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A new zinc(II) supramolecular square: synthesis, crystal structure, thermal behavior and luminescence

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Abstract: A new square-shaped Zn(II) complex, $[\text{Zn}_4(\text{L})_4(\text{phen})_4] \cdot 6\text{H}_2\text{O}$ (**1**, L = 2-hydroxynicotinate and phen = 1,10-phenanthroline), was synthesized under hydrothermal condition. The crystal of **1** belongs to triclinic, space group $P\bar{1}$ with $a = 10.773(2)$ Å, $b = 12.641(3)$ Å, $c = 13.573(3)$ Å, $\alpha = 107.44(3)^\circ$, $\beta = 102.66(3)^\circ$, $\gamma = 93.89(3)^\circ$, $\text{C}_{72}\text{H}_{56}\text{N}_{12}\text{O}_{18}\text{Zn}_4$, $FW = 1638.77$, $V = 1702.8(6)$ Å³, $Z = 1$, $D_c = 1.598$ g/cm³, $S = 1.045$, $\mu(\text{MoK}\alpha) = 1.475$ mm⁻¹, $F(000) = 836$, $R = 0.0472$ and $wR = 0.0919$. Four L ligands bridge four Zn(II) atoms to form a square-shaped structure, where four phen ligands are respectively located on the four corners of the square. The π - π stacking interactions extend adjacent squares into a 1D supramolecular chain. The thermal behavior of **1** was characterized. Moreover, the solid-state luminescence property of the complex was studied at room temperature.

Keywords: crystal structure; supramolecular square; luminescence; 2-hydroxynicotinate.

INTRODUCTION

Over the past few decades, precise control over the shape and size of supramolecular architectures *via* self-assembly has been a major driving force for chemists.^{1–6} Well-designed supramolecular architectures can show various physical properties and functionalities in molecular recognition, sensing and magnetism.^{7–10} To date, a number of complexes with regular arrays, such as grids, wires and rings, were synthesized using various synthetic methods.^{11,12} In a variety of typical cases, successful assemblies of molecular architectures with precise shapes and sizes mainly relied on the angles of the organic ligands and the coordination geometry of the metal ions.^{13–18} Therefore, through rational ligand design and metal ion selection, a controllable arrangement of metal ions in multinuclear complexes could be achieved.^{19,20} In this regard, tetranuclear

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complexes with square-shaped arrangements of metal ions are of intense interest to chemists owing to their potential application as molecular devices.²¹ By rationally combining the planar *N*-donor chelating ligand and the angular bridging carboxylate-containing ligand square grid-like complexes could be afforded.²²

Based on the above consideration, in this work a planar *N*-donor chelating 1,10-phenanthroline (phen) ligand and an angular bridging carboxylate-containing 2-hydroxynicotinate (L) were selected, and their complexation behavior was investigated. This paper describes the syntheses, crystal structure, and luminescent property of a new Zn(II) square-shaped complex, $[\text{Zn}_4(\text{L})_4(\text{phen})_4] \cdot 6\text{H}_2\text{O}$ (**1**). The compound was characterized by elemental analysis, IR spectrum, TG and X-ray crystallography. In addition, its luminescent property was also investigated.

EXPERIMENTAL

All the materials were of analytical reagent grade and used as received without further purification. The C, H and N elemental analyses were conducted on a Perkin–Elmer 240C elemental analyzer. The emission spectra were measured on a Renishaw inVia Raman Microscope at room temperature. The IR spectrum was recorded in the range of 4000–400 cm^{-1} on an Alpha Centauri FT-IR spectrophotometer using the KBr pellet technique. Thermal stability experiment was performed on a TG SDT2960 thermal analyzer (TA Instruments) under a nitrogen atmosphere.

*Synthesis of $[\text{Zn}_4(\text{L})_4(\text{phen})_4] \cdot 6\text{H}_2\text{O}$ (**1**)*

A mixture of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.2 mmol, 0.044 g), H_2L (0.15 mmol, 0.021 g), phen (0.1 mmol, 0.018 g) and KOH (0.1 mmol, 0.006 g) was dissolved in distilled water (10 mL). Then the mixture was transferred and sealed in a 25 mL Teflon-lined stainless steel container. The container was heated at 417 K for 4 days. After the mixture had been cooled to room temperature at a rate of 10 $^\circ\text{C} \cdot \text{h}^{-1}$, pale yellow crystals of **1** were obtained. Yield: 21 %. Anal. Calcd. for $\text{C}_{72}\text{H}_{56}\text{N}_{12}\text{O}_{18}\text{Zn}_4$: C, 52.76; H, 3.44; N, 10.75 %. Found: C, 52.31; H, 3.22; N, 10.26 %; IR (KBr, cm^{-1}): 3435(w), 1615(w), 1564(m), 1474(w), 1408(m), 1254(w), 1139(s), 1070(w), 994(w), 952(w), 850(w), 832(w), 786(w), 726(w), 618(m), 539(w), 515(w).

X-Ray crystallography

Single-crystal X-ray diffraction data for **1** was obtained on a Rigaku R-Axis-Rapid diffractometer with graphite-monochromatized MoK_α ($\lambda = 0.71073 \text{ \AA}$) radiation using an ω - ϕ scan method at 293(2) K. The structure was solved by direct methods with SHELXS-97 program and refined with SHELXL-97 by the full-matrix least-squares techniques on F^2 .^{23,24} Non-hydrogen atoms of the compound were refined with anisotropic temperature parameters. All H atoms on carbon atoms were positioned geometrically ($\text{C-H} = 0.93 \text{ \AA}$) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$. The H atoms of O1W and O2W were included in the model. A summary of the crystallographic data and structure analysis are given in Table S-I of the Supplementary material to this paper, and selected bond lengths and bond angles are listed in Table S-II of the Supplementary material.

RESULTS AND DISCUSSION

Crystal structure of 1

The asymmetric unit of **1** is composed of two Zn(II) atoms, two L ligands, two phen ligands, and three lattice water molecules. Noticeably, the two Zn(II) atoms are both in a penta-coordinated environment, completed by two oxygen atoms from one hydroxyl and one carboxylate of the same L anion, and three nitrogen atoms of one phen ligand and one L anion (Fig. 1). However, the two Zn(II) atoms exhibit different coordination spheres: Zn1 is in a slightly distorted square-pyramidal geometry with a τ value of 0.27, and Zn2 shows a nearly ideal trigonal-bipyramid sphere with a τ value of 0.90.²⁵

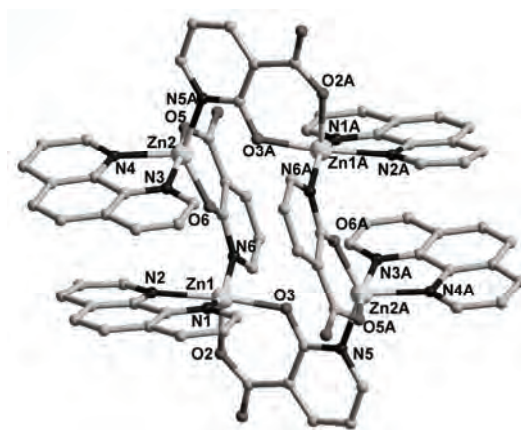


Fig. 1. View of square-shaped structure of **1** and the coordination environments of Zn(II) atoms in **1**.

As given in Table S-II, the Zn–O distances range from 1.971(3) to 2.057(3) Å, and the Zn–N distances vary from 2.023(4) to 2.196(4) Å, which are very similar to the ones found in other related compound [Zn(bpea)(phen)] (bpea = = 1,4,4'-(1*E*)-1,2-ethenediyl-bisbenzoate).²⁶ Each L ligand adopts a tridentate coordination mode by using its one pyridine nitrogen, one hydroxyl oxygen and one carboxylate oxygen. In this way, four L ligands bridge four Zn(II) atoms to yield a rare square-shaped molecular arrangements with the Zn(II)⋯Zn(II) distance of 4.66 Å. Four phen ligands are respectively located on the four corners of the square. It is clear that the bis-chelating phen ligands play a key role in the formation of the square.

Significantly, π – π stacking interactions exist among neighboring L ligands in adjacent squares (the face-to-face distance is *ca.* 3.51 Å). Furthermore, these π – π stacking interactions extend adjacent squares into a 1D supramolecular chain (Fig. 2). Moreover, in complex **1**, there are O–H⋯O hydrogen-bonding interactions among water oxygen atoms and the carboxylate oxygen atoms of the L ligands (Table I). These hydrogen-bonding interactions further stabilize the 1D supramolecular architecture of **1**.

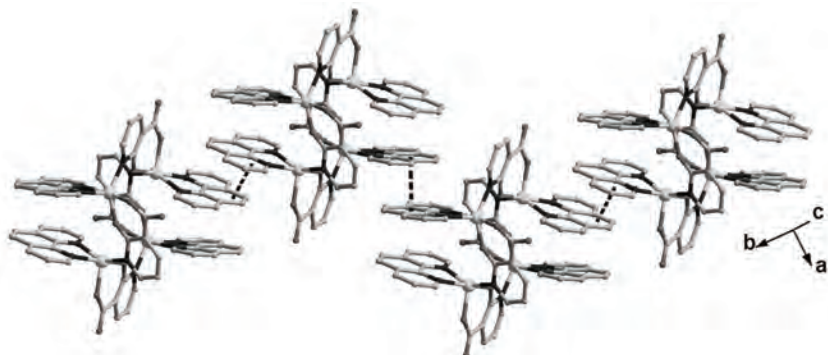


Fig. 2. View of the 1D supramolecular ladder structure of **1** constructed by π - π interactions.

TABLE I. Hydrogen-bonding parameters for **1**; symmetry transformations were used to generate equivalent atoms: B: $x+1, y-1, z$; C: $-x+2, -y, -z+2$; D: $-x+1, -y, -z+2$

D-H...A	$d(\text{D-H}) / \text{\AA}$	$d(\text{H}\cdots\text{A}) / \text{\AA}$	$d(\text{D}\cdots\text{A}) / \text{\AA}$	$\angle\text{DHA} / ^\circ$
O(2W)-HW21...O(3W) ^B	0.854(10)	2.027(14)	2.864(6)	167(5)
O(2W)-HW22...O(1W) ^C	0.854(10)	1.999(13)	2.845(6)	170(5)
O(1W)-HW11...O(2) ^D	0.848(10)	2.019(14)	2.862(5)	172(6)
O(1W)-HW12...O(1)	0.851(10)	1.926(16)	2.765(6)	168(6)

Notably in **1**, the L is a doubly deprotonated species coordinated to Zn(II) centers *via* two O atoms and one N atom. It is evident that the pH value of the reaction mixture plays an important role in the double deprotonation of the H₂L ligand and the formation of the final complex. In the present experiment, potassium hydroxide was used to adjust the pH value. Nevertheless, only at pH around 6.5 can be the reaction mixture produce single crystals of **1** with the completely deprotonated L dianion. Moreover, the hydrothermal reaction is necessary for the formation of **1**. At room temperature or under milder conditions, no crystals of **1** were obtained. It could be inferred that the hydrothermal reaction improved the solubility of the reaction mixture, and favored the crystallization of **1** during the cooling-down process. Moreover, the hydrothermal reaction accelerated the complete deprotonation of the H₂L ligand.

Thermal behavior

To know the stability of compound **1**, its thermogravimetric curve was recorded at a heating rate of 10 °C min⁻¹. As shown in Fig. 3, there were two main steps of weight loss. The first step of 6.5 % from 25 to 159 °C can be ascribed to the release of the free water molecules (calcd. 6.6 %), and the second step of 73.3 % in the temperature range of 178–598 °C corresponds to the removal of the organic ligands (L and phen; Calcd. 77.5 %). The residual weight 20.2 % (Calcd. 19.9 %) could probably be attributed to the formation of ZnO. These thermal behaviors agree with the formula of the title compound.

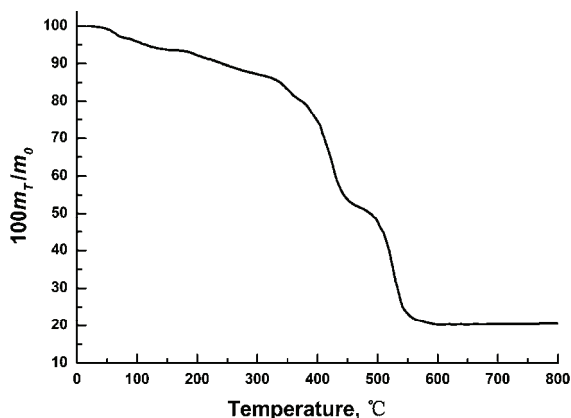


Fig. 3. TG curve of **1** recorded at a heating rate of 10 °C min⁻¹.

Luminescent property

The d¹⁰ metal-based luminescent compounds are of great interest because of their potential applications as chemical sensors and in photochemistry.^{27,28} In this work, the emission spectra of the free organic ligand H₂L and compound **1** were recorded in the solid state at room temperature (Fig. 4). The spectrum of H₂L shows a maximum emission peak at 393 nm ($\lambda_{\text{ex}} = 325$ nm) which could be attributed to a $\pi-\pi^*$ transition, together with a broad shoulder at about 480 nm tentatively attributable to an $n-\pi^*$ transition.²⁹ The spectrum of **1** exhibited a main peak at 523 nm ($\lambda_{\text{ex}} = 325$ nm) that was red-shifted by 25 nm with respect to the band shown by the phen ligand ($\lambda_{\text{em}} = 498$ nm).²⁶ The red shift may be attributed to a ligand to metal charge transfer (LMCT) transition.³⁰

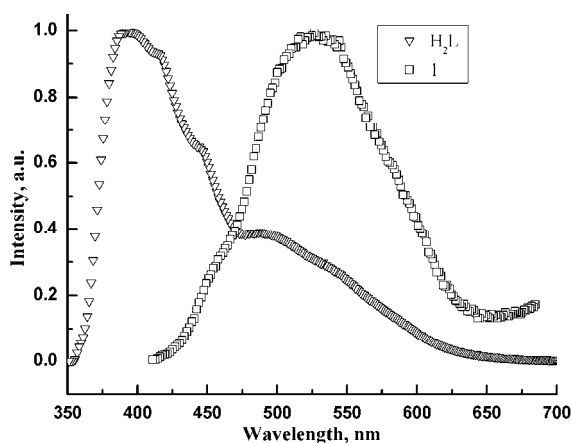


Fig. 4. Emission spectra of H₂L and **1** in the solid state at room temperature.

CONCLUSIONS

A new square-shaped molecule was prepared from a planar *N*-donor chelating ligand, 1,10-phenanthroline, and the angular bridging carboxylate-con-

taining 2-hydroxynicotinate under hydrothermal conditions. In **1**, the four L ligands bridge the four Zn(II) atoms to form a square-shaped structure, in which four phen ligands are respectively located on the four corners. The π - π stacking interactions extend adjacent squares into a 1D supramolecular chain. Moreover, compound **1** exhibits intense luminescence in the solid state at room temperature.

SUPPLEMENTARY MATERIAL

The supplementary crystallographic data for this paper are deposited at The Cambridge Crystallographic Data Centre under CCDC-1046844 (1). These data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

Crystal data and structure refinement, and selected bond lengths and angles for **1** are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

НОВИ СУПРАМОЛЕКУЛСКИ КВАДРАТНО-ПЛАНАРНИ ЦИНК(II) КОМПЛЕКС: СИНТЕЗА, КРИСТАЛНА СТРУКТУРА, ТЕРМИЧКО ПОНАШАЊЕ И ЛУМИНИСЦЕНЦИЈА

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Применом хидротермалних услова синтетизован је нови квадратно-планарни цинк(II) комплекс, опште формуле $[Zn_4(L)_4(phen)_4] \cdot 6H_2O$ (**1**, L = 2-хидроксинокотинат и phen = 1,10-фенантролин). Нађено је да комплекс **1** припада триклиничном кристалном систему са *P*-1 просторном групом и $a = 10,773(2) \text{ \AA}$, $b = 12,641(3) \text{ \AA}$, $c = 13,573(3) \text{ \AA}$, $\alpha = 107,44(3)^\circ$, $\beta = 102,66(3)^\circ$, $\gamma = 93,89(3)^\circ$, $C_{72}H_{56}N_{12}O_{18}Zn_4$, $FW = 1638,77$, $V = 1702,8(6) \text{ \AA}^3$, $Z = 1$, $D_c = 1,598 \text{ g/cm}^3$, $S = 1,045$, $\mu(MoK\alpha) = 1,475 \text{ mm}^{-1}$, $F(000) = 836$, $R = 0,0472$ и $wR = 0,0919$. У комплексу **1** четири лиганда L повезују четири Zn(II) јона мостом и граде структуру квадратно-планарне геометрије у којој се четири phen лиганда налазе на угловима квадрата. Преко π - π интеракција квадратно-планарне јединице су повезане у 1D супрамолекуларни ланац. Описано је термичко понашање комплекса **1**. Такође, испитивано је луминесцентно понашање овог комплекса на собној температури.

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