>-3</sup>,  $\mu$ (Mo- $K_a$ ) = 0.784 mm<sup>-1</sup>,  $\phi$  and  $\omega$  scans,  $\theta$  range = 2.63–27.91°, 12267 reflections collected, 7966 unique reflections [*R*(int) = 0. 0279] were used in all calculations, number of variables = 4680, *R* = 0.0524 (for [*I*>2sigma (*I*)], 0.1077 (for all data), *Rw* = 0.1460, *S* = 0.1234.

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