

Communication

# Structural Characterized Homotrimeric Zn<sup>II</sup> Bis(salamo)-Based Coordination Compound: Hirshfeld Surfaces, Fluorescent and Antimicrobial Properties

Yang Zhang, Ling-Zhi Liu, Ying-Qi Pan and Wen-Kui Dong \* 

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China; zhangy8124@163.com (Y.Z.); llz1009663202@126.com (L.-Z.L.); panyq0329@163.com (Y.-Q.P.)

\* Correspondence: dongwk@126.com

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**Abstract:** A homotrimeric Zn<sup>II</sup> bis(salamo) coordination compound, [LZn<sub>3</sub>(OAc)<sub>2</sub>(H<sub>2</sub>O)] of a new bis(salamo)-like ligand, has been synthesized and structurally characterized using elemental analyses, IR, UV-Vis and fluorescent spectra, and Hirshfeld surface analysis. Hirshfeld surface analysis and X-ray crystallography revealed that complexation between Zn<sup>II</sup> acetate dihydrate and the ligand H<sub>4</sub>L afforded a 3:1 (Zn<sup>II</sup>:L) type coordination compound. Moreover, the X-ray crystal structure analysis demonstrated that two  $\mu_2$ -acetate anions bridge three Zn<sup>II</sup> atoms in a  $\mu_2$ -fashion forming a homo-trimeric structure. There were two kinds of Zn<sup>II</sup> atoms coordination geometries (strongly distorted square pyramidal (Zn1) and distorted trigonal bipyramidal (Zn2 and Zn3)) in the Zn<sup>II</sup> coordination compound. In addition, a 3D supra-molecular structure was constructed by intermolecular C-H $\cdots$  $\pi$  and  $\pi\cdots\pi$  interactions in the Zn<sup>II</sup> coordination compound. Most importantly, the fluorescent and antimicrobial properties of H<sub>4</sub>L and its Zn<sup>II</sup> coordination compound were investigated.

**Keywords:** Zn<sup>II</sup> coordination compound; crystal structure; supra-molecular interaction; fluorescence property; antimicrobial activity

## 1. Introduction

In recent years, a great number of 3D metal coordination compounds with salen-like N<sub>2</sub>O<sub>2</sub> ligands have been widely investigated [1–8]. More recently, salamo-like N<sub>2</sub>O<sub>2</sub> chelating ligands and their analogues, using an O-alkyloxime (–CH=N–O–(CH<sub>2</sub>)<sub>n</sub>–O–N=CH–), have been explored [9–15]. Compared to salen-like coordination compounds, salamo-type coordination compounds are significantly more stable. The latter, salamo-like ligands, are more attractive candidates for metal-binding sites to be involved into metallohosts. Salamo-like ligands could coordinate to different transition metal ions in a tetradentate N<sub>2</sub>O<sub>2</sub>-type fashion to form stable metal coordination compounds, some of which are often as organic reaction catalysts [16], metal enzyme reaction center models [17,18], nonlinear optical and magnetic molecular materials [19–27], supramolecular architectures and host-guest chemistries [28–34], electrochemistries [35–37] and so on.

To utilize salamo units to control guest recognition, a better strategy distinguished from the macrocyclization has been proposed [38,39]. Thus, we designed and prepared a new C-shaped bis(salamo)-like chelating ligand that contained a O<sub>4</sub> site besides the two N<sub>2</sub>O<sub>2</sub> sites, to control guest binding via using the coordination-triggered conformational changes. When the ligand is metalated, our O<sub>4</sub> oxygen atoms are located in an acyclic, C-shaped arrangement. Moreover, the guest binding could be more effective owing to the negatively charged phenolates of the metal coordination

compounds having higher coordination ability to other metals than their phenol form. Interestingly, some studies have been devoted to research mono-, multi-, homo- or heteromultinuclear metal coordination compounds bearing salamo-type ligands or their derivatives [40,41].

Herein, on the basis of our previous studies [42–46], we have studied cooperative formation of a trinuclear Zn<sup>II</sup> bis(salamo)-like coordination compound, instead of the dinuclear bis(salamo)-like coordination compound reported before [47], via the metalation of bis(salamo)-like ligand H<sub>4</sub>L. IR, UV-Vis titration and X-ray crystallography clearly exhibited that complexation between Zn<sup>II</sup> acetate dihydrate and H<sub>4</sub>L can form a 3:1 [Zn<sub>3</sub>L]<sup>2+</sup> coordination compound. Meanwhile, the fluorescent and antibacterial properties of H<sub>4</sub>L and its Zn<sup>II</sup> coordination compound were also studied.

## 2. Experimental Section

### 2.1. Materials and Methods

2-Hydroxy-4-methoxybenzaldehyde (99%), 1,2-dibromopropane, 1,2-dimethoxybenzene, TMEDA, *n*-butyllithium, boron tribromide were bought from Alfa Aesar and used without further purification. Other solvents and reagents (DMF: *N,N*-dimethylformamide) were analytical grade reagents from Tianjin Chemical Reagent Factory.

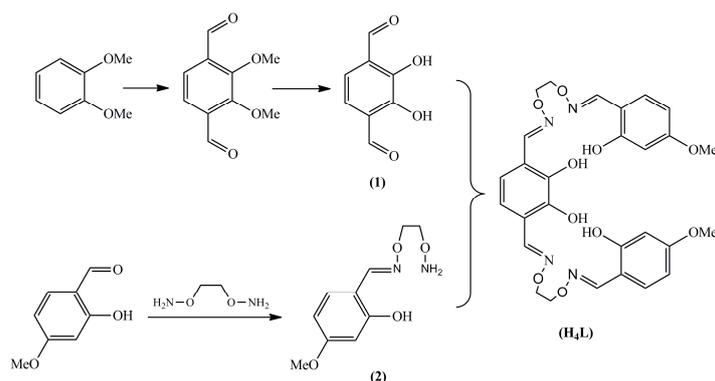
C, H and N analyses were gained using a GmbH VariuoEL V3.00 automatic elemental analysis instrument (Elementar, Berlin, Germany). Elemental analysis for Zn<sup>II</sup> was measured with an IRIS ER/S-WP-1 ICP atomic emission spectrometer (Elementar, Berlin, Germany). Melting points were obtained by the use of a microscopic melting point apparatus made by Beijing Taike Instrument Company Limited and were uncorrected. IR spectra (400–4000 cm<sup>-1</sup>) were recorded on a Vertex 70 FT-IR spectrophotometer (Bruker, Billerica, MA, USA), with samples prepared as KBr pellets. UV-Vis absorption spectra were recorded on a Shimadzu UV-3900 spectrometer (Shimadzu, Tokyo, Japan). <sup>1</sup>H NMR spectra were determined by German Bruker AVANCE DRX-400/600 spectroscopy. Single crystal X-ray structure diffraction for the Zn<sup>II</sup> coordination compound was carried out a Bruker Smart Apex CCD diffractometer. Fluorescent spectra were recorded on a F-7000 FL spectrophotometer.

### 2.2. Synthesis of the Ligand H<sub>4</sub>L

A synthetic route to the new ligand H<sub>4</sub>L is depicted in Scheme 1. Preparations of 2,3-dihydroxybenzene-1,4-dicarbaldehyde (1) and 2-[O-(1-ethoxyamide)] oxime-5-methoxyphenol (2) were in accordance with the literature [48–52]. A ethanol solution (15 mL) of 2-[O-(1-ethoxyamide)]oxime-5-methoxyphenol (452.46 mg, 2 mmol) was added dropwise to a ethanol solution (20 mL) of 2,3-dihydroxybenzene-1,4-dicarbaldehyde (166.13 mg, 1 mmol) under 55 °C, the mixture was heated to reflux and kept refluxing for 6 h, and then faint yellow solid of the bis(salamo)-like tetraoxime ligand (H<sub>4</sub>L) was obtained. After the solution was allowed to stand overnight at room temperature, precipitates were collected on a suction filter to afford H<sub>4</sub>L. Yield: 346.20 mg (65.5%). m.p. 148–149 °C. Anal. calcd. for C<sub>28</sub>H<sub>30</sub>N<sub>4</sub>O<sub>10</sub> (%): C, 57.73; H, 5.19; N, 9.62. Found (%): C, 58.92; H, 5.44; N, 9.47. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.91 (s, 2H, OH), 9.66 (s, 2H, OH), 8.23 (s, 2H, CH=N), 8.18 (s, 2H, CH=N), 7.06 (s, 2H, ArH), 6.77 (s, 2H, ArH), 6.49 (s, 2H, ArH), 6.47 (dd, *J* = 8.5, 2.6 Hz, 2H, ArH), 4.50 (s, 4H, CH<sub>2</sub>), 4.45 (s, 4H, CH<sub>2</sub>), 3.81 (s, 6H, CH<sub>3</sub>).

### 2.3. Synthesis of the Zn<sup>II</sup> Coordination Compound

A solution of Zn<sup>II</sup> acetate dihydrate (6.58 mg, 0.03 mmol) in methanol (1 mL) was added dropwise to a solution of H<sub>4</sub>L (5.88 mg, 0.01 mmol) in dichloromethane (3 mL), the color of the mixture turned to yellow immediately, the proper solvent ratio (methanol:dichloromethane = 1:3) was of utmost importance. After 0.5 h of stirring, the resulting yellow solution was filtered, and then left undisturbed. When the solution was partially evaporated, several yellow block-like single crystals suitable for X-ray crystallography were gained. Yield: 54% (4.92 mg). Anal. calcd. for C<sub>32</sub>H<sub>34</sub>Zn<sub>3</sub>N<sub>4</sub>O<sub>15</sub> (%): C, 42.20; H, 3.76; N, 6.15; Zn, 21.54. Found (%): C, 42.41; H, 3.85; N, 6.02; Zn, 21.84.

Scheme 1. Synthesis route of H<sub>4</sub>L.

#### 2.4. X-ray Crystallography

The single crystal of the Zn<sup>II</sup> coordination compound, with approximate dimensions of 0.38 × 0.40 × 0.48 mm was mounted on goniometer head of Bruker Smart 1000 diffractometer equipped with Apex CCD area detector. The diffraction data were collected using a graphite mono-chromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 298(2) K. The structure was solved by using the program SHELXS-97 and Fourier difference techniques, and refined by full-matrix least-squares method on  $F^2$  using SHELXL-2017. The structure contained large void, and the solvent and the positive or negative ions located in the void couldn't be identified because it was highly disordered and had so small residual peak. Therefore, SQUEEZE in PLATON program was performed to remove the highly disordered solvent and ions. (Solvent Accessible Volume = 1762.9, Electrons Found in S.A.V. = 104.2). The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were added in geometrical positions. Details of the data collection and refinements of the Zn<sup>II</sup> coordination compound are given in Table 1.

**Table 1.** Crystallographic data and collection parameters for the Zn<sup>II</sup> coordination compound.

Empirical Formula	C <sub>32</sub> H <sub>34</sub> ZnN <sub>3</sub> N <sub>4</sub> O <sub>15</sub>
Formula weight	910.74
Temperature, K	298(2)
Wavelength, $\text{\AA}$	0.71073
Crystal system	Monoclinic
Space group	C 2/c
Cell dimensions, ( $\text{\AA}$ , deg)	$a = 26.702(2)$ $b = 21.6859(19)$ , $c = 14.8470(13)$ , $\beta = 101.253(2)$
Volume, $\text{\AA}^3$	8432.0(13)
Z	8
Density (calculated), $\text{mg/m}^3$	1.435
Absorption coefficient, $\text{mm}^{-1}$	1.759
$F(000)$	3712.0
Index ranges	$-28 \leq h \leq 31$ , $-22 \leq k \leq 25$ , $-17 \leq l \leq 16$
Reflections collected	20,924/7426 [ $R(\text{int}) = 0.0496$ ]
Independent reflections	5335
Data/restraints/parameters	7426/36/514
Goodness of fit indicator	0.944
$R$ [ $I > 2\sigma(I)$ ]	$R_1 = 0.0366$ , $wR_2 = 0.0903$
Largest diff. peak and hole, $\text{e} \cdot \text{\AA}^{-3}$	0.357 and $-0.382$

$$R_1 = \frac{\sum \|F_o| - |F_c|\|}{\sum |F_o|}; wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}{w}; w = \frac{1}{[\sigma^2(F_o^2) + (0.0784P)^2 + 1.3233P]^{-1}}$$

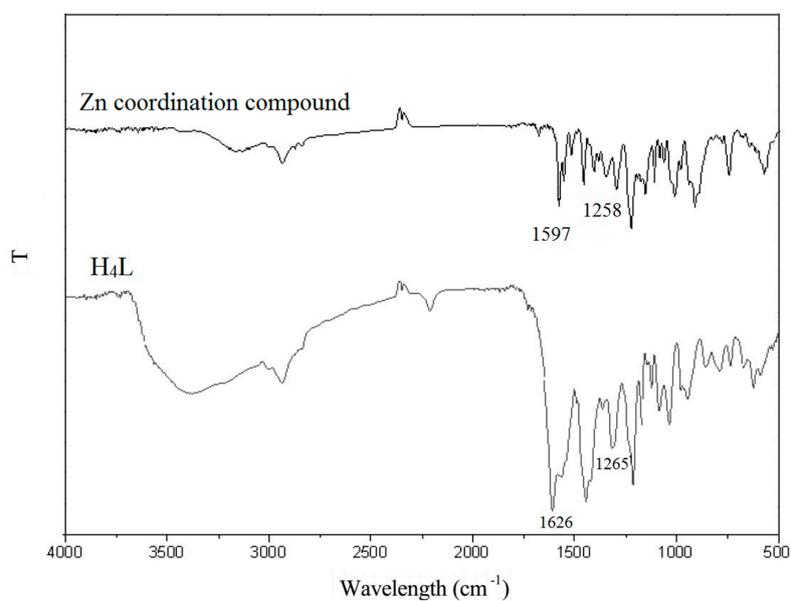
where  $P = (F_o^2 + 2F_c^2)/3$ ;  $\text{GOF} = \frac{[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}}{}$ .

Supplementary crystallographic data have been deposited at Cambridge Crystallographic Data Centre (CCDC: 890890). Copies of the data could be gained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Telephone: +44-01223-762910; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk). The data could be also gained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html).

### 3. Results and Discussion

#### 3.1. IR Spectra

As depicted in Figure 1, the IR spectra of  $H_4L$  and its  $Zn^{II}$  coordination compound exhibited different bands in the  $4000\text{--}500\text{ cm}^{-1}$  region. A typical  $C=N$  stretching band of  $H_4L$  appeared at  $1626\text{ cm}^{-1}$ , however that of the  $Zn^{II}$  coordination compound was observed at  $1597\text{ cm}^{-1}$ , indicating that the oxime nitrogen atoms are coordinated to the  $Zn^{II}$  atoms [53–57].



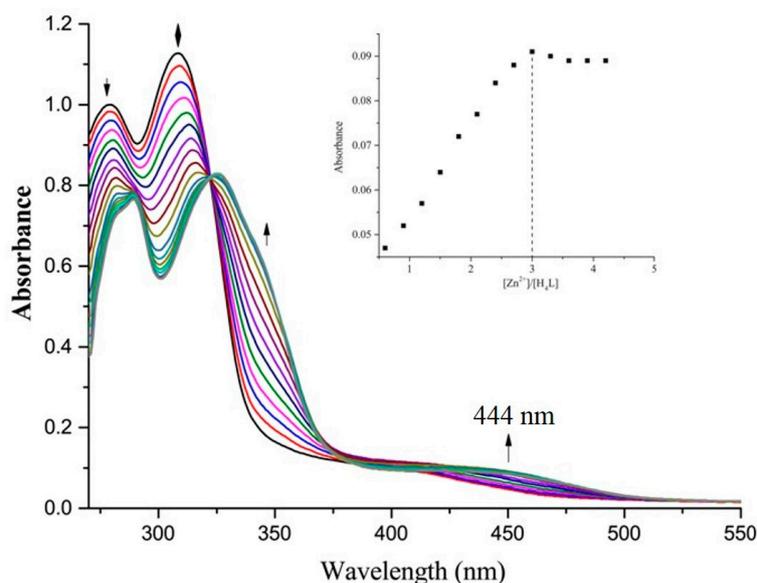
**Figure 1.** IR spectra of the ligand  $H_4L$  and its  $Zn^{II}$  coordination compound.

Meanwhile, the free ligand  $H_4L$  displayed a typical  $Ar-O$  stretching frequency at  $1265\text{ cm}^{-1}$ , while the  $Ar-O$  stretching frequency of the  $Zn^{II}$  coordination compound was observed at  $1258\text{ cm}^{-1}$ . This frequency was shifted to high frequency, which can be an evidence of formation of the  $Zn^{II}-O$  bonds between the  $Zn^{II}$  atoms and the phenolic oxygen atoms [58–60].

#### 3.2. UV-Vis Absorption Spectra

UV-Vis absorption spectra of the ligand  $H_4L$  and its  $Zn^{II}$  coordination compound were measured in  $5 \times 10^{-5}\text{ mol/L}$  DMF solution (Figure 2).

In the UV-Vis titration experiment of the  $Zn^{II}$  coordination compound, the spectroscopic titration clearly showed the reaction stoichiometry ratio to be 3:1. Absorption spectra of the  $Zn^{II}$  coordination compound were clearly different from that of  $H_4L$  upon complexation. The absorption maxima at ca. 278 and 313 nm were shifted bathochromically upon coordination to the  $Zn^{II}$  atoms, and a new absorption maxima at ca. 444 nm was absent in the spectrum of the  $Zn^{II}$  coordination compound, which should be assigned to LMCT [61–65].



**Figure 2.** Absorption spectra of  $H_4L$  in DMF with the increase of  $Zn^{II}$ . Inset: the absorbance at 444 nm varied as a function of  $[Zn^{2+}]/[H_4L]$ .  $[H_4L] = 5 \times 10^{-5}$  mol/L.

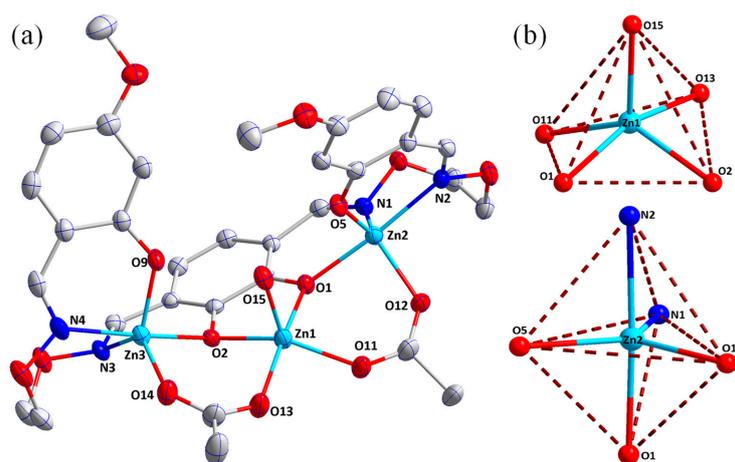
### 3.3. Crystal Structure Description

From a 3:1 mixture of  $Zn^{II}$  acetate dihydrate and the ligand  $H_4L$ , a yellow crystalline coordination compound was obtained. X-ray crystallography obviously displayed that the  $Zn^{II}$  coordination compound included one completely deprotonated ligand ( $L$ )<sup>4-</sup> unit, three  $Zn^{II}$  atoms, two  $\mu_2$ -acetate ligands, and one coordinated water molecule (Figure 3).

Two of the three  $Zn^{II}$  ( $Zn2$  and  $Zn3$ ) atoms sat in the salamo  $N_2O_2$  moieties, while  $Zn1$  was located in the central  $O_4$  site. Two oxygen ( $O1$  and  $O2$ ) atoms bridged  $Zn1$ - $Zn2$  and  $Zn1$ - $Zn3$ , respectively. In addition, two  $\mu_2$ -acetato ligands linked  $Zn1$  to  $Zn2$  and  $Zn1$  to  $Zn3$  stabilizing the homotrimeric structure. The central  $Zn^{II}$  ( $Zn1$ ) atom was found to have an aqua molecule. Thus, two of the three  $Zn^{II}$  ( $Zn2$  and  $Zn3$ ) atoms possess pentacoordinate distorted trigonal bipyramidal geometries ( $\tau = 0.8038$ ) in which the axial positions were held by  $N2-O1$  and  $N4-O2$ , respectively. Besides,  $Zn1$  atom possesses a strongly distorted square pyramidal ( $\tau = 0.3128$ ) coordination environment where the axial position was held by the  $O15$  atom of the aqua molecule [17,23]. Selected bond distances and angles are listed in Table 2. It can be seen from the data that the different positions of the substituents can lead to slightly different changes in the structure [11].

**Table 2.** Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for the  $Zn^{II}$  coordination compound.

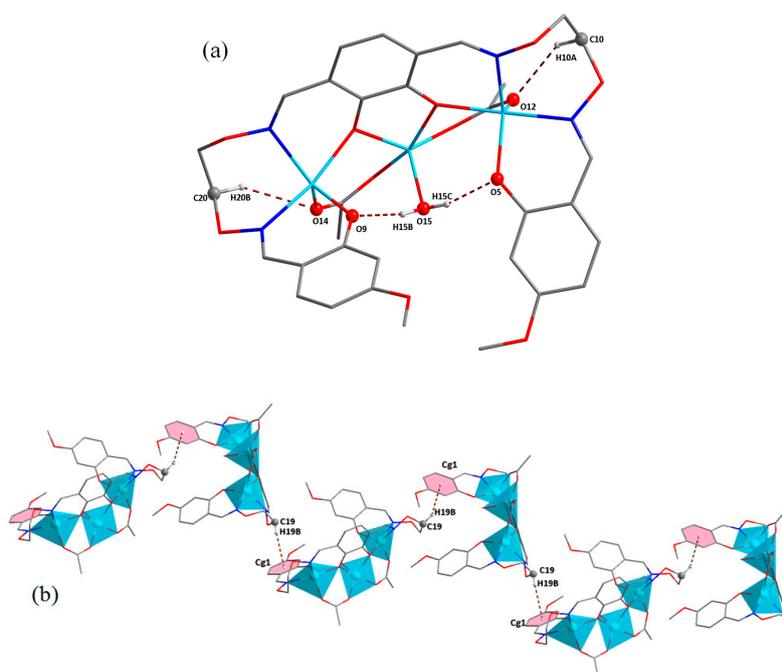
Bond	Lengths	Bond	Lengths	Bond	Lengths
Zn1-O11	1.975(3)	Zn1-O13	1.998(3)	Zn1-O15	2.021(3)
Zn1-O2	2.042(2)	Zn1-O1	2.079(2)	Zn2-O5	1.962(2)
Zn2-O12	1.985(3)	Zn2-O1	2.052(2)	Zn2-N1	2.091(3)
Zn2-N2	2.135(3)	Zn3-O9	1.959(3)	Zn3-O14	1.971(3)
Zn3-O2	2.057(2)	Zn3-N4	2.104(3)	Zn3-N3	2.150(3)
Bond	Angles	Bond	Angles	Bond	Angles
O11-Zn1-O13	89.62(13)	O11-Zn1-O15	114.09(13)	O13-Zn1-O15	99.82(11)
O11-Zn1-O2	145.43(15)	O13-Zn1-O2	93.15(10)	O15-Zn1-O2	99.38(9)
O11-Zn1-O1	88.93(11)	O13-Zn1-O1	164.20(13)	O15-Zn1-O1	95.13(10)
O2-Zn1-O1	79.31(9)	O5-Zn2-O12	114.15(11)	O5-Zn2-O1	92.43(9)
O12-Zn2-O1	90.61(10)	O5-Zn2-N1	126.79(11)	O12-Zn2-N1	118.97(11)
O1-Zn2-N1	84.29(10)	O5-Zn2-N2	87.16(10)	O12-Zn2-N2	94.10(11)
O1-Zn2-N2	175.02(10)	N1-Zn2-N2	91.98(11)	O9-Zn3-O14	112.13(11)
O9-Zn3-O2	93.72(10)	O14-Zn3-O2	95.00(10)	O9-Zn3-N4	88.47(11)
O14-Zn3-N4	96.81(11)	O9-Zn3-N3	121.50(11)	O2-Zn3-N3	81.51(10)
O2-Zn3-N4	166.17(11)	O14-Zn3-N3	126.37(11)	N4-Zn3-N3	85.70(12)



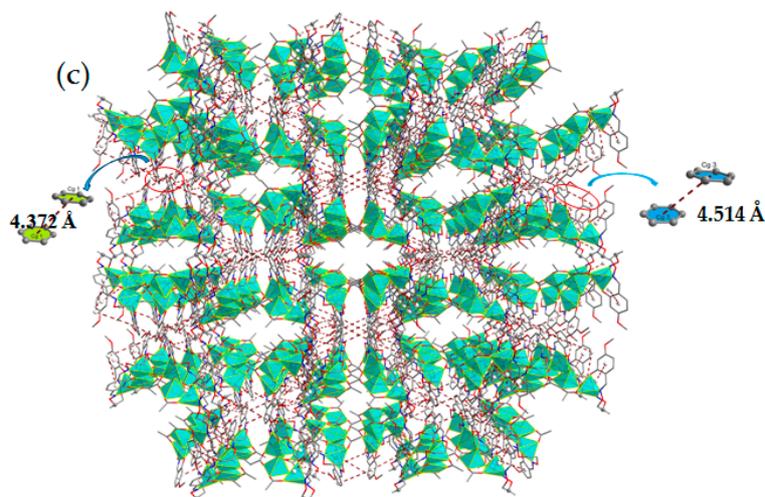
**Figure 3.** (a) Representation of the  $Zn^{II}$  coordination compound structure; (b) The coordination polyhedra of Zn1 and Zn2 centers.

### 3.4. Supra-Molecular Interaction

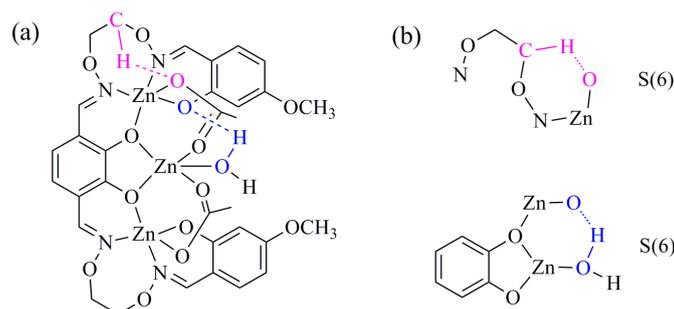
As illustrated in Table 3 and Figure 4, there were four pairs of intra-molecular O15-H15B...O9, O15-H15B...O5, C10-H10A...O12 and C20-H20B...O14 hydrogen bond interactions and a pair of C-H... $\pi$  inter-molecular hydrogen bonds in the  $Zn^{II}$  coordination compound. The  $Zn^{II}$  coordination compound molecules were inter-linked effectively via C-H... $\pi$  hydrogen bonds (C19-H19B...Cg1) into a 1D supermolecular structure. Furthermore, one molecule could link four adjacent molecules into an infinite 3D net-like supramolecular structure by two pairs of intermolecular Cg1...Cg1 and Cg3...Cg3 interactions [66–72]. The weak hydrogen bonds existing in the  $Zn^{II}$  coordination compound have been described in graph sets (Figure 5) [73]. Additionally, the hydrogen bonding scheme of the  $Zn^{II}$  coordination compound is defective due to suppression of the electron density originating from solvent molecules (used SQUEEZE) and subsequent exclusion of these solvent molecules from the refinement model.



**Figure 4.** Cont.



**Figure 4.** (a) Intra-molecular hydrogen bondings of the  $Zn^{II}$  coordination compound unit (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity); (b) One-dimensional supra-molecular structure of the  $Zn^{II}$  coordination compound, mediated by inter-molecular  $C-H\cdots\pi$  (pink) interactions; (c) 3-D supramolecular structure of the  $Zn^{II}$  coordination compound, mediated by intermolecular  $C-H\cdots\pi$  and  $\pi\cdots\pi$  interactions.



**Figure 5.** (a) Graph set assignments for the  $Zn^{II}$  coordination compound; (b) Partial enlarged drawing of hydrogen bonds.

**Table 3.** Hydrogen bonding and  $\pi\cdots\pi$  stacking interactions [ $\text{\AA}$ ,  $^\circ$ ] for the  $Zn^{II}$  coordination compound.

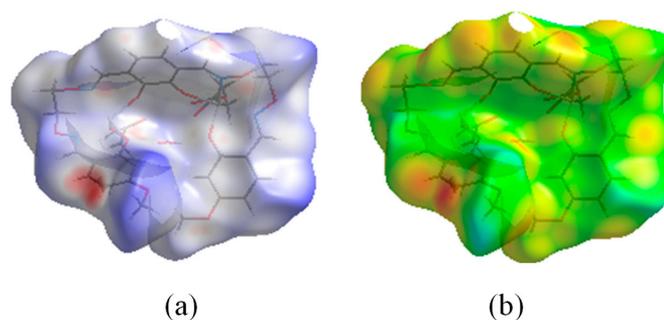
D-H...A	d(D-H)	d(H-A)	d(D-A)	$\angle D-X-A$	Symmetry Code
O15-H15B...O9	0.85	1.84	2.675(4)	168	
O15-H15C...O5	0.85	1.80	2.625(4)	162	
C10-H10A...O12	0.97	2.49	3.367(5)	150	
C20-H20B...O14	0.97	2.42	3.296(6)	150	
C19-H19B...Cg1	0.97	2.84	3.601(5)	136	$1/2 - X, 1/2 + Y, 1/2 - Z$
Cg1...Cg1			4.372		$1/2 - X, 1/2 - Y, 1 - Z$
Cg3...Cg3			4.541		$1/2 - X, 1/2 - Y, -Z$

Note: Cg1 is the centroids for benzene ring C12–C17, Cg3 is the centroids for benzene ring C22–C27.

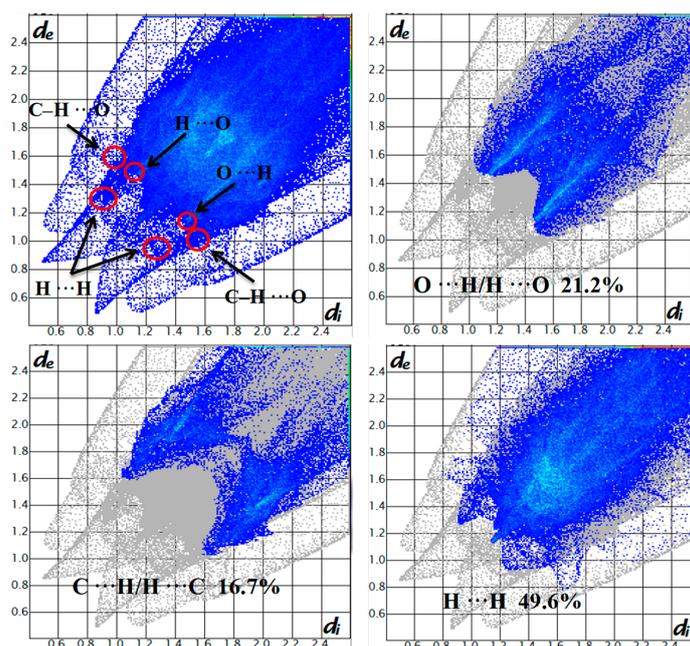
### 3.5. Hirshfeld Surfaces

The Hirshfeld surfaces of the  $Zn^{II}$  coordination compound are depicted in Figure 6, exhibiting surfaces that have been mapped over  $d_{norm}$  and  $d_i$  [74,75]. The interactions between hydroxyl oxygen in the  $Zn^{II}$  coordination compound can be seen as bright red areas in the Hirshfeld surface in Figure 7.

The light red spots are owing to C–H···O interactions, and other visible spots correspond to C···H and H···H contacts on the surface. Figure 7 shows the 2D plots generated [76–78] which correspond to the C···H, O···H and H···H interactions from the Hirshfeld surface of the Zn<sup>II</sup> coordination compound. To provide context, the overview of the full fingerprint is depicted in grey and the blue area showing the separate contact. The proportions of O···H/H···O, C···H/H···C and H···H interactions are composed of 22.3, 12.1 and 49.7% of the all Hirshfeld surfaces for each Zn<sup>II</sup> coordination compound molecule, respectively. It is because of the existence of these hydrogen bondings that the Zn<sup>II</sup> coordination compound can be stable.



**Figure 6.** Hirshfeld surfaces mapped with (a)  $d_{norm}$  and (b)  $d_i$  of the Zn<sup>II</sup> coordination compound. The surfaces are depicted as transparent to allow visualization of the molecule structure.

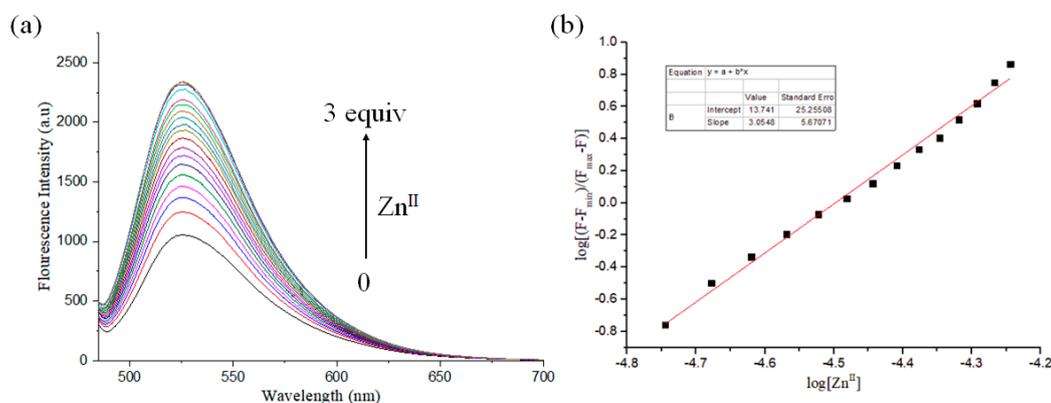


**Figure 7.** Fingerprint plot of the Zn<sup>II</sup> coordination compound: full and resolved into full and resolved into O···H, C···H and H···H contacts exhibiting the percentages of contacts contributed to the total Hirshfeld surface area of the Zn<sup>II</sup> coordination compound molecule.

### 3.6. Fluorescent Spectra

The fluorescence titration experiment of the Zn<sup>II</sup> coordination compound with H<sub>4</sub>L was studied. Figure 8 shows gradual changes in the fluorescence spectra of H<sub>4</sub>L upon addition of Zn<sup>II</sup> ions. The ligand exhibited an intense emission at ca. 525 nm upon excitation at 380 nm based on global maximum determined from three-dimensional fluorescence spectra, which could be attributed to

intra-ligand  $\pi-\pi^*$  transition [79–81]. Figure 8 obviously indicates that fluorescence emission of the ligand  $H_4L$  was very weak, probably owing to isomerization of C=N double bond, intramolecular hydrogen bond between azomethine and hydroxyl moieties of the aromatic group. Upon incremental addition of  $Zn^{II}$  ions to the solution of  $H_4L$ , fluorescence emission intensity at 523 nm gradually increased, and this peak remained relatively constant after the addition of 3 equiv.

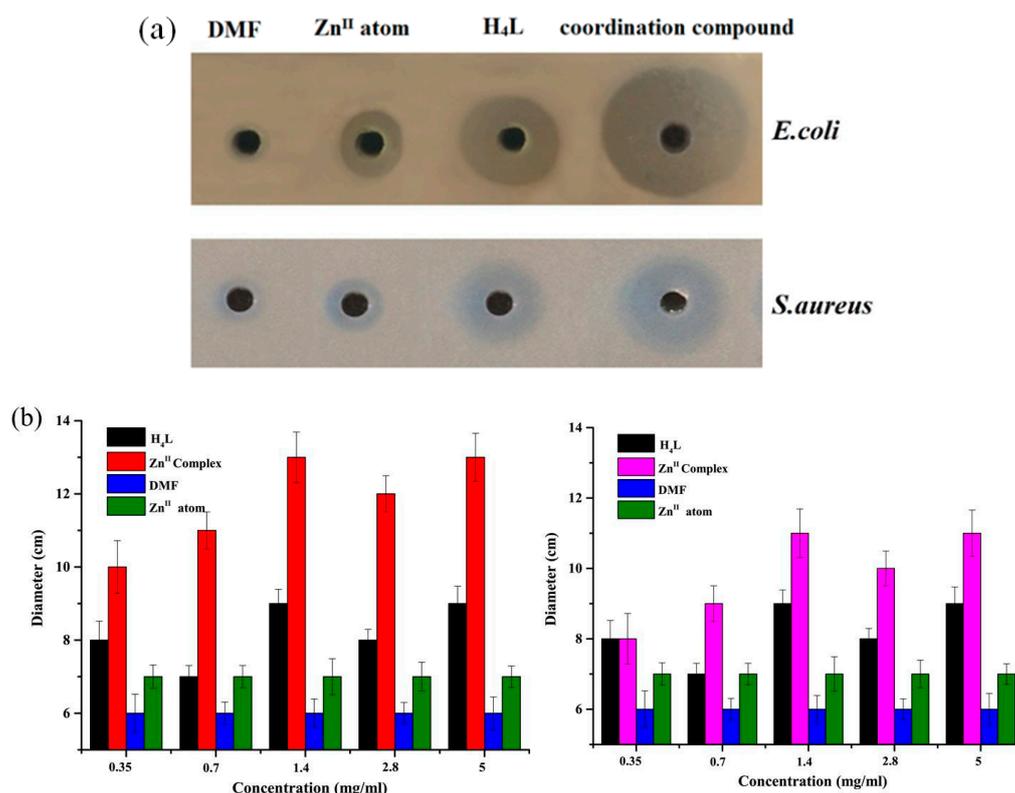


**Figure 8.** (a) Fluorescence spectrum changes of the  $H_4L$  solution ( $c = 5 \times 10^{-5}$  mol/L) upon addition of different amounts of  $Zn^{II}$  ions (0–3.0 equiv) in dilute dichloromethane:methanol ( $v:v = 1:1$ ) solutions at room temperature; (b) The linear relationship between fluorescence intensity and the concentrations of  $Zn^{II}$  ions. ( $\lambda_{ex} = 380$  nm,  $\lambda_{em} = 523$  nm).

The  $Zn^{II}$  coordination compound showed a strong and broad luminescence with maximum emission at ca. 523 nm upon excitation at 380 nm, which is moved bathochromically to that of  $H_4L$ . Compared with the emission spectrum of  $H_4L$ , enhanced fluorescent intensity of the  $Zn^{II}$  coordination compound was observed, displaying that intra-ligand transition has been affected owing to the introduction of the  $Zn^{II}$  atoms [82,83]. No emissions coming from ligand-to-metal/metal-to-ligand charge-transfer or metal-centered excited states are expected for the  $Zn^{II}$  coordination compound, since  $Zn^{II}$  is a  $d^{10}$  ion. Therefore, the emission of the  $Zn^{II}$  coordination compound observed is tentatively assigned to the intra-ligand  $\pi-\pi^*$  fluorescence. From the emission intensity by following the modified Benesi–Hildebrand equation, the association constant of compound was calculated as  $1.59 \times 10^4$   $M^{-1}$  [31–34].

### 3.7. Antimicrobial Activities

The antimicrobial properties of  $H_4L$  and its  $Zn^{II}$  coordination compound were detected against *Escherichia coli* as *Staphylococcus aureus* and Gram-negative bacteria as Gram-positive bacteria via a punch method. The bacterial suspension was mixed in sterile LB (lysogeny broth agar) plates (2% agar), then made four holes with a hole punch, last added DMF,  $Zn^{2+}$ ,  $H_4L$ , and the  $Zn^{II}$  coordination compound into every holes. After 7 h of incubation at 37 °C, the growth-inhibitory effect was monitored and diameters of the inhibition zones were measured. The discs measuring 5 mm in diameter were dissolved in DMF. The diameters of inhibition zones of  $H_4L$  and its  $Zn^{II}$  coordination compound are given in Figure 9, the  $Zn^{II}$  coordination compound proved more enhanced antimicrobial activities than the bis(salamo)-like tetraoxime  $H_4L$  under the same concentrations.



**Figure 9.** (a) The diameters of inhibition zones of *E. coli* and *S. aureus* at different concentrations; (b) the diameter of inhibition zones of *E. coli* and *S. aureus* in different concentrations.

As shown in Figure 9, the inhibitory effect of the Zn<sup>II</sup> coordination compound at different concentrations was studied, the results showed that the antibacterial effect of the Zn<sup>II</sup> coordination compound increased with increasing concentrations. The increase in the antibacterial activity of the Zn<sup>II</sup> coordination compound with increase in concentration can be explained according to the chelation theory. Chelation reduces the polarity of the metal atom mainly owing to partial sharing of positive charge of Zn<sup>II</sup> atom with donor groups and possible delocalization of  $\pi$ -electron within the whole chelate ring. Further, it enhances the lipophilic character of the central atom. These results are similar to earlier reports of biological activities of similar salamo-like Co<sup>II</sup> coordination compounds [84].

#### 4. Conclusions

A newly designed symmetric bis(salamo)-like chelating tetraoxime ligand H<sub>4</sub>L, possessing a C-shaped O<sub>4</sub> site besides the two N<sub>2</sub>O<sub>2</sub> sites, has been synthesized, and its Zn<sup>II</sup> coordination compound [LZn<sub>3</sub>(OAc)<sub>2</sub>(H<sub>2</sub>O)] has been determined by X-ray crystallography. The UV-Vis titration experiment clearly showed the reaction stoichiometry ratio to be 3:1. In the Zn<sup>II</sup> coordination compound, Zn1 is pentacoordinate with a strongly distorted square pyramidal geometry, while Zn2 and Zn3 possess pentacoordinates with distorted trigonal bipyramidal geometries. Furthermore, the Hirshfeld surface analysis indicated that the Zn<sup>II</sup> coordination compound could be stable due to intramolecular hydrogen bonds and some weaker interactions. Fluorescence behaviors of H<sub>4</sub>L and its Zn<sup>II</sup> coordination compound were investigated, compared with the ligand H<sub>4</sub>L, the emission intensity of the Zn<sup>II</sup> coordination compound increased obviously, which indicated that the Zn<sup>II</sup> ions possess a quality of fluorescent enhancement. Antimicrobial experiments showed that the Zn<sup>II</sup> coordination compound demonstrated more enhanced antimicrobial activities than H<sub>4</sub>L under the same conditions.

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