

氧桥桥连四核 $M_4[2\times 2]$ 格子状结构锌(II)配合物的自组装、 晶体结构及荧光性质

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摘要: 以席夫碱碳腙类配体 H_2L 自组装合成了一个新的 $M_4[2\times 2]$ 四方格子状结构锌(II)配合物 $[Zn_4(HL)_4](ClO_4)_4\cdot 2MeCN\cdot 2MeOH$ ($H_2L=1,5$ -bis(1-(pyridine-2-yl)ethylidene)carbohydrazide), 并对其进行了元素分析、红外光谱、紫外可见光谱和 X-射线单晶衍射法表征。单晶结构分析结果表明配合物中, $Zn(II)$ 离子具有 N_4O_2 型扭曲的八面体配位构型, 4 个配体分别失去 1 个质子后以醇式与金属离子配位, 由 4 个酚氧原子桥连 4 个 $Zn(II)$ 离子形成 $[2\times 2]$ 格子状结构四核配合物。固态荧光测试表明配合物在 530 nm 附近有强的荧光发射峰。

关键词: 锌(II)配合物; 四核配合物; 晶体结构; 荧光性质

中图分类号: O614.24*1

文献标识码: A

文章编号: 1001-4861(2013)12-2609-06

DOI: 10.3969/j.issn.1001-4861.2013.00.360

Oxygen-Bridged Tetranuclear Zn(II) Complex of $M_4[2\times 2]$ Square Grid: Self-Assembly, Crystal Structure and Fluorescent Property

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Abstract: A novel tetranuclear $M_4[2\times 2]$ square grid complex $[Zn_4(HL)_4](ClO_4)_4\cdot 2MeCN\cdot 2MeOH$ ($H_2L=1,5$ -bis(1-(pyridine-2-yl)ethylidene)carbohydrazide) was constructed via self-assembly using Schiff base ligand based on carbohydrazone derivative. The complex was characterized by elemental analyses, IR spectra, UV-Vis absorption spectra and single crystal X-ray diffraction. Single crystal structure analysis showed that all metal atoms have N_4O_2 distorted octahedral coordination spheres and four ligands are monodeprotonated with four enolyl oxygen atoms direct bridging the Zn ions to form a tetranuclear $[2\times 2]$ square grid complex. Furthermore, the fluorescent spectra analysis indicated the tetranuclear $Zn(II)_4$ complex exhibits intense fluorescence emission band at around 530 nm in the solid state. CCDC: 922042.

Key words: zinc(II) complex; tetranuclear complex; crystal structure; fluorescence property

In recent years, variety of metallosupramolecular arrays, particularly, grid-type metal-ion structures and the self-assembly processes involved in their formation

have attracted a considerable amount of attention^[1-5]. Meanwhile, a large number of square and rectangle $[n\times n]$ ($n=2\sim 4$) grid-type complexes with intriguing

收稿日期: 2013-02-16。收修改稿日期: 2013-06-07。

新疆自治区自然科学基金面上项目(No.2012211A009)资助项目。

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electronic or magnetic properties have been reported^[3-12]. In order to construct such grid complexes, the design of the ligands is pivotal, which must provide linear sequences of bidentate and/or tridentate binding sites in combination with different metal ions that favor tetrahedral or octahedral coordination geometry. Ligands based on carbohydrazone cores, modified with pyridine, carboxylate and oxime ends, which display a tautomeric versatility based on the flexible nature of the hydrazone linkages, leading to varied coordination motifs. Furthermore, the bridging oxygen atom makes it capable of generating self-assembled molecular squares. To date, however, only a few studies in the literature concerning the preparation, structural characterization and magnetic and fluorescent properties of transitional metal complexes of this type of carbohydrazone based ligands.

Examples of square and rectangle M_4 $[2 \times 2]$ grid complexes have been obtained through the carbohydrazone based ligands reacted with metal ions for octahedral centers including Fe(II)^[13-14], Co(II)^[14], Ni(II)^[15], and Zn(II)^[16]. In tetranuclear μ -O bridged Fe(II) $[2 \times 2]$ grid complex, $[Fe_4(HL)_4](BF_4)_4 \cdot (H_2O)_2 \cdot CH_3OH$ ($H_2L=1,5$ -bis(1-(pyridine-2-yl)ethylidene)carbonhydrazone) exhibits spin crossover behaviour at ~ 170 K occurring on the two Fe^{II} on the same side of the Fe^{II} square^[13]. It is worth noting that μ -O/ μ -N-N bridged Co_4 rectangle contains two high-spin (HS) and two low-spin (LS) Co(II) ions, which is a rather unusual observation in polynuclear cobalt cluster chemistry^[14]. And the square $[2 \times 2]$ grid Ni(II) complex exhibits intramolecular anti-ferromagnetic exchange^[15]. The differences of magnetic properties of the complexes might arise from different anions, the kind of central metal ions and different substitutions on the ligands. Furthermore, μ -O bridged Zn(II)₄ $[2 \times 2]$ grid complex also reveals interesting frameworks through self-assembly^[16].

Herein, inspired by these investigations, we select ditopic carbohydrazone based ligands: 1,5-bis(1-(pyridine-2-yl)ethylidene)-carbonhydrazone as building block for self-assembly a Zn_4 $[2 \times 2]$ square grid complex. In the complex, all metal centers are in distorted octahedral environment with N_4O_2 coordi-

ation spheres with enolyl oxygen atoms acting as connector between the two adjacent metal atoms. In addition, the complex **1** exhibits intense fluorescence emission band at around 530 nm upon excitation at 350 nm in the solid state.

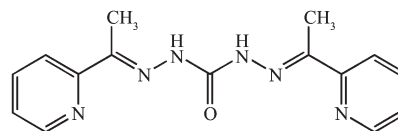
1 Experimental

1.1 Materials and physical measurements

All reagents and solvents in the syntheses were of reagent grade and used without further purification. Elemental analyses of carbon, hydrogen, and nitrogen were carried out on Thermo Flash EA-1112. FT-IR spectra were recorded in the range $600 \sim 4\,000\text{ cm}^{-1}$ region on a BRUKER EQUINOX-55 spectrophotometer with single crystal samples. UV-Vis measurements were performed on a Hitachi U-3010 Spectrophotometer at room temperature. The fluorescence behavior of the ligand and its Zn(II) complex have been studied using Hitachi F-4500 Fluorescence Spectrophotometer with an Xe arc lamp as the light source at room temperature. The excitation and emission band widths are of 5 nm.

1.2 Synthesis of the ligand

The ligand 1,5-bis(1-(pyridine-2-yl)ethylidene)carbonhydrazone (H_2L), as shown in Scheme 1, was synthesized according to the literature^[13]. 2-Acetylpyridine (20.0 mmol, 2.422 8 g) was added dropwise to a solution of carbohydrazone (10 mmol, 0.900 8 g) in methanol (40 mL). The resulting solution was reflux for 3 h and white solids was formed on cooling, which was filtered off, washed with methanol and dried in vacuum. Yield: (75%). Anal. Calcd.(%) for $C_{15}H_{16}N_6O$ ($M=296.33$): C, 60.80; H, 5.44; N, 28.36. Found (%): C, 61.41; H, 5.04; N, 28.28.



Scheme 1

1.3 Preparation of the complex **1**

$[Zn_4(HL)_4](ClO_4)_4 \cdot 2MeCN \cdot 2MeOH$ (**1**): $Zn(ClO_4)_2 \cdot 6H_2O$ (0.40 mmol, 0.144 8 g) dissolved in methanol (10 mL) was added dropwise to the H_2L solution (0.20

Table 1 Crystal and structure refinement data for complex 1

Complex	1	V / nm^3	3.922 46(13)
Formula	$\text{C}_{66}\text{H}_{74}\text{Cl}_4\text{N}_{26}\text{O}_{22}\text{Zn}_4$	Z	2
Formula weight	1 986.79	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.682
Crystal system	Triclinic	μ / mm^{-1}	1.437
Space group	$P\bar{1}$	Reflections collected	42 026
a / nm	1.360 07(3)	Unique reflections (R_{int})	13 750 (0.031 7)
b / nm	1.364 22(3)	Observed reflections	11 805
c / nm	2.125 55(4)	GOF on F^2	1.038
$\alpha / (^\circ)$	93.235 8(16)	$R_1 (I > 2\sigma(I))$	0.043 5
$\beta / (^\circ)$	94.910 9(16)	$wR_2 (I > 2\sigma(I))$	0.104
$\gamma / (^\circ)$	90.737 9(15)	Residuals / ($\text{e} \cdot \text{nm}^{-3}$)	-1 033, 1 563

mmol, 0.059 3 g) in methanol-acetonitrile solution (5 mL:50 mL) with equimolar Et_3N under stirring. The resulting mixture was filtered after stirring for ca. 1 h and the filtrate was allowed to evaporate slowly at ambient temperature. Yellow block crystals suitable for X-ray diffraction were grown after several days. Yield: 63%. IR (single crystal, cm^{-1}): 3 505, 3 250, 3 088, 1 630, 1 573, 1 546, 1 354, 1 086, 780, 621. Anal. Calcd.(%) for $\text{C}_{66}\text{H}_{74}\text{Cl}_4\text{N}_{26}\text{O}_{22}\text{Zn}_4$ ($M_r=1\ 986.79$): C, 39.90; H, 3.75; N, 18.33. Found (%): C, 40.46; H, 3.48; N, 18.66.

1.4 X-ray crystallography

The crystallographic data of complex **1** was collected at 100 K on an Agilent Super Nova Atlas Dual System with a Mo microfocus source and focusing multilayer optics. The crystal structure was solved by direct method using SHELXS-97 program and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXTL-97 crystallographic software package^[17-18]. Hydrogen atoms were constrained to ideal geometries and were included in the refinement in the riding model approximation. Details of the data collection parameters and crystallographic information for complex **1** are summarized in Table 1.

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2 Results and discussion

2.1 IR spectrum

Fig.1 illustrates the IR spectrum of the complex **1**. The IR spectrum shows strong peaks at 3 250,

1 573 and 1 354 cm^{-1} , which are assigned to $\nu(\text{N-H})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{C-O}^-)$ of HL^- , respectively^[10,12]. It is inferred that the ligand reacted in the enol form instead of keto form by deprotonation of N-H proton and coordinated to the metal ion Zn^{II} . Moreover, the band at around 1 086 cm^{-1} in IR spectrum of this complex is the characteristic absorption peak ClO_4^- . From these observations, it is concluded that ClO_4^- are present in the complex for charge balance. The compound was also characterized by elemental analysis and single-crystal X-ray diffraction, which confirm that the four ligands bind to zinc(II) as monodeprotonated HL^- . Thermo-gravimetric data was not obtained, due to the explosive of perchlorate compound.

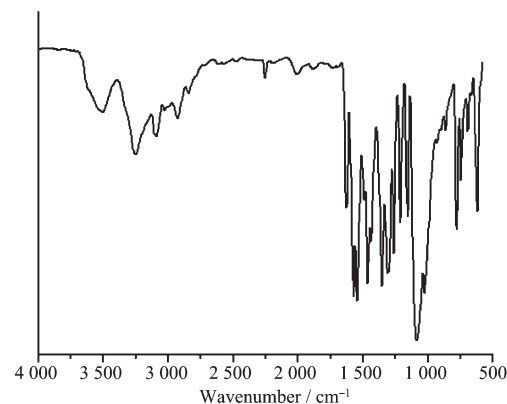


Fig.1 FI-IR spectrum of the complex 1

2.2 Crystal structural description of complex 1

Complex **1** consists of a $[2 \times 2]$ square grid involving four Zn(II) centers bridged by four μ -O atoms. The structural representation of tetranuclear cation $[\text{Zn}_4(\text{HL})_4]^{4+}$ in the complex is shown in Fig.2a, with the core structure depicted in Fig.2b. Important

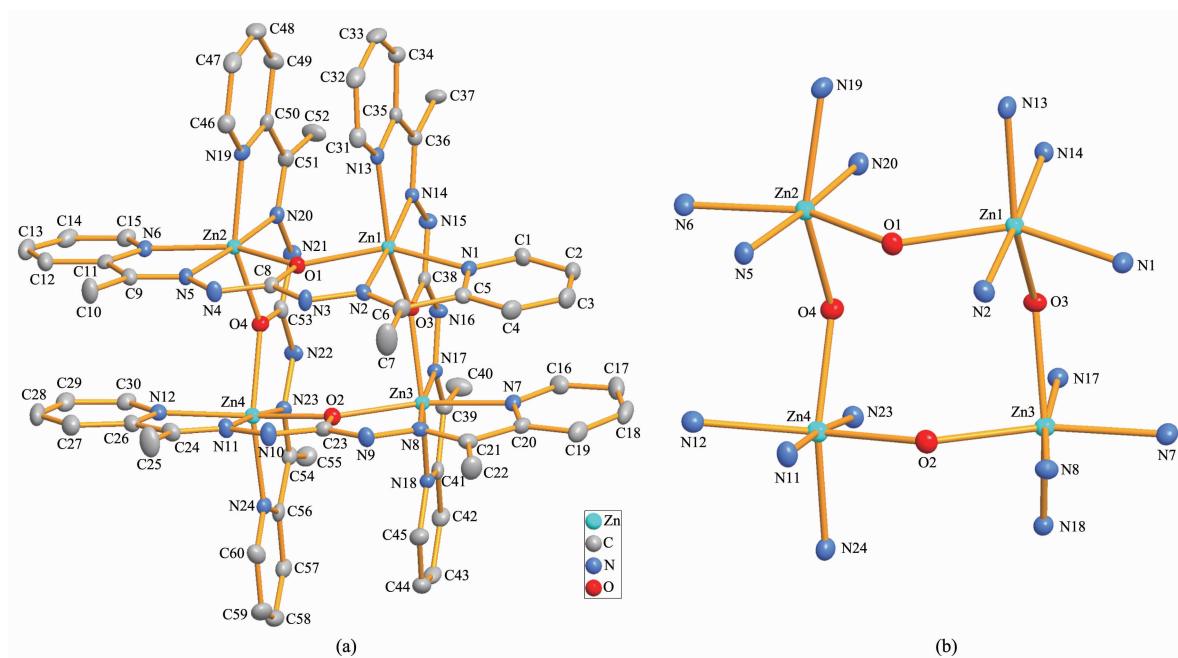


Fig.2 (a) Structural representation of cationic complex with 50% probability displacement ellipsoids and hydrogen atoms were omitted for clarity; (b) Structural representation of the tetranuclear core in the complex **1** with 50% probability displacement ellipsoids

Table 2 Important bond lengths (nm) and angles (°) for complex **1**

Zn(1)-O(1)	0.212 8(2)	Zn(1)-N(1)	0.214 8(3)	Zn(1)-N(2)	0.211 6(3)
Zn(1)-O(3)	0.217 6(2)	Zn(1)-N(13)	0.218 5(3)	Zn(1)-N(14)	0.205 7(3)
Zn(2)-O(1)	0.215 7(2)	Zn(2)-O(4)	0.213 8(2)	Zn(3)-O(2)	0.211 5(2)
Zn(3)-O(3)	0.213 0(2)	Zn(4)-O(2)	0.216 0(2)	Zn(4)-O(4)	0.210 1(2)
N(14)-Zn(1)-N(2)	173.98(11)	N(2)-Zn(1)-O(3)	111.88(10)	N(14)-Zn(1)-O(1)	106.86(10)
N(1)-Zn(1)-O(3)	90.83(10)	N(2)-Zn(1)-O(1)	73.88(10)	N(14)-Zn(1)-N(13)	75.91(11)
N(14)-Zn(1)-N(1)	105.97(11)	N(2)-Zn(1)-N(13)	98.09(11)	N(2)-Zn(1)-N(1)	74.16(11)
O(1)-Zn(1)-N(13)	95.21(10)	O(1)-Zn(1)-N(1)	146.54(10)	N(1)-Zn(1)-N(13)	98.80(11)
N(14)-Zn(1)-O(3)	74.13(10)	O(3)-Zn(1)-N(13)	150.00(10)	Zn(1)-O(1)-Zn(2)	133.07(11)
Zn(4)-O(4)-Zn(2)	132.87(11)	Zn(3)-O(2)-Zn(4)	134.81(11)	Zn(3)-O(3)-Zn(1)	134.59(11)
O(1)-Zn(1)-O(3)	92.00(9)	O(4)-Zn(4)-O(2)	91.80(9)	O(2)-Zn(3)-O(3)	90.46(9)
O(4)-Zn(2)-O(1)	91.65(9)				

bond lengths (nm) and angles (°) for complex **1** are listed in Table 2. The cation is composed of four zinc ions and four partially deprotonated ligands; each distorted octahedral zinc atom is located at a corner of the square. Each ligand loses one proton upon coordination to Zn (II) in monoanionic forms after enolization with pyridyl N atoms, azomethine N atoms and enolyl O atoms belonging to two perpendicular HL⁻ ligands. All the ligands are in *cis*-configurations (Fig.2) and arranged in two parallel pairs, above and

below the tetra zinc square arrangements. All the six-coordinate zinc(II) centers are surrounded by two sets of N₂O tridentate units from different ligands. The Zn-Zn bond lengths are in the range of 0.388 6~0.397 2 nm forming a Zn₄ [2×2] square grid (Fig.2), with the oxygen atoms acting as a bridging atoms between the two adjacent zinc(II) centers. Relative to the Zn₄ mean plane, the zinc(II) ions of the square are shifted by *ca.* 0.028 nm in an up-down-up-down fashion leading to a small tetrahedral distortion of the Zn₄ square, resulting

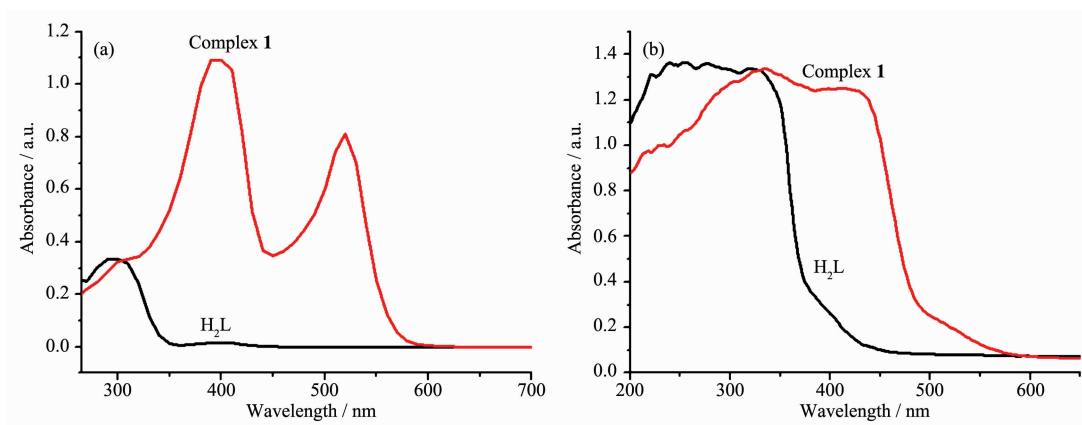


Fig.3 UV-Vis spectra of ligand H_2L and complex **1** at room temperature: (a) in DMF solution, (b) in the solid state

a boat like arrangement. The Zn-O bonds have alternating long and short distances (from 0.210 1(2) to 0.217 6 (2) nm) around the Zn_4O_4 arrangement and the Zn-O-Zn angles are in the range of $132.87 (11)^\circ \sim 134.81 (11)^\circ$. In comparison, the structure of the complex is similar to the reported complex $[Zn(HL)]_4 (BF_4)_4 \cdot 10H_2O$ (H_2L = bis (2-benzoylpyridine ketone) carbohydrazone)^[16].

2.3 UV-Vis absorption spectra

The UV-Vis spectra recorded for ligand H_2L and complex **1** dissolved in N,N -dimethyl formamide (DMF) (concentration $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) and in the solid state at room temperature are shown in Fig.3a and 3b, respectively. In DMF solution, the H_2L shows an absorption band at 298 nm, which attributed to the π - π^* transition of the ligand, and the complex **1** displays two intense bands at 396 and 519 nm, arising mainly from the K band of the $L \rightarrow M$ (charge transfer) transition^[19-20]. The intense bands suggest that the ligand H_2L coordinate to metal Zn(II) to form complex **1**, which increased the molecular conjugate system and reduced the energy system^[20]. Therefore, the absorption spectrum of complex **1** exhibits a large red shift. In the solid state, both of the ligand and complex **1** present broad absorption bands in the range of 200 to 600 nm, as shown in Fig.3b, which is attributed to intraligand transition and charge transfer^[21].

2.4 Fluorescent properties

The fluorescent spectra of the free ligand H_2L and complex **1** in the solution of DMF did not display evident fluorescence emission band, due to the

coordination effect of the solvents, namely solvate effect, which results to the formation of fluorescence quenching phenomenon. However, in the solid state, the complex **1** exhibits one intense fluorescence emission band at around 530 nm, and the ligand shows a weak wide emission band at around 360~550 nm, as shown in Fig.4. Compared with the luminescence of ligand, the emission energy of complex **1** is much higher and shows a large red shift, which may be attributed to the coordination of Zn(II) center to the ligand^[22]. The good fluorescence efficiency indicated that **1** may be a good candidate for green fluorescent materials.

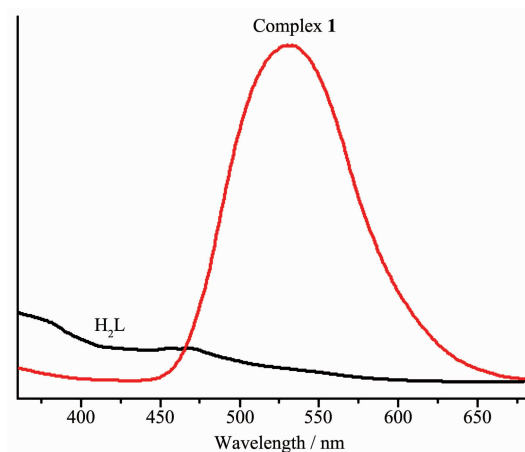


Fig.4 Emission spectra of ligand H_2L and complex **1** in the solid state at room temperature

3 Conclusions

In this work, a novel tetranuclear complex was constructed via self-assembly using ligand based on carbohydrazone derivative, in which the bridging

oxygen atom makes it capable of generating molecular square Zn_4 [2×2] grid structure. In the complex, all the metal centers have distorted octahedral geometry with N_4O_2 coordination spheres. The results demonstrate that carbohydrazone ligands can be well used to build a series of novel polynuclear complexes. Moreover, the complex **1** shows maximum fluorescence emission at around 530 nm in the solid state at room temperature. Our future work will continue to focus on the self-assembly of supramolecular architectures by the carbohydrazone derivatives ligands possessing different coordination sites and different metal ions.

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