

Synthesis and Fluorescence Properties of Asymmetrical Salamo-Type Tetranuclear Zinc(II) Complex

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Abstract: A new tetranuclear zinc(II) complex with an asymmetrical Salamo-type chelating ligand, H₃L (5-methoxy-6'-hydroxy-2,2'-(ethylenedioxybis(nitrilomethylidyne))diphenol), was synthesized and characterized using FT-IR, elemental analyses, X-ray single crystal diffraction method, UV-Vis, and fluorescence spectra. The zinc(II) complex possesses the cell parameters $a = 8.1960(7)$ Å, $b = 9.8127(8)$ Å, $c = 16.5428(15)$ Å, $Z = 1$, $V = 1172.5(2)$ Å³, $R_1 = 0.0722$, and $wR_2 = 0.1558$, and crystallizes in the triclinic system, with space group $P-1$. X-ray crystal structure analysis reveals that Zn1 and Zn2 atoms are all pentacoordinated and adopt slightly twisted tetragonal pyramidal and trigonal bipyramidal geometries. The zinc(II) complex forms a 1D supramolecular chain via intermolecular hydrogen bonds along the b axis. Besides, the fluorescence properties have been discussed.

Keywords: Salamo-type ligand; zinc(II) complex; synthesis; crystal structure; fluorescence property

1. Introduction

Over the past years, research has shown the Salen-type [1–8] and Salamo-type [9–17] compounds to be exceptionally good chelating ligands in the fields of organometallic chemistry and coordination chemistry. The Salamo metal complexes are widely utilized in various fields such as industrial catalyses [18,19], biological fields [20,21], ion recognitions [22–24], environmental sciences [25–28], and magnetic [29,30] and luminescent materials [31–39]. Recently, a lot of researchers have tried many approaches to change the $(-\text{CH}=\text{N}-(\text{CH}_2)_n-\text{N}=\text{CH}-)$ instead of $(-\text{CH}=\text{N}-\text{O}-(\text{CH}_2)_n-\text{O}-\text{N}=\text{CH}-)$ unit in order to make the exchange reaction and hydrolysis reaction rate of the compounds greatly reduced and the balance level raised to a very great extent, so the Salamo-type compounds are more stable than the Salen-type compounds [40–42]. Research on Salen-type compounds has yet to be fully explored. Besides, their complexes often form supramolecular systems that have unique structures, a novel bonding pattern, a specific microstructure, and excellent macroscopic properties by the intermolecular association of the weak non-covalent bonding [43–45]. More ideal structural variations, drastic changes in characteristics of the previous complexes, and novel properties could be obtained through the asymmetric configuration. Herein, a new asymmetrical Salamo-type compound, 5-methoxy-6'-hydroxy-2,2'-(ethylenedioxybis(nitrilomethylidyne))diphenol (H₃L) and its zinc(II) complex, were designed and synthesized and structurally characterized.

2. Experimental

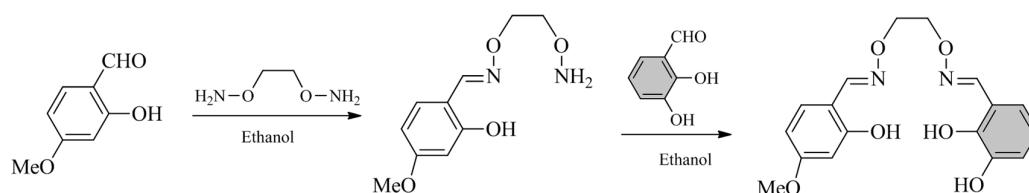
2.1. Materials and Measurements

3-hydroxysalicylaldehyde (99%) and 4-Methoxysalicylaldehyde (98%) were purchased from Alfa Aesar (New York, NY, USA), while Tianjin Chemical Reagent Factory supplied the remaining reagents. Elemental analysis for zinc was detected by IRIS ER/S-WP-1 ICP atomic emission spectrometer (Elementar, Berlin, Germany). C, H, and N were analyzed using GmbH VariuoEL V3.00 automatic elemental analysis instrument (Elementar, Berlin, Germany). IR spectra ($400\text{--}4000\text{ cm}^{-1}$) 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). ^1H NMR spectra were determined by German Bruker AVANCE DRX-400/600 spectroscopy (Bruker AVANCE, Billerica, MA, USA). Fluorescence spectra were recorded on an F-7000 FL spectrophotometer (Hitachi, Tokyo, Japan). X-ray single crystal structure determination of the zinc(II) complex was carried out on a SuperNova Dual (Cu at zero) four-circle diffractometer.

2.2. Synthesis of H_3L

The synthesis of 5-methoxy-6'-hydroxy-2, 2'-[ethanedioxybis(nitrilomethylidyne)]diphenol (H_3L) is given (Scheme 1).

1,2-Bis(aminooxy)ethane and 2-[O-(1-ethyloxyamide)]oxime-5-methoxyphenol were synthesized according to an analogous method reported earlier [15,46]. A colorless ethanol solution (4 mL) of 2,3-dihydroxybenzaldehyde (256.32 mg, 2.0 mmol) was slowly added to the ethanol solution (4 mL) of 2-[O-(1-ethyloxyamide)]oxime-5-methoxyphenol (425.05 mg, 2.0 mmol), and the mixture was stirred at $52\text{ }^\circ\text{C}$ for 6 h. After cooling to room temperature, the precipitate was filtered and washed successively with ethanol and ethanol-hexane (1:4) ($3 \times 4\text{ mL}$), respectively. The product was purified with recrystallization from ethanol and dried in vacuo to get a yellow powder. Yield: 80.7%. m.p. $110\text{--}111.5\text{ }^\circ\text{C}$. Anal. calcd. for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_6$ (%): C 59.84, H 6.21, N 7.41; found: C 59.66, H 6.12, N 7.73. ^1H NMR (400 MHz, CDCl_3) δ 9.92 (d, $J = 7.8\text{ Hz}$, 2H), 8.19 (d, $J = 18.3\text{ Hz}$, 1H), 7.05 (d, $J = 8.4\text{ Hz}$, 1H), 6.96 (d, $J = 7.2\text{ Hz}$, 1H), 6.87–6.71 (m, 2H), 6.53–6.44 (m, 2H), 4.47 (d, $J = 6.7\text{ Hz}$, 3H), 3.81 (s, 4H).



Scheme 1. Routes to the synthesis of ligand H_3L .

2.3. Synthesis of the Zinc(II) Complex

A dropwise solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (8.78 mg, 4 mmol) in ethanol (9 mL) was added to a solution of H_3L (6.84 mg, 2 mmol) in chloroform (5 mL) at r.t., after which the mixed solution was stirred for 6 h at $60\text{ }^\circ\text{C}$ and was then filtered off. The filtrate was allowed to stand at r.t. for several days, and yellow prismatic single crystals suitable for X-ray crystallographic analysis were obtained. Yield: 51.6%. Anal. calcd. for $\text{C}_{42}\text{H}_{48}\text{N}_4\text{Zn}_4\text{O}_{18}$ (%): C, 43.54; H, 4.19; N, 4.89; Zn, 22.55. Found: C, 43.55; H, 4.18; N, 4.84; Zn, 22.58. Table 1 shows the data collection and refinements of the zinc(II) complex.

2.4. X-ray Crystallography

Single crystal X-ray diffraction data were collected at 173 K on a SuperNova Dual (Cu at zero) four-circle diffractometer with graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The

structure was solved by the direct methods and all hydrogen atoms were added. All non-hydrogen atoms were refined anisotropically using a full-matrix least-squares procedure on F^2 with SHELXL-2014 [47,48]. The LP factor and semi-empirical absorption correction by SADABS were applied to the intensity data. The crystal data and experimental parameters relevant to the structure determination are listed in Table 1, and the final positional and thermal parameters are available as supplementary material.

Table 1. Crystal data and structure refinement for the zinc(II) complex.

Molecular Formula	$C_{42}H_{48}N_4Zn_4O_{18}$
Formula weight	1158.32
Temperature (K)	221
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P-1$
a (Å)	8.1960(7)
b (Å)	9.8127(8)
c (Å)	16.5428(15)
α (°)	106.392(8)
β (°)	92.669(8)
γ (°)	111.299(8)
V (Å ³)	1172.5(2)
Z	1
D_{calc} (g·cm ^{−3})	1.640
μ (mm ^{−1})	2.099
$F(000)$	592
Crystal size (mm)	$0.21 \times 0.23 \times 0.25$ $-10 \leq h \leq 8,$ $-12 \leq k \leq 12,$ $-18 \leq l \leq 20$
Index range	
Reflections collected	7315
Independent reflections	4569
Rint	0.0620
Completeness to θ	3.43 to 26.02
Data/ restraints/parameters	4569/3/313
GOF	1.027
Final R_1 , wR_2 indices	$R_1 = 0.0722$, $wR_2 = 0.1127$
R_1^a , wR_2^b indices (all data)	$R_1 = 0.1493$, $wR_2 = 0.1555$
Largest differences peak and hole (e Å ^{−3})	0.918 and -0.493

$$a. R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; b. wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}.$$

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, with CCDC-1519979 for the zinc(II) complex. Copies of the data can be obtained 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). These data can be also obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

3. Results and Discussion

3.1. FT-IR Spectra

The most important features in the FT-IR spectra data of H₃L and its zinc(II) complex are listed in Table 2.

Table 2. Infrared absorption spectra of H₃L and its zinc(II) complex (cm^{−1}).

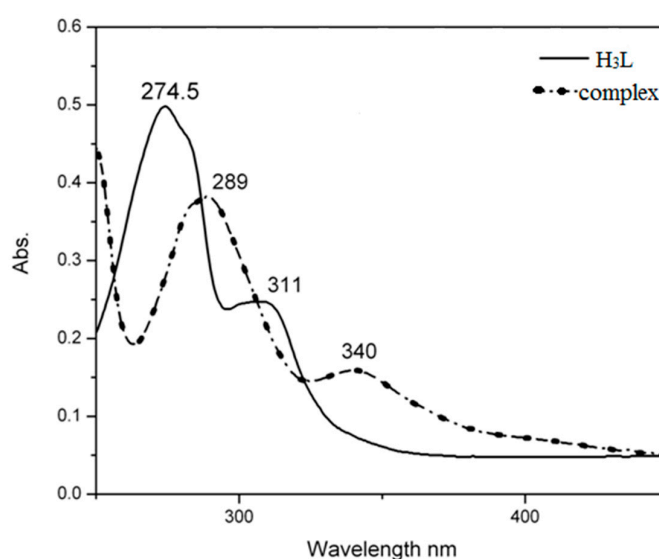
Compound	$\nu(\text{O-H})$	$\nu(\text{C=N})$	$\nu(\text{Ar-O})$	$\nu(\text{Zn-N})$	$\nu(\text{Zn-O})$
H ₃ L	3439	1631	1283	-	-
[{Zn(L)(μ -OAc)Zn(CH ₃ CH ₂ OH)} ₂]	3424	1600	1265	509	467

Data obtained from the FT-IR spectra show differences between H₃L and its zinc(II) complex, and the analysis gives hint about the coordination reaction between H₃L and zinc(II) atoms, and thus suggests formation of a new zinc(II) complex. The characteristic C=N stretching band of H₃L is found at 1631 cm^{−1}, and that of zinc(II) complex appears at 1600 cm^{−1} [49–51]. Upon complexation, this band shifts by a ca. 31 cm^{−1} to a lower frequency, and thus indicates that C=N bond order decreases owing to the binding of the zinc(II) atom to oxime nitrogen atoms [40]. The stretching frequency band of the Aromatic-O atom appears at 1283 cm^{−1} for H₃L, while for the zinc(II) complex the band appears at 1265 cm^{−1} [40,52]. The frequency shift in the Aromatic-O stretching band shows that interaction between the oxygen atoms of phenolic group and zinc(II) atom results in the Zn–O bonds formation [46]. Besides, the O–H stretching band of H₃L is observed at 3439 cm^{−1}, while the absorption broad band at 3424 cm^{−1} in the zinc(II) complex could be ascribed to the –OH group of coordinated ethanol molecules.

3.2. UV-Vis Absorption Spectra

The data and absorption spectra of H₃L and its zinc(II) complex in diluted ethanol solution were presented in Figure 1. The spectrum of the zinc(II) complex is different from that of the free ligand H₃L. The UV-Vis spectrum of the free ligand H₃L exhibits one absorption peak at ca. 275 nm and could be attributed to the π – π^* transition of the benzene rings.

The zinc(II) complex exhibits maximum absorption peak at 289 nm, which indicates that coordination reaction occurs between the zinc(II) atoms and H₃L [46]. Moreover, a new absorption peak at 340 nm was observed in the zinc(II) complex, contrary to the peak observed at 311 nm in H₃L, which could be attributed to the π – π^* transition of the oxime group [46].

**Figure 1.** UV-Vis absorption spectra of H₃L and its zinc(II) complex in ethanol (3.0×10^{-5} mol/L).

3.3. Crystal and Supramolecular Structure of the Zinc(II) Complex

The zinc(II) complex crystal structure is depicted in Figure 2, while Table 3 shows the list of important bond distances and bond angles.

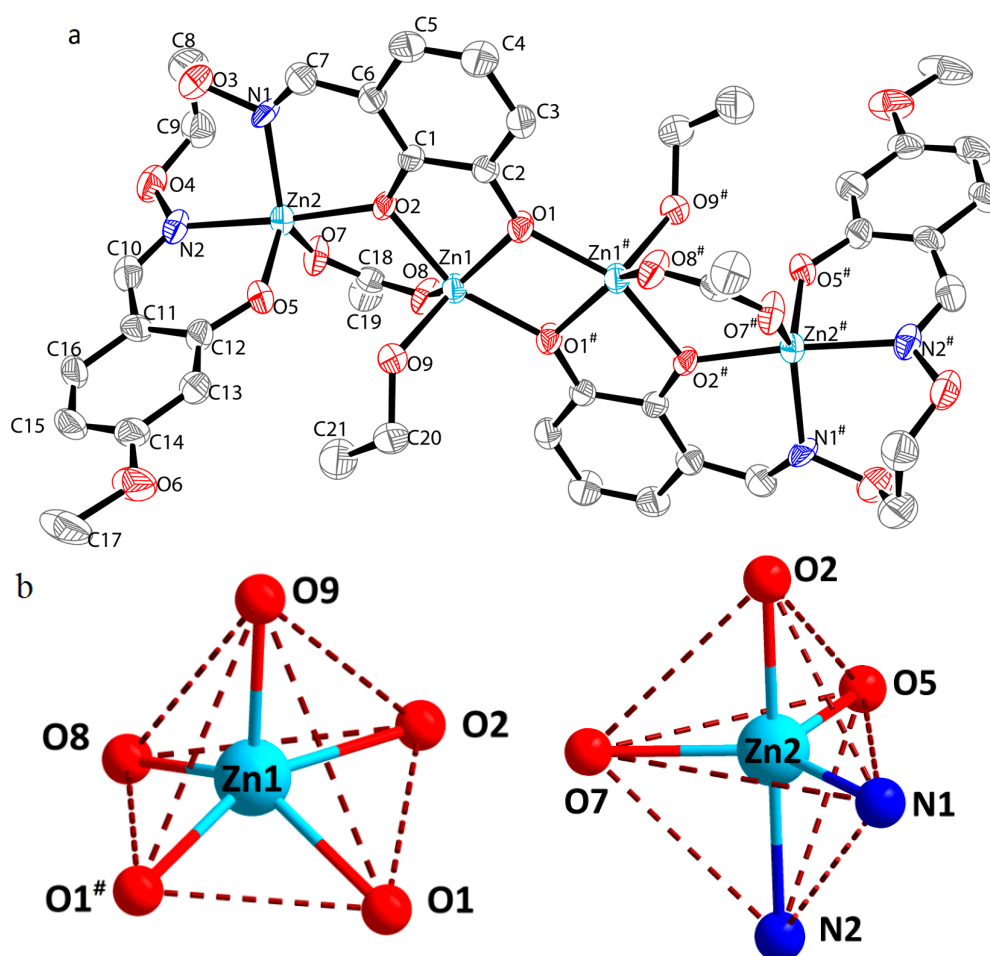


Figure 2. (a) View of the molecular structure of the zinc(II) complex with atom labeling (hydrogen atoms are omitted for clarity purpose and are drawn at the 30% probability level). (b) View of zinc(II) atoms of the zinc(II) complex showing coordination polyhedrons.

Table 3. Selected bond distances (Å) and bond angles (°) of the zinc(II) complex.

Bond	Lengths	Bond	Lengths	Bond	Lengths
Zn1-O1	2.039(5)	Zn1-O2	2.058(5)	Zn1-O8	1.963(6)
Zn1-O9	2.026(5)	Zn1-O1 #	2.002(5)	Zn2-O2	2.010(5)
Zn2-N1	2.083(7)	Zn2-O5	1.940(5)	Zn2-O7	1.981(6)
Zn2-N2	2.127(7)				
Bond	Angles	Bond	Angles	Bond	Angles
O1-Zn1-O2	79.6(2)	O1-Zn1-O8	140.6(2)	O1-Zn1-O9	111.2(2)
O1-Zn1-O1 #	77.7(2)	O2-Zn1-O8	96.3(2)	O2-Zn1-O9	89.6(2)
O2-Zn1-O1 #	156.63(2)	O8-Zn1-O9	107.8(2)	O8-Zn1-O1 #	97.9(2)
O9-Zn1-O1 #	103.6(2)	O2-Zn2-O5	94.0(2)	O2-Zn2-O7	91.8(2)
O2-Zn2-N1	85.0(3)	O2-Zn2-N2	175.8(2)	O5-Zn2-O7	113.1(2)
O5-Zn2-N1	117.4(3)	O5-Zn2-N2	89.7(3)	O7-Zn2-N1	129.5(3)
O7-Zn2-N2	88.7(2)	N1-Zn2-N2	91.5(3)		

Symmetry transformations used to generate equivalent atoms: # : $2 - x, 1 - y, -z$.

The complex $[\{Zn(L)(\mu-OAc)Zn(CH_3CH_2OH)\}_2]$ belongs to the triclinic system, with space group $P-1$, and consists of four zinc(II) atoms and two completely deprotonated $(L)^{3-}$ linkers, with two ethanol molecules and two bonded acetate ions. As far as we know, this new 2:4 ($(L)^{3-}$: zinc(II))

Salamo-type zinc(II) coordination complex ratio is rarely reported when compared to its counterpart complexes that have the coordination ratio of 1:1 [46], 2:3 [43], and 4:8 [45] (L: zinc(II)). The terminal zinc(II) atom (Zn2 or Zn2[#]) is penta-coordinated, and situated at an N₂O₂ site of the deprotonated ligand moiety with one O7 atom from μ -acetate ion adopting a slightly twisted trigonal bipyramidal geometry ($\tau_2 = 0.772$) [11]. The central zinc(II) atom (Zn1 or Zn1[#]) is also penta-coordinated via the three oxygen atoms (O1, O2 and O1[#]), one O9 atom from the coordinated EtOH molecule, and one O8 atom from μ -acetate ion forming a slightly distorted tetragonal pyramidal geometry ($\tau_1 = 0.265$) [11]. The Zn1 and Zn2 atoms are connected through μ -acetate ion in a familiar M-O-C-O-M fashion.

Table 4 summarizes the inter- and intramolecular hydrogen bonds in the zinc(II) complex. From Figure 3, the proton (–C9H9B or –C9[#]H9B[#]) of ethylenedioxime carbon atom (C9 or C9[#]) of (L)^{3–} unit is hydrogen bonded to oxygen atom (O7) of the μ -acetate ions, and the proton (–O9H9 or –O9[#]H9[#]) of the coordinated ethanol molecule is hydrogen bonded to one of phenolic oxygen atom (O5 or O5[#]) of the (L)^{3–} unit. Thus, two pairs of intramolecular hydrogen bonds C9–H9B...O7, C9[#]–H9B[#]...O7[#], O9–H9...O5 and O9[#]–H9[#]...O5[#] [53–59] are formed. Under the intermolecular force of C7–H7...O6 and C7[#]–H7[#]...O6[#], a 1D supramolecular chain that extends infinitely in the *b* axis direction is formed by the crystal of [Zn(L)(μ -OAc)Zn(CH₃CH₂OH)]₂, as depicted in Figure 4 [60–67].

Table 4. The intra- and intermolecular hydrogen bonds of the Zn(II) complex.

D–H...A	d(D–H) (Å)	d(H...A) (Å)	d(D...A) (Å)	\angle D–H...A (°)	Symmetry Code
O9–H9...O5	0.86	1.88	2.64 8(2)	147	<i>x</i> , 1 + <i>y</i> , <i>z</i>
C9–H9B...O7	0.97	2.53	3.33 6(5)	141	
C7–H7...O6	0.93	2.55	3.47 3(4)	171	

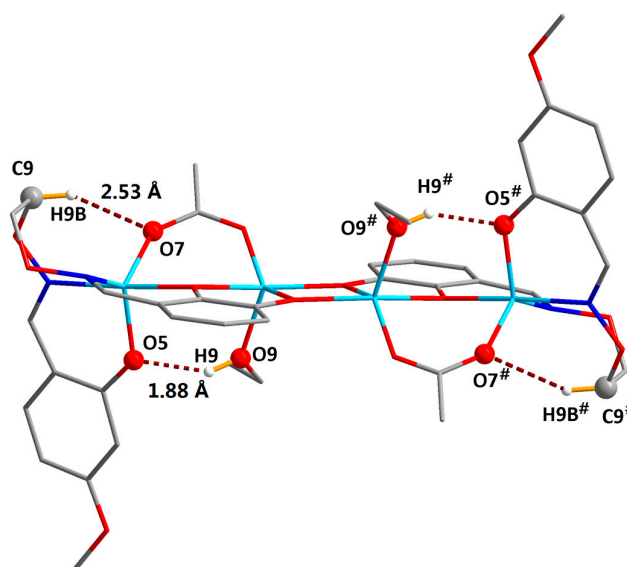


Figure 3. View of the intramolecular hydrogen bonds of the zinc(II) complex unit (for clarity's sake, hydrogen atoms are omitted except those forming hydrogen bonds).

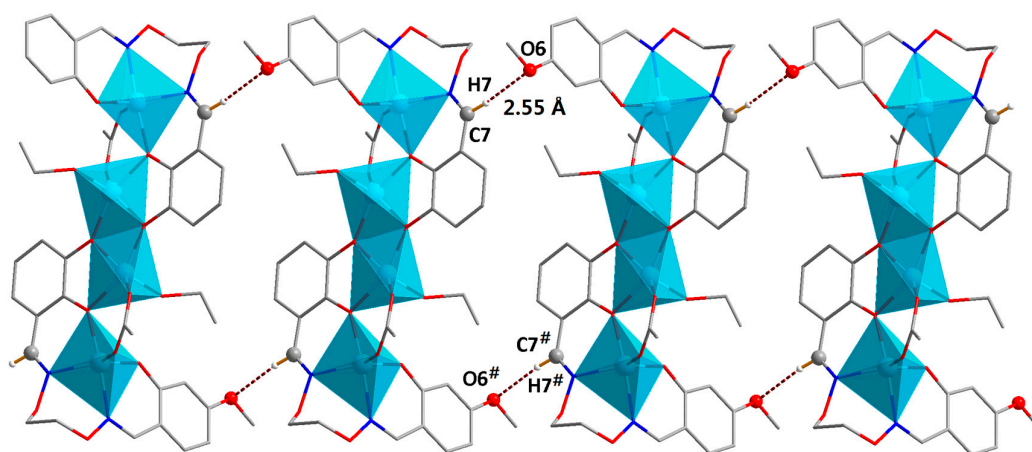


Figure 4. A 1D chain of the zinc(II) complex viewed along the *b* axis (for clarity's sake, hydrogen atoms are omitted except those forming hydrogen bonds).

3.4. Fluorescent Properties

As shown in Figure 5, H_3L exhibits a broad emission at 406 nm upon excitation at 268 nm, while the zinc(II) complex displays an intense photoluminescence with maximum emission peak at ca. 415 nm upon excitation at 268 nm, which is considered to be bathochromically shifted when compared to that of H_3L , indicating that molecular inter-atomic forces and degree of conjugation are better in the zinc(II) complex internal molecules, due to the intraligand π - π^* transition [18]. The Zn(II) complex has a greater fluorescence intensity, and it may have potential as a luminescent material.

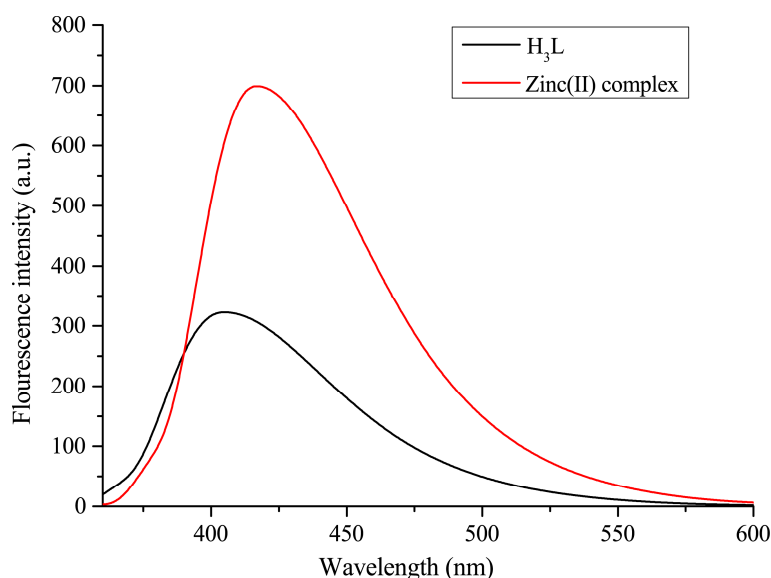


Figure 5. The Fluorescence spectra of H_3L and its zinc(II) complex in methanol (3.0×10^{-5} mol/L).

4. Concluding Remarks

In this paper, A new tetranuclear zinc(II) complex has been successfully prepared and characterized. X-ray crystal structure analysis reveals that the four zinc(II) atoms are all penta-coordinated, in which two of the zinc(II) atoms lie in the N_2O_2 coordination spheres of Salamo-type bis-oxime (L) $^{3-}$ moieties and adopt slightly distorted trigonal bipyramid geometries ($\tau_2 = 0.772$), and the remaining two zinc(II) atoms adopt slightly distorted tetragonal pyramidal geometries ($\tau_1 = 0.265$). Moreover, the zinc(II) complex molecules assemble to form an infinite 1D

chain-like supramolecular structure via intermolecular C7–H7···O6 and C7[#]–H7[#]···O6[#] hydrogen bonding interactions. The fluorescence properties show that the Zn(II) complex may have the potential to be used as a luminescent material.

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Author Contributions: Wen-Kui Dong conceived and designed the experiments; Quan-Peng Kang performed the experiments; Gao-Xian An analyzed the data; Yang Zhang contributed reagents/materials/analysis tools; Yun-Dong Peng and Xiao-Yan Li wrote the paper.

Conflicts of Interest: The authors declare no competing financial interests.

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