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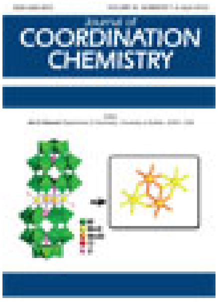

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An unprecedented tetranuclear Zn(II) complex with an unsymmetric Salen-type bisoxime ligand: synthesis, crystal structure, and spectral properties

Wen-Kui Dong [a] , Si-Jia Xing [a] , Yin-Xia Sun [a] , Li Zhao [a] , Lan-Qin Chai [a] & Xiong-Hou Gao [b]

[a] School of Chemical and Biological Engineering, Lanzhou Jiaotong University , Lanzhou 730070 , P.R. China

[b] Lanzhou Petrochemical Research Center , PetroChina , Lanzhou 730060 , P.R. China

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An unprecedented tetranuclear Zn(II) complex with an unsymmetric Salen-type bisoxime ligand: synthesis, crystal structure, and spectral properties

WEN-KUI DONG*†, SI-JIA XING†, YIN-XIA SUN†, LI ZHAO†,
LAN-QIN CHAI† and XIONG-HOU GAO‡

†School of Chemical and Biological Engineering, Lanzhou Jiaotong University,
Lanzhou 730070, P.R. China
‡Lanzhou Petrochemical Research Center, PetroChina, Lanzhou 730060, P.R. China

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A tetranuclear Zn(II) complex, $[Zn_4L_2(OAc)_2(CH_3OH)_2]$ with an unsymmetric Salen-type bisoxime (H_3L = 6-hydroxy-4′,6′-dibromo-2,2′-[ethylenediyldioxybis(nitrilomethylidyne)] diphenol), has been synthesized and structurally characterized. There are two kinds of coordination geometry (trigonal bipyramidal and square pyramidal) in the Zn(II) complex. The molecule has serious distortion probably from the asymmetry. The complex exhibits blue emission with the maximum emission wavelength $\lambda_{max} = 423$ nm when excited with 340 nm.

Keywords: Unsymmetric Salen-type bisoxime ligand; Zn(II) complex; Synthesis; Spectral property

1. Introduction

Transition metal complexes bearing Salen-type ligands [1–6] or its derivatives (R-CH=N–O–$(CH)_2$–O–N=CH-R) [7–11] have been reported, as their catalytic activity and spectral characteristics have attracted interest. Zn(II) complexes with Salen-type ligands also draws attention for their photoluminescent characteristics [12–14]. Zn(II) complexes with symmetrical Salen-type bisoxime ligands often show structures of 1 : 1 [15], 1 : 2 [16], 2 : 2 [17], and 8 : 4 [18] (Zn : L). However, complex with an unsymmetrical Salen-type bisoxime composition (R^1-CH=N–O–$(CH)_2$–O–N=CH-R^2) has not been reported. Selective synthesis of unsymmetrical ligands is important because electronic and steric effects of Salen-metal-assisted catalysis may be controlled by introduction of different substituents into the two benzene rings [19–21]. In this article, we report a five-coordinate tetranuclear Zn(II) complex, $[Zn_4L_2(OAc)_2(CH_3OH)_2]$, with the asymmetric Salen-type ligand 6-hydroxy-4′,6′-dibromo-2,2′-[ethylenediyldioxybis (nitrilomethylidyne)]diphenol (H_3L); the 4 : 2 (Zn : L) complex by five-coordination is unusual.

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*Corresponding author. Email: dongwk@126.com

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2. Experimental

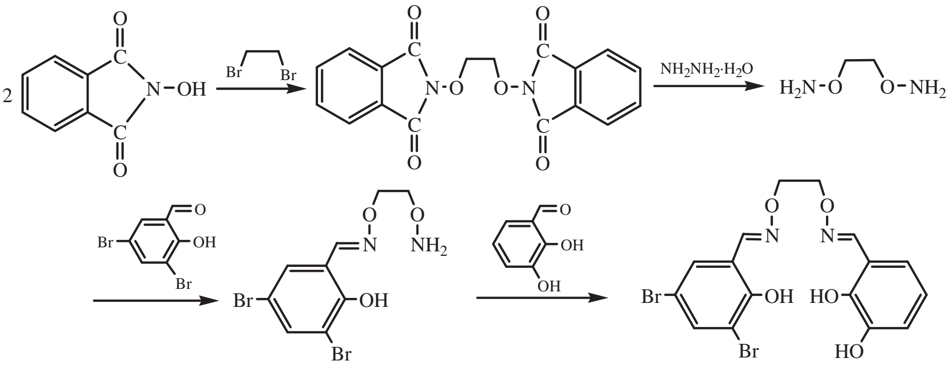
2.1. *Materials and physical measurements*

3,5-Dibromo-2-hydroxybenzaldehyde and 2,3-dihydroxybenzaldehyde from Aldrich were used without purification. 1,2-Dibromoethane was dried and redistilled before use. Other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. Elemental analysis for Zn was detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. C, H, and N analyses were carried out with a GmbH VarioEL V3.00 automatic elemental analyzer. Infrared (IR) spectra from 500 to 4000 cm^{-1} were recorded on a VERTEX70 FT-IR spectrophotometer using KBr pellets. ^{1}H NMR spectra were recorded on a Mercury-400BB spectrometer. UV-Vis absorption and fluorescence spectra were recorded on a Shimadzu UV-2550 spectrometer and Perkin-Elmer LS-55 spectrometer, respectively. X-ray single-crystal structure was determined on a Bruker Smart APEX CCD area detector. Electrolytic conductance measurement was made with a DDS–11D type conductivity bridge using a $1.0 \times 10^{-3}\,mol\,L^{-1}$ solution in DMF at room temperature. Melting points were measured by use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company, and the thermometer was uncorrected.

2.2. *Preparation of H_3L and its complex*

2.2.1. Preparation of 6-hydroxy-4′,6′-dibromo-2,2′-[ethylenediyldioxybis (nitrilomethylidyne)]diphenol (H_3L). 1,2-Bis(aminooxy)ethane was synthesized by a reported method [15, 20]. Yield: 75.2%. Anal. Calcd for $C_2H_8N_2O_2$ (Mw 92.1) (%): C, 26.08; H, 8.76; N, 30.42. Found (%): C, 25.98; H, 8.90; N, 30.38. The synthetic route of the asymmetric Salen-type bisoxime (H_3L) is shown in scheme 1 [22].

First, synthesis for monoxime, a solution of 1,2-bis(aminooxy)ethane (4 mmol) in ethanol (10 mL) was added to a solution of 3,5-dibromo-2-hydroxybenzaldehyde (2 mmol) in ethanol (20 mL) and the mixture was heated at 50–55°C for 5 h. The solution was concentrated *in vacuo* and the residue purified by column chromatography (SiO_2, chloroform/ethyl acetate, 50 : 3) to afford crystals of monoxime. Yield: 59.3%;



Scheme 1. The synthetic route of H_3L.

m.p. 102.5–103.5°C. Anal. Calcd for $C_9H_{10}Br_2N_2O_3$ (Mw 354) (%): C, 30.54; H, 2.85; N, 7.91. Found (%): C, 30.60; H, 2.79; N, 7.87. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.98 (t, $J=4.5$ Hz, 2H), 4.39 (t, $J=4.5$ Hz, 2H), 5.54 (brs, 2H), 6.89 (d, $J=9.0$ Hz, 1H), 7.36 (dd, $J=9.0$, 2.5 Hz, 1H), 8.12 (s, 1H), 9.85 (s, 1H).

Second, a solution of the monoxime (1 mmol) from the first step in ethanol (20 mL) was added to a solution of 2,3-dihydroxybenzaldehyde (1 mmol) in ethanol (20 mL) and the mixture was heated at 50–55°C for 5 h. After cooling to room temperature, white precipitates were collected on a suction filter to give colorless powder. Yield: 68.2%; m.p. 127–128°C. Anal. Calcd for $C_{16}H_{14}Br_2N_2O_5$ (Mw 474.1) (%): C, 40.53; H, 2.98; N, 5.91. Found (%): C, 40.60; H, 2.89; N, 5.96. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.48–4.50 (m, 4H, CH_2), 6.88 (d, $J=8.6$ Hz, 1H), 6.92 (t, $J=7.8$ Hz, 1H), 6.98 (d, $J=7.8$ Hz, 1H), 7.16 (dd, $J=7.8$ Hz, 1.5 Hz, 1H), 7.35 (dd, $J=8.6$ Hz, 2.5 Hz, 1H), 8.16 (s, 1H), 8.23 (s, 1H), 9.72 (s, 1H), 9.77 (s, 1H), 10.38 (s, 1H).

2.2.2. Preparation of $[Zn_4L_2(OAc)_2(CH_3OH)_2]$. A solution of zinc(II) acetate dihydrate (22.0 mg, 0.1 mmol) in methanol (10 mL) was added dropwise to a solution of H_3L (23.69 mg, 0.05 mmol) in chloroform/methanol (1 : 2) (15 mL) at room temperature. The color of the solution turned to bright yellow immediately, was filtered and the filtrate was allowed to stand at room temperature for about 2 weeks. Several yellow block-shaped single-crystals suitable for X-ray crystallographic analysis were obtained. Yield: 18.89%. Anal. Calcd for $C_{38}H_{36}Br_4N_4O_{16}Zn_4$ (Mw 1385.89) (%): C, 32.93; H, 2.62; N, 4.04; Zn, 18.87. Found (%): C, 33.01; H, 2.48; N, 3.95; Zn, 19.09.

2.3. *X-ray structure determination of $[Zn_4L_2(OAc)_2(CH_3OH)_2]$*

Crystal diffraction intensities for $[Zn_4L_2(OAc)_2(CH_3OH)_2]$ were collected at 298(2) K on a CCD area detector with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved with direct methods and refined with full-matrix least-squares based on F^2 using the SHELXTL program package. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically and the methanol hydrogen atoms were located from difference maps and refined with isotropic temperature factors. A summary of parameters for data collection is given in table 1.

3. Results and discussion

3.1. *Crystal structure of $[Zn_4L_2(OAc)_2(CH_3OH)_2]$*

The molecular structure of $[Zn_4L_2(OAc)_2(CH_3OH)_2]$ along with the atom-numbering scheme is represented in figure 1, and selected bond lengths and angles are summarized in table 2.

Zn(II) complex crystallizes in the triclinic system, space group *P*-1, with four Zn(II) ions, two L^{3-}, two acetates, and two methanols resulting in a tetranuclear Zn(II) complex. The structure can be described as two $[Zn_2L(OAc)(CH_3OH)]$ units connected with a diphenoxy-bridge. The coordination sphere of terminal Zn(1) or Zn(1)^i was

Table 1. Crystallographic data and data collection parameters for $[Zn_4L_2(OAc)_2(CH_3OH)_2]$.

Empirical formula	$C_{38}H_{36}Br_4N_4O_{16}Zn_4$
Formula weight (gm^{-1})	1385.83
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	9.1930(8)
b	9.7309(9)
c	15.7301(13)
α	102.6420(10)
β	95.1820(10)
γ	116.991(2)
Volume (Å^3), Z	1194.03(18), 1
Calculated density ($Mg\,m^{-3}$)	1.927
Absorption coefficient (mm^{-1})	5.402
$F(000)$	680
Crystal size (mm^3)	$0.26 \times 0.15 \times 0.12$
θ range for data collection (°)	2.43–25.02
Limiting indices	$-10 \le h \le 10$; $-11 \le k \le 10$; $-18 \le l \le 16$
Reflections collected	6314
Independent reflection	4159 [$R(\text{int}) = 0.0210$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4159/0/311
Goodness-of-fit on F^2	1.043
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0328$, $wR_2 = 0.0722$
R indices (all data)	$R_1 = 0.0512$, $wR_2 = 0.0762$
Largest difference peak and hole ($e\,Å^{-3}$)	0.722 and −0.404

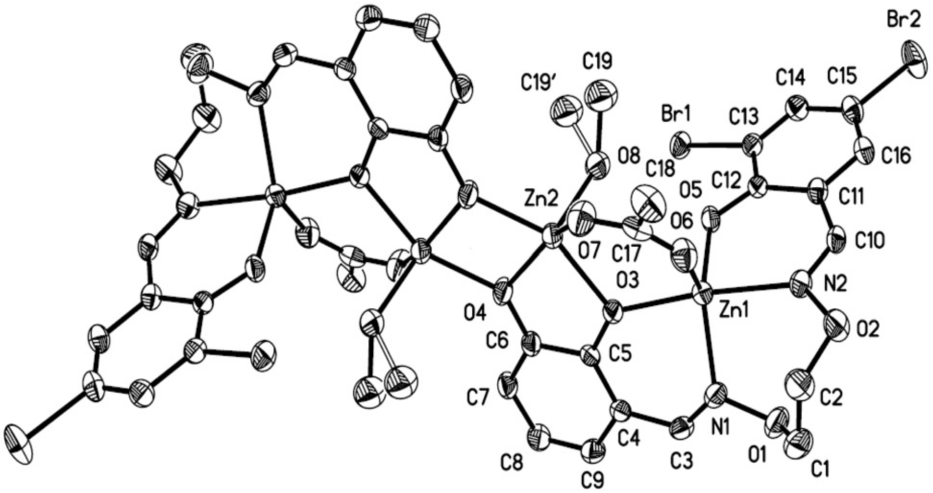


Figure 1. Molecular structure of Zn(II) complex.

completed by N_2O_2 donors and one oxygen (O6) of acetate. The sphere of Zn(2) or Zn(2)^i was completed by three μ-phenolic oxygen atoms, one oxygen acetate, and one oxygen of methanol. Two units serve both as tetradentate N_2O_2 donors for the two terminal zinc(II)'s (Zn(1) and Zn(1)^i), and at the same time as bidentate moieties for the

Table 2. Selected bond lengths (Å) and angles (°) of Zn(II) complex.

Zn(1)–O(5)	1.972(3)	Zn(1)–N(2)	2.134(3)	Zn(2)–O(4)	2.027(3)
Zn(1)–O(6)	1.997(3)	Zn(2)–O(7)	1.973(3)	Zn(2)–O(3)	2.045(3)
Zn(1)–O(3)	2.015(3)	Zn(2)–O(4)#1	1.997(3)	Zn(2)–Zn(2)#1	3.149(1)
Zn(1)–N(1)	2.091(4)	Zn(2)–O(8)	2.029(3)		
O(5)–Zn(1)–O(6)	111.2(1)	N(1)–Zn(1)–N(2)	89.6(1)	O(4)#1–Zn(2)–O(3)	154.5(1)
O(5)–Zn(1)–O(3)	96.4(1)	O(7)–Zn(2)–O(4)#1	98.2(1)	O(8)–Zn(2)–O(3)	93.4(1)
O(6)–Zn(1)–O(3)	92.3(1)	O(7)–Zn(2)–O(8)	103.2(2)	O(4)–Zn(2)–O(3)	79.2(1)
O(5)–Zn(1)–N(1)	122.5(1)	O(4)#1–Zn(2)–O(8)	102.5(1)	O(7)–Zn(2)–Zn(2)#1	129.8(1)
O(6)–Zn(1)–N(1)	126.2(1)	O(7)–Zn(2)–O(4)	148.8(1)	O(4)#1–Zn(2)–Zn(2)#1	38.83(8)
O(3)–Zn(1)–N(1)	85.1(1)	O(4)#1–Zn(2)–O(4)	77.0(1)	O(8)–Zn(2)–Zn(2)#1	109.7(1)
O(5)–Zn(1)–N(2)	88.0(1)	O(4)–Zn(2)–O(8)	108.0(1)	O(4)–Zn(2)–Zn(2)#1	38.16(7)
O(6)–Zn(1)–N(2)	89.5(1)	O(7)–Zn(2)–O(3)	97.4(1)	O(3)–Zn(2)–Zn(2)#1	116.86(8)
O(3)–Zn(1)–N(2)	174.4(1)				

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

Table 3. Hydrogen-bonding distances (Å) and angles (°) for Zn(II) complex.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠D–H···A
O8–H8D···O5	0.820	1.927	2.747	178.23
O8–H8D···Br1	0.820	3.050	3.423	110.39
C3–H3···Br1	0.930	3.042	3.901	154.20

central zinc(II)'s (Zn(2) and Zn(2)^{i}). Acetate coordinates to the two zinc(II)'s *via* a familiar Zn(1)–O–C–O–Zn(2) coordination.

Zn(1) adopts trigonal bipyramidal geometry with axial O(3) and N(2) ($\tau = 0.803$) [23], which deviates from the mean plane (O(6)–N(1)–O(5)) by 0.033 Å. The distances of Zn1 to the five donors are all different (1.972–2.134 Å). The dihedral angle of N(1)–Zn(1)–O(3) and N(2)–Zn(1)–O(5) is 57.50°, which indicates L^{3-} has serious distortion probably as a result of the asymmetry. The geometry of Zn(2) is different from Zn(1). The value of $\tau = 0.095$ clearly indicates that the environment of the Zn(2) atom is close to square pyramidal in which the axial site is occupied by O(8) from methanol. The four donors (O(3), O(4), O(4)^{i}, and O(7)) in the basal plane deviate slightly from the mean plane (O(3) and O(4)^{i} above average by 0.132 Å and 0.137 Å, O(4) and O(7) below average by 0.158 Å and 0.111 Å, respectively), and Zn(2) deviates by 0.404 Å. The dihedral angle of O(7)–Zn(2)–O(3) and O(4)–Zn(2)–O(4)^{i} is 34.32°. Zn(2) and Zn(2)^{i} connected with two μ-phenolic oxygen atoms (O(4) and O(4)^{i}). The configuration of the four atoms (Zn(2), O(4), Zn(2)^{i}, and O(4)^{i}) is a parallelogram (Zn(2)–O(4), 2.027 Å; Zn(2)–O(4)^{i}, 1.997 Å; ∠O(4)–Zn(2)–O(4)^{i}, 77.0(1)°; ∠Zn(2)–O(4)–Zn(2)^{i}, 103.0(1)°). Thus, two types of coordination geometry (trigonal bipyramidal and square pyramidal) exist in the Zn(II) complex.

In this complex, two pairs of intramolecular O8–H8D···Br1 and O8–H8D···O5 hydrogen bonds form two five-membered rings. Moreover, each molecule links two other molecules into an infinite 1-D supramolecular chain *via* a pair of intermolecular C3–H3···Br1 hydrogen bonds which are formed between substituted bromine on the aromatic ring and –CH of the oxime (table 3; figure 2).

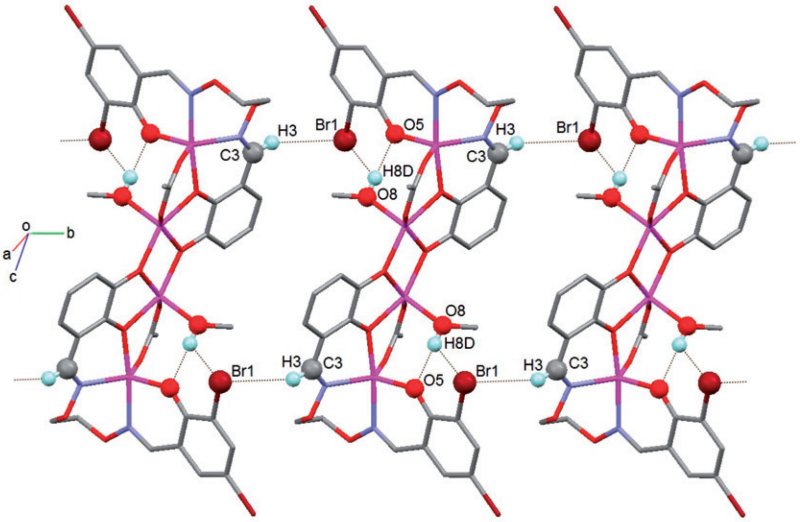


Figure 2. View of the 1-D supramolecular chain within the Zn(II) complex along the *a*-axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

3.2. *Molar conductance*

Molar conductance value of Zn(II) complex at 25°C of $10^{-3}\,\mathrm{mol\,dm^{-3}}$ DMF solution is $4.0\,\mathrm{S\,cm^2\,mol^{-1}}$, indicating a non-electrolyte, implying that all Zn(II) ions in the complex are firmly held in the coordination sphere in solution.

3.3. *IR spectra*

IR spectra of H_3L and its corresponding Zn(II) complex exhibit various bands from 500 to $4000\,\mathrm{cm^{-1}}$. The free ligand exhibits characteristic C=N stretching band at $1612\,\mathrm{cm^{-1}}$, while C=N of the complex is observed at $1603\,\mathrm{cm^{-1}}$. The C=N stretching frequency shifted to a lower frequency by *ca* $9\,\mathrm{cm^{-1}}$ upon complexation indicates a decrease in C=N bond order due to the coordination of zinc(II) with oxime nitrogen [24].

The Ar–O stretching frequency is a strong band at $1263–1213\,\mathrm{cm^{-1}}$ as reported for similar ligands [25–27], occurring at $1238\,\mathrm{cm^{-1}}$ for H_3L and at $1215\,\mathrm{cm^{-1}}$ for Zn(II) complex. The Ar–O stretching frequency is shifted to lower frequency, indicating that Zn–O bond was formed between zinc(II) and oxygen of phenol [24, 28]. The IR spectrum of Zn(II) complex shows the expected strong absorption due to ν(O–H) at *ca* $3432\,\mathrm{cm^{-1}}$, evidence for the existence of methanol.

3.4. *UV-Vis absorption spectra*

UV-Vis absorption spectra of H_3L and complex were determined in $5.0 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ DMF solution (figure 3). Absorptions of Zn(II) complex are obviously different from H_3L upon complexation. Absorptions at 272 and 320 nm are red-shifted upon

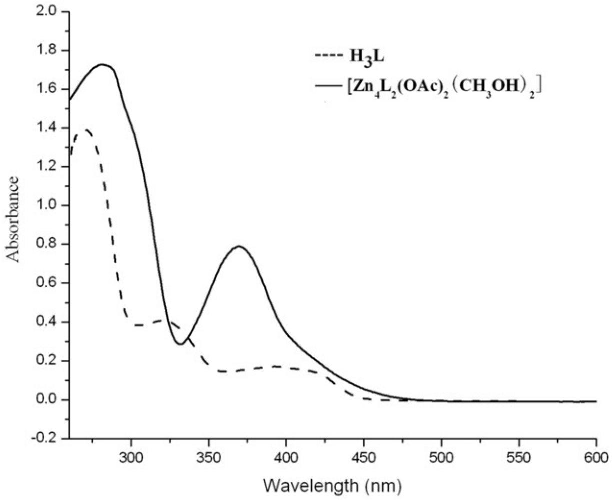


Figure 3. UV-Vis absorption spectra of H_3L (- - - -) and Zn(II) complex (—) in DMF ($c = 5 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$).

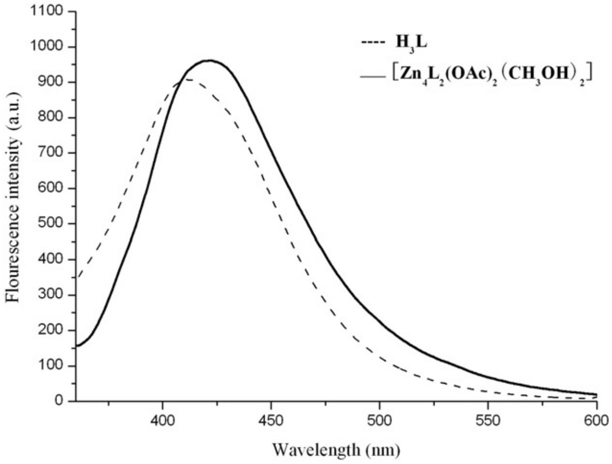


Figure 4. Emission spectra of H_3L (- - - -) ($\lambda_{ex} = 310$ nm) and corresponding Zn(II) complex (—) ($\lambda_{ex} = 340$ nm) in dilute DMF solutions at room temperature ($c = 5 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$).

coordination to Zn(II), which can be assigned to π–π^* transitions of the Salen-type ligand. The absorption at 393 nm is absent in the spectrum of Zn(II) complex.

3.5. *Fluorescence spectra*

The fluorescent properties of H_3L and its corresponding Zn(II) complex were investigated at room temperature (figure 4). The ligand exhibits an intense emission at 411 nm upon excitation at 310 nm, which should be assigned to intraligand π–π^*

transition [29]. Zn(II) complex shows an intense broad photoluminescence with maximum emission at *ca* 423 nm upon excitation at 340 nm, which is slightly red-shifted to that of H_3L. Since the emission peak position of Zn(II) complex is similar to that of free ligand, the emission band in the spectrum of the Zn(II) complex may also arise from the intraligand transition. Compared with the emission spectrum of H_3L, enhanced fluorescence intensity of Zn(II) complex is observed, indicating that intraligand transition has been influenced because of the introduction of metal ions in the structure [30]. No emission originating from metal-centered or metal-to-ligand/ligand-to-metal charge-transfer excited states are expected for Zn(II) complex, since Zn(II) is d^{10}. Thus, the emission observed in Zn(II) complex is tentatively assigned to the (π–π^*) intraligand fluorescence.

4. Conclusion

We have reported a tetranuclear Zn(II) complex, $[Zn_4L_2(OAc)_2(CH_3OH)_2]$, with an asymmetric Salen-type bisoxime. The complex can be described as two $[Zn_2L(OAc)(CH_3OH)]$ units connected with a diphenoxy-bridge. Spectral properties of Zn(II) complex have also been studied and it shows blue emission with maximum emission wavelength $\lambda_{max} = 423$ nm when excited with 340 nm. This emission is tentatively assigned to the intraligand fluorescence.

Supplementary material

Further details of the crystal structure investigation(s) may be obtained from the Cambridge Crystallographic Data Centre, Postal Address: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Telephone: (44) 01223 762910; Facsimile: (44) 01223 336033; E-mail: deposit@ccdc.cam.ac.uk on quoting the depository number CCDC 852420.

Acknowledgments

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