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Syntheses, Crystal Structures and Fluorescence Properties of Zn(II) Complexes with Pyrazolone Derivatives

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Abstract *N*-(1,3-Diphenyl-4-benzal-5-pyrazolone)-salicy lidene hydrazone(H₂L¹) and its zinc complex Zn (HL¹)₂ · 2CH₃OH (1) have been synthesized and characterized by elemental analyses, IR spectra, thermal analyses and single-crystal X-ray diffraction studies. The X-ray diffraction analyses of the complex Zn(HL¹)₂ · 2CH₃OH (1) and the known compound Zn₄(L²)₄ (2) (H₂L² = *N*-(1,3-diphenyl-4-phenylethylene-5-pyrazolone)-salicylidene hydrazone) show that different acyl groups in position 4 of pyrazolones may lead to the different coordination mode of the ligands and distinctive structures of the same central metal Zn(II) complexes, of which **1** is a mononuclear complex while **2** is a tetranuclear complex. Meanwhile, two Zn(II) complexes have different thermal stabilities and fluorescence properties.

Keywords Crystal structures · Fluorescence · Pyrazolone derivatives · Zinc complexes

Introduction

The multidentate ligand is a critical factor in the design and synthesis of polynuclear metal complexes, which have attracted much attention from the chemists in recent years. Meanwhile, pyrazolones, especially 4-acyl pyrazolones, display several different coordination modes with respect to classical β -diketonates [1–4]. Meanwhile, 4-acyl pyrazolone and its derivatives are widely used in many fields in the society, especially in biological, clinical and

analytical applications [4–7]. On the other hand, compounds containing salicylidene hydrazone and their complexes also possess biological activity and their phenoxy is capable of chelate and bridge properties. So we expect the formation of polyfunctional ligands by the combination of the 4-acyl pyrazolones and salicylidene hydrazone.

Information about the structural properties of the complexes with different 4-acyl pyrazolone-5 derivatives is important to understand the structural features and coordination abilities of the ligands in the complexes. In previous, we have synthesized a series of 4-acyl pyrazolone derivatives with a methyl group or phenyl group in position 3 of pyrazolone [8-10] and reported several transition metal complexes [11-16]. In order to further examine the complexation behaviors of pyrazolone derivatives, we have extended the study to the syntheses of various pyrazolone derivations ligands and their transition metal complexes. Hence, in this paper, the syntheses, crystal structures, fluorescence and thermal stability of N-(1,3-diphenyl-4-benzal-5-pyrazolone)-salicylidene hydrazone (H_2L^1) and the complex $Zn(HL^1)_2 \cdot 2CH_3OH$ (1) are reported. Compared 1 with the tetranuclear complex $Zn_4(L^2)_4$ (H₂L² = N-(1,3-diphenyl-4-phenylethylene-5-pyrazolone)-salicylidene hydrazone) (2), the different acyl groups in position 4 of pyrazolones may lead to the different coordination mode of the ligands and distinctive structures of the same central metal Zn(II) complexes.

Experimental Section

Physical Measurements

Elemental analyses of carbon, hydrogen and nitrogen were performed on a PE-2400 analyzer. IR spectra were

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recorded on a BRUKER EQUINOX-55 spectrophotometer within 400-4000 cm⁻¹ using the samples prepared as pellets with KBr. Melting point was measured with a model Tech X-6 melting point apparatus. Thermogravimetric measurements were carried out on a Netzsch STA 449C Model instrument in dynamic air atmosphere $(30 \text{ cm}^3 \text{ min}^{-1})$, the rate of heating was 15 °C min⁻¹. The crystal structures were determined by a Siemens P4 diffractometer and SHELXL-97 crystallographic software package of molecular structure. The emission and excitation spectra were taken with a Hitachi F-4500 fluorescence spectrophotometer with a xenon arc lamp as the excitation light source. Excitation and emission bandwidths of 2.5 nm were employed and the fluorescence spectra were corrected for nonlinear instrumental response and blank solvents.

Materials

All chemicals and solvents were of analytical grade and commercially available. Salicylal hydrazone (SAH) was prepared according to a published procedure [9]. 1,3-Dipheny 1-4-benzoyl-pyrazolone-5 (DPBP) and $Zn_4(L^2)_4$ ($H_2L^2 = N$ -(1,3-diphenyl-4-phenylethylene-5-pyrazolone)-salicylidene hydrazone) (**2**) were prepared according to the reference [12, 17].

Synthesis of the Ligand H₂L¹ (DPBP-SAH)

The ligand H_2L^1 was prepared by refluxing equimolar DPBP and SAH in methanol for ca. 3 h, adding a few drops of glacial acetic acid as a catalyst. On cooling, the yellow solid obtained was filtered, washed with ethanol, and dried in vacuum. Suitable X-ray diffraction quality single crystals were obtained by slow evaporation of ligand in CH₃OH. M.p. = 252–254 °C. *Anal.* Calcd. for $C_{29}H_{22}N_4O_2$ (%): C, 75.97; H, 4.84; N, 12.22; Found: C, 75.93; H, 4.71; N, 12.09.

Synthesis of $Zn(HL^1)_2 \cdot 2CH_3OH(1)$

The ligand H_2L^1 (1 mmol) was dissolved by the addition of an aqueous solution of 3 M NaOH in 100 mL of methanol. To this solution was added dropwise the aqueous solution of $Zn(OAc)_2$ ·4H₂O (1 mmol) with constant stirring. The mixture was further refluxed for 1 h. The resulting yellow precipitate was filtered off, washed with methanol and dried naturally. Yellowish single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of **1** in CH₃OH. *Anal.* calcd. for C₆₀H₅₀N₈O₆Zn (%): C, 69.00; H, 4.83; N, 10.73. Found: C, 68.94; H, 4.89; N, 10.70.

X-Ray Crystallography

Crystals suitable for X-ray diffraction analyses were mounted on a glass fiber and diffraction experiments were performed on a Siemens P4 four-circle diffractometer using graphite monochromated MoK α radiation ($\lambda =$ 0.71073 Å). The crystal structures were solved by direct method, and refined by full-matrix least squares on F^2 . Empirical absorption corrections were applied to 1. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were placed in calculated positions and refined isotropically with a riding model. All calculations were performed using SHELXL-97 program package. Crystal data and information about the data collection and structure refinement for H₂L¹ and 1 are given in Table 1. The selected bond lengths and angles are listed in Table 2.

CCDC: 613452 (H₂L¹); 232658(1)

Table 1 Crystallographic Parameters for H_2L^1 and 1

Compound	H_2L^1	1	
Empirical formula	$C_{29}H_{22}N_4O_2$	C60H50N8O6Zn	
Formula weight	458.51	1044.45	
Temperature (K)	294(2)	292(2)	
Wavelength (Å)	0.71073	0.71073	
Crystal system	Monoclinic	Monoclinic	
Space group	Cc	C2/c	
a (Å)	12.958(3)	27.274(4)	
b (Å)	21.961(4)	12.478(1)	
<i>c</i> (Å)	8.754(1)	17.330(2)	
β (°)	110.38(1)	120.95(7)	
Volume (Å ³)	2335.25(71)	5058.0(14)	
Ζ	4	4	
Density (calculated) (g/cm ³)	1.304	1.372	
Absorption coefficient (mm^{-1})	0.084	0.548	
<i>F</i> (000)	960	2176	
Crystal size (mm)	$0.60 \times 0.36 \times 0.10$	$0.44 \times 0.40 \times 0.36$	
Reflections collected	3453	5102	
Independent reflections	3108 [$R_{\rm int} = 0.0147$]	4581 [$R_{\rm int} = 0.0171$]	
Data/restraints/ parameters	3108/4/325	4581/1/349	
Goodness-of-fit on F^2	0.801	0.854	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0405$	$R_1 = 0.0347$	
	$wR_2 = 0.0711$	$wR_2 = 0.0695$	
R indices (all data)	$R_1 = 0.0961$	$R_1 = 0.0627$	
	$wR_2 = 0.0808$	$wR_2 = 0.0745$	
Largest diff. peak and hole $(e \cdot A^{-3})$	0.146 and -0.130	0.205 and -0.347	

Table 2 Selected bond lengths (Å) and angles (°) for H_2L^1 and 1

H_2L^1			
O(1)–C(7)	1.252(3)	N(3)–N(4)	1.369(3)
O(2)–C(29)	1.369(4)	C(7)–C(8)	1.448(4)
N(1)–C(7)	1.373(4)	C(8)–C(16)	1.380(4)
N(1)–N(2)	1.414(3)	C(8)–C(9)	1.443(4)
N(3)–C(16)	1.344(3)	N(2)–C(9)	1.304(3)
C(7)–N(1)–N(2)	111.6(2)	C(9)–C(8)–C(7)	105.1(3)
C(9)–N(2)–N(1)	106.7(2)	N(2)-C(9)-C(8)	111.5(2)
O(1)–C(7)–C(8)	127.9(3)	N(3)-C(16)-C(8)	117.9(3)
N(1)-C(7)-C(8)	105.1(3)	N(4)-C(23)-C(24)	120.8(3)
C(16)–N(3)–N(4)	121.2(3)	C(23)-N(4)-N(3)	116.5(2)
1			
Zn-O(1)	2.0022(14)	Zn-N(3)	2.1764(18)
Zn-O(1A) ^a	2.0022(14)	Zn-O(3)	2.2135(18)
Zn-N(3A) ^a	2.1764(18)	Zn-O(3A) ^a	2.2135(18)
O(1)–Zn–O(1A) ^a	168.01(8)	O(1)–Zn–O(3A) ^a	86.54(6)
O(1)–Zn–N(3A) ^a	100.20(6)	N(3) ^a –Zn–O(3)	174.63(7)
O(1)-Zn-N(3)	88.41(6)	N(3)–Zn–O(3)	94.01(6)
O(1)–Zn–O(3)	84.53(6)	O(3)–Zn–O(3A) ^a	83.70(10)

Symmetry transformations used to generate equivalent atoms: a: -x + 1, y, -z + 1/2

Results and Discussion

IR Spectra

In the spectrum of the free ligand H_2L^1 , the bands at around 3141, 1626 and 1585 cm⁻¹ are assigned to v(NH) [18], v(C=O) [3] and the v(C=N) [6] stretching vibration, respectively. While in the spectrum of complex 1, the bands of 3141 and 1626 cm⁻¹ are both disappeared, and new bands are observed at 1335 cm⁻¹ due to $v(C=O^-)$ [19] and around 1605 cm⁻¹ assigned to v(C=N-N=C) of hydrazone [20]. From these observations, it is concluded that the ligand react in the enol form and the enolic proton is replaced by metal ion in the complex with new bands of v(C=N) and v(M-N) around 480 cm⁻¹ are appeared in the spectrum of complex 1, which is confirmed that nitrogen atom of azomethine group of hydrazone is coordinated to the metal ion [21].

Crystal Structure of H_2L^1 (DPBP-SAH)

The molecular structure and the packing arrangement in the unit cell of the ligand H_2L^1 are shown in Figs. 1 and 2, respectively. Similar with *N*-(1-phenyl-3-methyl-4-benzal-5-pyrazolone)-salicylidene hydrazone (PMBP-SAH) [9], the crystal structure of H_2L^1 shows that free ligand does not exist in form of Schiff base (II) but in another tautomer keto-form (I) in the solid state (see Scheme 1). There are two

kinds of intramolecular hydrogen bonds, $[N(3)-H\cdots O(1),$ 2.699(3) Å, $143(3)^{\circ}$] and $[O(2)-H\cdots N(4), 2.641(4) Å,$ $147(4)^{\circ}$ in the free ligand. Compared the relevant bond lengths in the H_2L^1 with PMBP-SAH, we can see that the equalization degree of corresponding double bond and single bond are increase. In addition to that, the dihedral angles between pyrazolone ring plane (N1,N2,C9,C8,C7), plane (O1,C7,C8,C16,N3,H3 N), plane (N4,C23,C24,C29,O2, H2O) in H₂L¹ are only in the range of $2-7^{\circ}$, which are smaller than the corresponding dihedral angles in PMBP-SAH. All the above observations confirm that the main skeleton of the ligand molecule are nearly planar and this quasi-coplanarity cause the higher electron dislocalization in H_2L^1 . We have thought that the introduction of aromatic moieties in 3- position of pyrazolone might increase the π -conjugation effect in the molecule so that the coordinating activity of the ligand may be improved. However, a phenyl in 3- position doesn't seem to increase the π -conjugation effect as we have expected before this work, because the dihedral angle between pyrazolone ring plane (N1,N2,C9,C8,C7) and 3- phenyl ring plane (C10–C15) are 60.9° , which is far from 0° or 180° .

In the packing diagram of molecule H_2L^1 , weak C–H…O kind hydrogen bonding interactions have been observed between O1 on pyrazolone rings and hydrogen of 1-phenyl rings C2–H, with the length of 3.401 Å and angle of 148.8°. Thus, a zigzag chain comes into being under the assistance of the weak hydrogen-bonding interactions (Fig. 2).

Crystal Structure of $Zn(HL^1)_2 \cdot 2CH_3OH(1)$

The structure of complex 1, together with the atom-numbering scheme, is illustrated in Fig. 3. Zn(II) atom is coordinated by two oxygen and two nitrogen atoms from two monoanionic bidentate ligands HL¹ and another two oxygen atoms of two methanol molecules. The N3, N3A, O3, O3A atoms occupy the equatorial positions of octahedron and O1, O1A atoms occupy two axial positions, whilst Zn(II) is located in the center of the octahedral geometry. The axial bond lengths of 2.0022(14) Å (Zn–O1) are shorter than the equatorial bond lengths of 2.1764(18) Å (Zn-N3) and 2.2135(18) Å (Zn-O3). The bond angles of O1-Zn-O1A and N3A-Zn-O3 are 168.01(8)° and 174.63(7)°, respectively, which deviated from ideal value 180°. Moreover, the angles found within the equatorial plane are in the range from $83.70(10)^\circ$ to $94.01(6)^\circ$. From the above observations, we conclude that the coordination geometry around Zn(II) is slightly distorted shortened octahedron.

The crystal structure of H_2L^1 shows that free ligand does not exist in form of Schiff base (II) but in another tautomer form (I) in the solid state, while during the formation of the complex 1, keto form of the ligand isomerizes to the



enol form and loses one proton acting as a one-charged bidentate ligand coordinating to Zn(II) atom. Furthermore, intramolecular H-bond interaction $[O(2)-H\cdots N(4), 2.593(3) \text{ Å}, 152(3)^{\circ}]$ still exist in the complex **1**, which is 0.05 Å shorter than the same H-bond in the free ligand. All these results showed that this hydroxyl proton is less prone to dissociate in neutral, acidic or mildly alkaline conditions. The crystal packing diagram of **1** is shown in Fig. 4, the mononuclear complex units are connected by the C20–H…O2 intermolecular hydrogen bonding interactions to give the formation of a 1D chain structure.

Comparing the crystal structures of complexes $Zn(HL^{1})_{2} \cdot 2CH_{3}OH(1)$ and $Zn_{4}(L^{2})_{4}(2)$ [12], we can find that the structure of these compounds are greatly depend on

the nature of the organic ligand. The X-ray diffraction analysis of complex 2 shows that it is a phenoxy-bridged tetranuclear zinc(II) complex without solvent in it. Four penta-coordinated Zn(II) centers are bonded simultaneously to four deprotonated two-charged tridentate ligands arranged in a rectangular shape. The only difference between the two ligands lies in the substitutes on position 4 of pyrazolones, of which a benzal group in ligand H_2L^1 and a phenylethylene group in ligand H_2L^2 , while mononuclear complex 1 and tetranuclear complex 2 were obtained respectively. Entirely different structures between 1 and 2 indicate that substitute groups in ligands might influence the spatial position of the lateral chain and the coordination probability of the atoms in the ligands.





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Fluorescent Spectrum of the Compounds

Free ligands and their corresponding zinc complexes 1 and 2 all exhibit fluorescence in the solid state at room temperature. The emission spectra of them are shown in Fig. 5. The very strong emissions of the free ligand H_2L^1 and H_2L^2 with wavelength from 460 to 660 nm ($\lambda_{max,H2L1} = 532$ nm, $\lambda_{\text{max,H2L2}} = 539 \text{ nm}$) upon excitation at 350 nm are observed, which may due to the chemical structures of the ligands, which contain aromatic ring, fused aromatic rings and two kind of intramolecular hydrogen bonds [22-25]. In the contrast to the case for the free ligand, the emission spectra of complex 1 shows a broad emission band centered at 552 nm with a red-shifted by ~ 20 nm and a mediumintensity emission band occurring at 493 nm with a blue-shifted by ~ 40 nm. The bathochromic shift of the maximum peak position of 552 nm for complex 1 in the solid state may arise from the different fields around H_2L^1 , which also have an intramolecular hydrogen bond after coordination to zinc ion and forming a mononuclear complex 1 [25]. While the significant blue shift emission band at 493 nm for 1 and a very broad emission band (bandwidth at half-height 110 nm) with λ_{max} at 455 nm in compound 2, might be ascribed to the photo-induced charge transfer accompanied with internal charge transfer (ICT) from the donor to the acceptor [25]. The substitution of benzal group with a phenylethylene group may decrease the electron conjugate system to yield a ligand with a higher triplet energy level, so that charge-transfer may occur towards lower energy [25]. This also affects the fluorescence properties of the complexes [26].

Thermal Decomposition

Thermal analysis curve of complex **1** showed that it begins to decompose at around 120 °C corresponding to the endothermic loss of the methanol molecules ($DTG_{max.} = 180$ °C) and then followed with the ligand decomposition by giving broad and strong exothermic. The final solid product of the thermal decomposition was identified as ZnO (found. 8.99, calcd. 7.71%).

Thermal decomposition curve of the complex 2 revealed that it is stable up to 390 °C. The thermal decomposition appears to take place in the temperature range 390–600 °C to give zinc oxide as the final decomposition product,

Fig. 3 Molecular structure of 1 (hydrogen atoms are omitted for clarity)



Fig. 4 Packing diagram of **1** showing supramolecular weak hydrogen-bonding interactions

which indicates the oxidative nature of the decomposition reaction. A sharp peak appears in the DTA curve, which may due to the explosive decomposition of the complex.

The final solid product was found to be zinc oxide for the test value (15.5%) is corresponding to the theoretical mass (15.0%) of ZnO.



Fig. 5 Emission spectra in the solid state of the ligand H_2L^1 , H_2L^2 and complexes 1 and 2

The reason why Zn(II) complex 2 is so stable may be that the μ -phenoxo bridges cause the molecule becoming a big sphere and the bond force between them is so strong that it needs higher energy to break them. As a result, the decomposition temperature of 2 is high and the exothermic peak so wide and strong. It can also be deduced from the result of the crystal structure.

Conclusion

In this paper, N-(1,3-diphenyl-4-benzal-5-pyrazolone)salicylidene hydrazone H₂L¹ and its Zn(II) complex were synthesized and characterized. The results showed that different groups in position 4 of pyrazolones may lead to the formation of Zn(II) complexes with entirely different structures, thermal stabilities and diverse fluorescence properties. It might give a new way to design and synthesis of functional polynuclear metal complexes by using pyrazolone derivatives ligand.

Supplementary Material

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 613452 and 232658. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code_(1223)336033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

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