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КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF A NEW TRANSITION METAL-ORGANIC Zn(II) COMPLEX

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A novel Zn(II) coordination polymer $[Zn_2(phen)_2]L_4 \cdot 3H_2O$(1) is synthesized by the reaction of $Zn(NO_3)_2$, Phen(1,10-phenanthroline), and L(2-mercaptonicotinic acid) at room temperature and structurally characterized by X-ray single crystal diffraction along with IR spectra and elemental analysis. Title complex **1** belongs to the triclinic system with the space group (P-1), $a = 10.9373(11)$ Å, $b = 11.6201(12)$ Å, $c = 13.1371(14)$ Å; $\alpha = 116.100(1)°$, $\beta = 97.717(2)°$, $\gamma = 108.652(2)°$, $V = 1344.4(2)$ Å^3; $Z = 2$, $\rho_{calcd} = 1.596$ g·cm^{-3}, $F(000) = 664$, $R_1 = 0.0708$ and $wR_2 = 0.1823$ independent reflections for 18523 observed ones ($I > 2\sigma(I)$), and the zinc atom is rendered five-coordinated in a distorted tetragonal pyramid coordination geometry by two nitrogen atoms from the phen molecule, two oxygen atoms from two L molecules, and an oxygen atom from the H_2O molecule. Complex **1** forms a 1D chain by O—H···O hydrogen bonds from free-water, while the 2D layer structure is formed by C—H···O hydrogen bonds through the L ligand of adjacent chains. These compounds further result in a 3D network structure by the intermolecular π···π stacking interaction of the neighbouring layers.

Keywords: Zn(II) complex, 2-mercaptonicotinic acid, crystal structure, coordination.

Since coordination theory was established in 1893, coordination chemistry was being one of the most active and vitality subjects of current issues in the chemical field [1]. Coordination compounds have received more and more attention [2—4] because of their perfect framework and admirable properties such as catalysis, anticancer activity, etc. [5—9].

The molecular engineering of transition-metal-based coordination compounds with an extended network is a rapidly growing area of research because of their functional properties and potential applications [10]. In this habit, the use of heteronuclear polydentate and polynucleating ligands is of particular interest because they can lead to the formation of extended systems with unusual electronic and optical properties [11, 12]. Compared to the vast literature on the synthesis of coordination polymers and metal-organic frameworks (MOFs) based on N- and O-coordinating ligands [13, 14], reports focusing on complexes of bifunction S- and O-donors are rather scarce [15]. The latter class of ligands is particularly interesting because they are in principle able to accomplish new coordination fashions with still unexplored electronic and optical properties. In this respect, it has to be mentioned that even if many examples of bridging S—M—O bonds have been reported in the literature, most of them imply a bidentate bridging coordinate mode [16]. A functionalized heterocyclic ligand of 2-mercaptonicotinic acid with potential oxygen, nitrogen, and sulfur donors has recently attracted our attention to the construction of translation-metal organothiolate coordination polymer.

Phenanthroline has long been used as the main component of hemoglobin in the chemical model. It has a strong coordination ability and biological activity that were widely used in the synthesis and

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Table 1

Crystallographic data and experimental details for complex **1**

Empirical formula	$C_{54}H_{48}Zn_2O_{14}N_8S_4$
Formula weight	1198.01
Temperature, K	293(2)
Crystal system; space group	Triclinic; *P*-1
Wavelength, Å	0.71073
Unit cell dimensions *a*, *b*, *c*, Å;	10.9373(11), 11.6201(12), 13.1371(14);
α, β, γ, deg.	116.100(1), 97.717(2), 108.652(2)
V, Å^3	1344.4(2)
Z	2
ρ_{calcd}, g cm^{-3}	1.596
$F(000)$	664
Crystal size, mm	0.10×0.08×0.06
θ range for data collection, deg.	$1.82 < \theta < 26.02$
Limiting indices	$-12 \le h \le 13$, $-14 \le k \le 9$, $-14 \le l \le 16$
Reflections collected / unique, $I > 2\sigma(I)$	7599 / 5181 [R(int) = 0.0215]
Completeness, %	97.7
Data / restraints / parameters	5181 / 2 / 385
Goodness-of-fit on F^2	1.038
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0708$, $wR2 = 0.1823$
R indices (all data)	$R1 = 0.0877$, $wR2 = 0.1979$
Largest diffraction peak and hole, e/Å^{-3})	2.591 and –2.073

research of transition metal complexes. Our laboratory has reported a series of transition metal compounds with the phenanthroline ligand partially embedded in the adjacent DNA base pairs, making the conformation of DNA change [17, 18]. Zinc is one of the most important metals in biological systems, which is a cation of special relevance. An adult human body contains ca. 3 g of Zn(II) and it is involved in many human diseases [19, 20]. Herein, in this paper we selected L, phen as a ligand and transition metal Zn(II) to synthesize the $[Zn_2(phen)_2]L_4\cdot 3H_2O$(1) complex with two coordination modes of L and phen ligands, intramolecular $\pi\cdots\pi$ stacking, and the intermolecular hydrogen bond weak interaction were observed.

Experimental. Materials and measurements. All chemicals were of reagent grade, were purchased from commercial sources and used without further purification. Elemental analyses (C, H, N) were performed on a model SQ-201 instrument. IR spectra were recorded in the 4000—400 cm^{-1} region as KBr pellets on a Nicolet IR-470 instrument. The crystal determination was recorded on a Bruker Smart 1000 CCD X-ray single crystal diffractometer. The structure analysis was performed on a computer with the SHELX-97 program package.

Synthesis of Zn(II) complex 1. In the experiment, an aqueous $Zn(NO_3)_2$ solution (1.0 mmol, 10 ml) was mixed with a 2-mercaptonicotinic acid solution (1.0 mmol, 10 ml) dissolved by an aqueous KOH solution. Along with stirring, the pH value was adjusted to 7.53 using a HCl solution (1 M), and then the mixture continuously reacted at room temperature. After about four hours of fully blending, an EtOH solution of 1,10-phenaanthroline (1.0 mmol, 10 ml) was added. It was mixed constantly for yet another 4 h; the final pH value of the solution was 7.38, and then it was slowly evaporated at normal temperature. Four weeks later, numerous colorless columnar crystals were obtained from the filtrated concentrated solution.

The FT-IR spectrum (ν, cm^{-1}): 3346s, 2397w, 1764w, 1606s, 1387s, 1243m, 1020m, 854m, 825m, 776m, and 726m. The absence of IR bands at 1652 cm^{-1} belongs to >C=O, indicating that both 2-mercaptonicotinic acid carboxyl groups have been coordinated.

Table 2

Selected bond lengths and bond angles for complex **1**

Bond	*d*, Å	Angle	ω, deg.	Angle	ω, deg.
Zn(1)—O(6)	1.961(4)	O(6)—Zn(1)—O(2)	95.31(17)	N(1)—Zn(1)—O(3)#1	102.95(16)
Zn(1)—O(2)	1.999(3)	O(6)—Zn(1)—N(2)	169.41(17)	N(2)—Zn(1)—O(3)#1	85.58(15)
Zn(1)—O(3)#1	2.206(4)	O(2)—Zn(1)—N(2)	95.18(16)	O(2)—Zn(1)—O(3)#1	100.87(15)
Zn(1)—N(2)	2.007(4)	O(6)—Zn(1)—N(1)	89.83(18)	O(6)—Zn(1)—O(3)#1	91.00(15)
Zn(1)—N(1)	2.047(4)	O(2)—Zn(1)—N(1)	155.52(16)	N(2)—Zn(1)—N(1)	81.20(17)

For $C_{51}H_{54}N_8O_{12}S_4Zn_2$, Anal. calcd, %: C, 51.13; H, 4.54; N, 9.36; Found, %: C, 51.08; H, 4.61; N, 9.29.

X-ray crystallography. The structure measurement of complex **1** was carried out on a Bruker Smart 1000 CCD diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å) at 273 K, and intensity data were obtained ranging from $1.82 < \theta < 26.02°$ with a ω scan method. The corrections for the Lp factor and empirical absorption were applied. A direct approach was adopted in the structure analysis using the SHELXS-97 instrument. All hydrogen atoms were obtained by the theoretical hydrogenation method, and non-hydrogen atoms were revised with anisotropy displacement parameters and goodness-of-fit on F^2 (SHELXL-97).

Crystal data and structure refinement details were summarized in Table 1. Selected bond lengths and bond angles were listed in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no.875563; deposit@ccdc.cam.ac.uk).

Results and discussion. Single crystal X-ray analyses revealed that complex **1** crystallized in the triclinic system with the space group (*P*-1). The basic structure of complex **1** was shown in Fig. 1.

One H_2O molecule dissociated from the zinc atom, while other two were connected to the central zinc cation. Phen was firmly connected to the zinc atom whose coordination ability was much stronger than that of L. Moreover, two L molecules condensed together by desulfhydryl reaction. As shown in Fig. 1, the Zn(II) atom was coordinated by two nitrogen atoms (N1, N2) from Phen, two oxygen atoms (O2, O3A) from two different L molecules, and one oxygen atom (O6) from the H_2O molecule respecti-

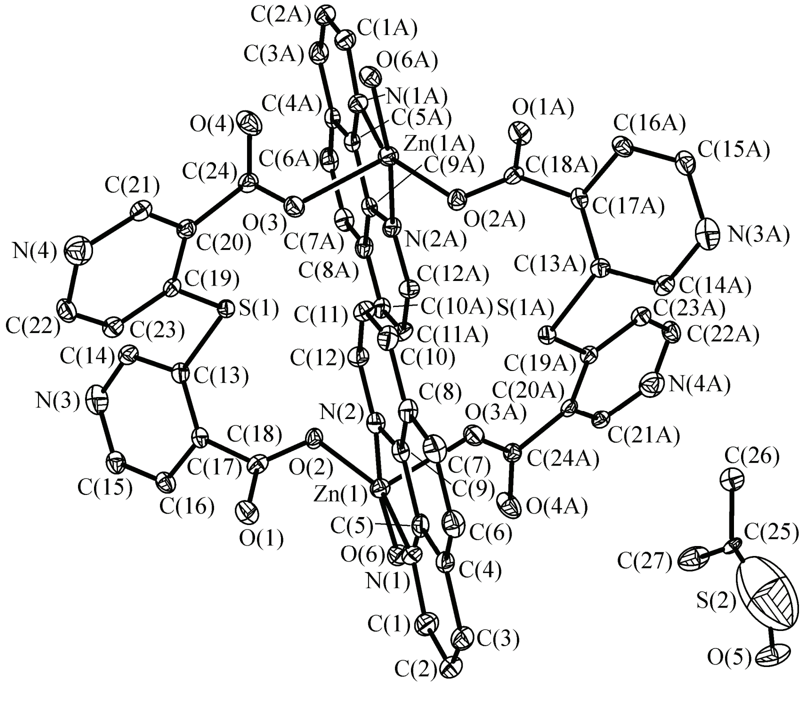

Fig. 1. Basic structure of complex **1**

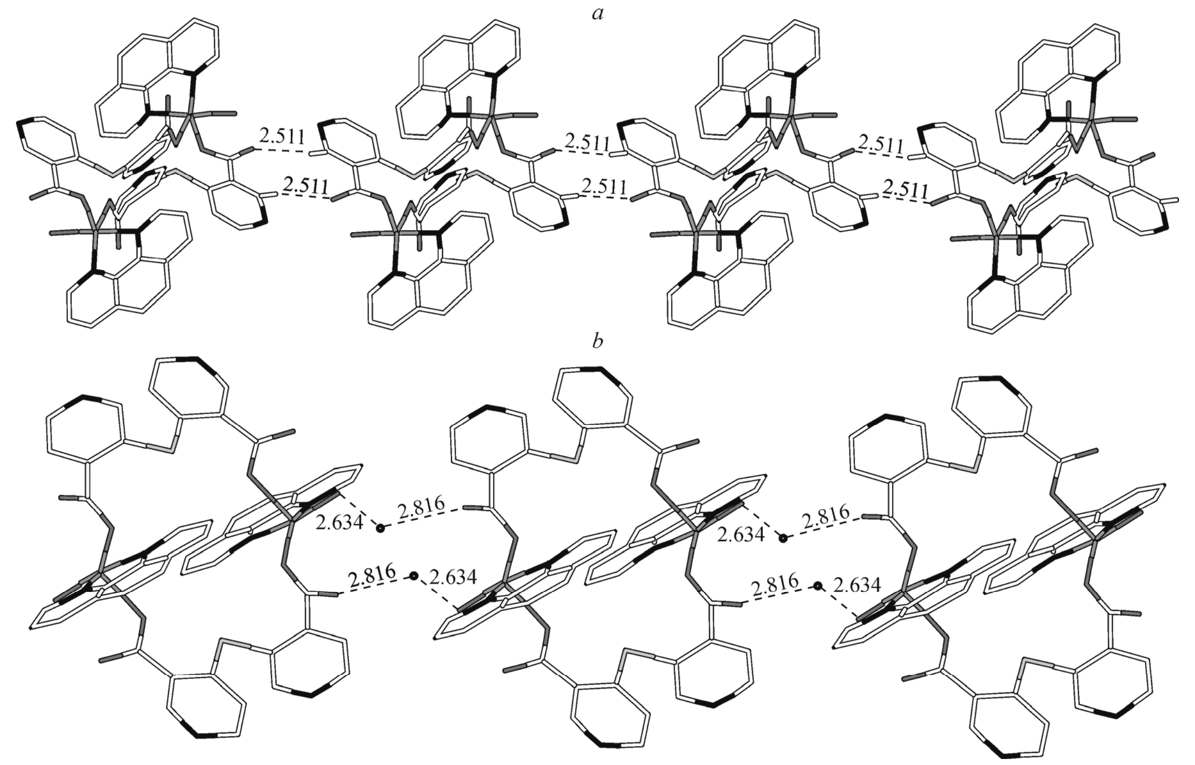

Fig. 2. C—H···O interactions (2.511 Å) of the 1D chain of complex **1** (H atoms were omitted for clarity) (*a*); O—H···O interactions (2.816 or 2.634 Å) of the 1D chain of complex **1** (H atoms were omitted for clarity) (*b*)

vely. The formation of the dinuclear complex was bridged by Zn1 and Zn1A via the condensation reaction of two L molecules. The Zn—O bond lengths ranged from 1.9612 Å to 2.206 Å (Zn—O3A 2.206 Å; Zn—O2 1.9986 Å; Zn—O6 1.9612 Å) and Zn—N were 2.0479 Å and 2.0068 Å, which were similar to those reported. O2—Zn—N1 and O6—Zn—N2 bond angles were 155.52(16)° and 169.41(17)°. Therefore, O2, Zn, N1 and O6, Zn, N2 were located nearly in a line; what is more important, N1, N2, O6, O2 were nearly located in the same plane. Thus, the Zn ion center was in the distorted tetragonal pyramidal environment.

As shown in Fig. 1, the Zn fragments of complex **1** were connected through the O—H···O interaction between one dissociative H_2O (O1w) and the L ligand (O1) (bond length was 2.816 Å), forming a basic build unit. The basic units formed a one-dimensional chain (shown in Fig. 2) via the O—H···O interaction between one dissociative H_2O (O1w) and combined H_2O(O6) or the L ligand (O1) (bond length was 2.816 or 2.634 Å).

Interestingly, the adjacent one-dimensional chains were connected into a two-dimensional structure through the C—H···O interaction (bond length is 2.511 Å), shown in Fig. 3. The 2D layers were further connected through π···π stacking between the Phen fragments (the center-to-center distance was 3.439 Å), forming a 3D framework shown in Fig. 4.

Conclusions. Zinc complex $[Zn_2(phen)_2]L_4\cdot 3H_2O$ (**1**) has been synthesized and structurally characterized by X-ray single crystal diffraction along with the IR spectra and elemental analysis. This research on the synthesis and crystal structure of complex **1** provides an important method that may lead to further understanding of the mechanism of transition-metal-based coordination compounds.

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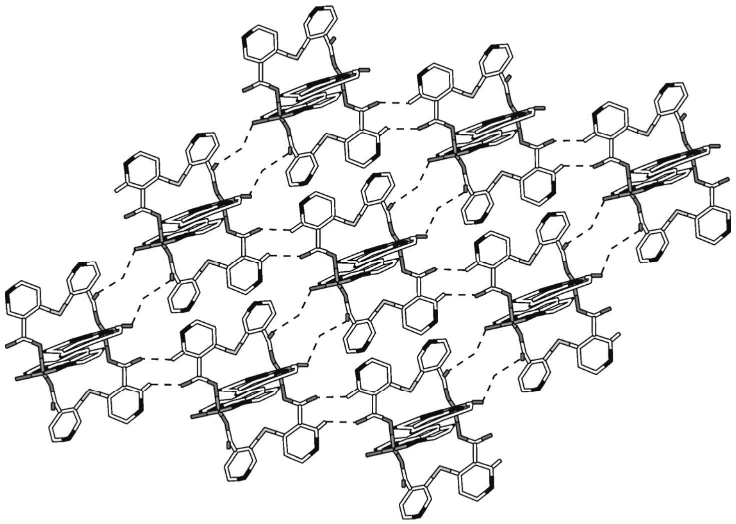

Fig. 3. 2D framework diagram of complex **1** and C—H···O interactions (2.511 Å) (H atoms were omitted for clarity)

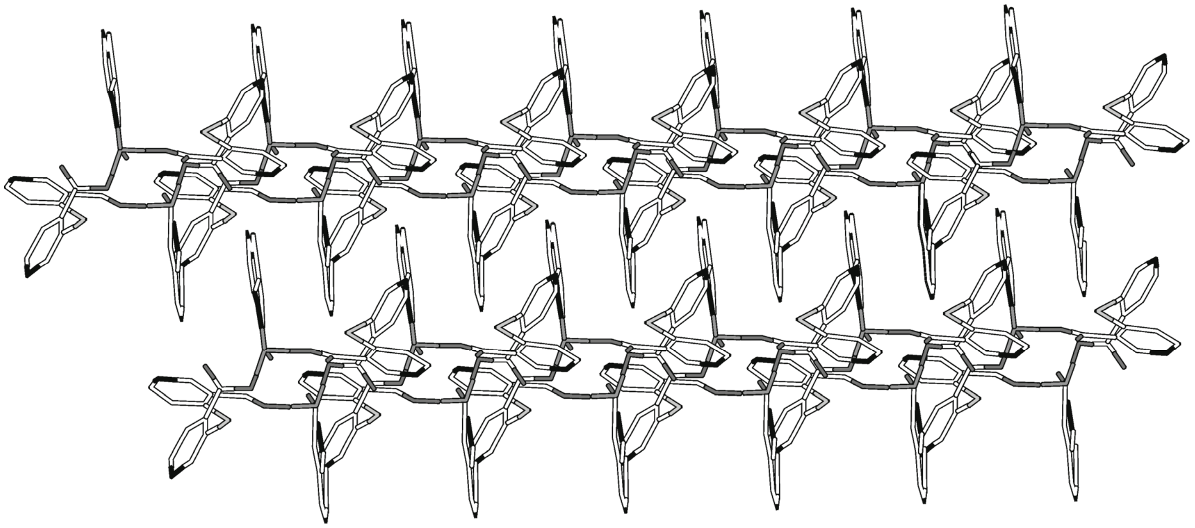

Fig. 4. π—π stacking interactions (3.439 Å) between the layer with the hydrogen bonding interactions in the structure (H atoms were omitted for clarity)

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