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Novel multinuclear transition metal(II) complexes based on an asymmetric Salamo-type ligand: syntheses, structure characterizations and fluorescent properties

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ABSTRACT

Three multinuclear complexes, $[{Cu(HL)(OAc)Cu}_2] \cdot CH_3OH$, [Zn(HL)(OAc)Zn(CH₃CH₂OH)] and $[{Cd(HL)(OAc)Cd(CH_3CH_2OH)}_2] \cdot 2CHCl_3$, have been synthesized with an asymmetric Salamo-type ligand H₄L, and characterized by FT-IR, UV-vis spectra and X-ray crystallography. The Cu(II) complex contains two crystallographically independent but chemically identical dinuclear complexes (molecules 1 and 2). Meanwhile, self-assembled infinite 1D, 2D and 3D structures are formed by intermolecular hydrogen bonds and C-H··· π interactions of neighboring complexes in the solid state. The Zn(II) complex also forms a novel dinuclear structure. And a self-assembled infinite 2D structure is formed by C-H··· π interaction of neighboring complexes in the solid state. Otherwise, the Cd(II) complex forms an infinite 1D structure by C-H··· π interaction of the neighboring complex molecules. In addition, the photophysical properties of the Cu(II), Zn(II) and Cd(II) complexes have also been discussed.

Keywords: Salamo-type ligand; Transition metal(II) complex; Synthesis; Crystal structure; Fluorescent property

1. Introduction

Transition metal(II) complexes with Salen-type ligands have been studied for many decades, which have been attracted much interest for their catalytic activities [1,2], medical imaging, optical materials [3,4], etc. Photoluminescence has been one of the highlights in

modern coordination chemistry owing to potential applications in luminescent device [5,6], which have been also observed for Salen-type compounds and their transition metal(II) complexes [7,8]. Noticeably, several excellent works have been devoted to synthesize and characterize mononuclear, homo- or heteropolynuclear transition metal(II) complexes bearing Salamo-type ligand or its derivatives [9-15].

Compared with symmetric salamo-type ligands, the asymmetric configuration would afford the opportunities for a greater structural variation and infinite coordination polymers, which would be expected to lead to novel characteristics [16]. As selective synthesis of asymmetrical Salamo-type ligands is important because electronic and steric effect of the ligands on Salen-metal-assisted catalysis may be controlled by introduction of different substituents into the two benzene rings [17]. In order to study the structural feature and fluorescent characteristics of the transition metal(II) complexes with asymmetric Salamo-type ligands, herein we have synthesized a new asymmetric Salamo-type ligand and its corresponding Cu(II), Zn(II) and Cd(II) complexes. And the structures of the Cu(II), Zn(II) and Cd(II) complexes have been characterized by X-ray single crystal diffraction.

2. Experimental

2.1. Materials and instruments

2,3-Dihydroxybenzaldehyde, 2-hydroxy-3-aminoacetophenone and 2-hydroxy-3-methoxybenzaldehyde were purchased from Alfa Aesar and used without further purification. The other reagents and solvents are of analytical grade from Tianjin Chemical Reagent Factory.

C, H, and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. Elemental analyses for Cu(II), Zn(II) and Cd(II) ions were detected by an IRIS ER/S·WP–1 ICP atomic emission spectrometer. FT-IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr (400-4000 cm⁻¹) and CsI (100-500 cm⁻¹) pellets. UV-Vis absorption spectra in the 200-600 nm range were recorded on a Hitachi UV-3010 spectrophotometer in chloroform solution. ¹H NMR spectra were determined by German Bruker AVANCE DRX-400 spectrometer. Melting points were

obtained by use of an X4 microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and were not corrected. Fluorescent spectra were taken on a LS-55 fluorescence photometer. X-ray single crystal structures were determined on a Bruker Smart Apex CCD diffractometer.

2.2. Synthesis of the ligand H_4L

1,2-Bis(phthalimidoxy)ethane was synthesized according to the literature [8,11].

1,2 -Bis(aminooxy)ethane was prepared according to an analogous method reported earlier [11,16].

The asymmetric Salamo-type ligand H_4L was synthesized by a modified method reported in the earlier literature (Scheme 1) [18,19].

Scheme 1. Synthetic route to H₄L.

To an ethanol solution (30 ml) of 2-hydroxy-3-methoxybenzaldehyde (304.3 mg, 2 mmol) was added an ethanol solution (20 ml) of 1, 2-bis(aminooxy)ethane (276.0 mg, 3 mmol). The mixture solution was heated at 50 – 55 °C for 6 h. The solution was concentrated *in vacuo* and the residue was purified by column chromatography (SiO₂, chloroform/ethyl acetate, 10:1) to afford colorless flocculent crystalline solid of 2-hydroxy-3-methoxybenzaldehyde O-(2-(aminooxy)ethyl) oxime (327.2 mg, 1.45 mmol). Yield, 72.3%. M.p. 91-92 °C. *Anal.* Calc. for C₁₀H₁₄N₂O₄: C, 53.09; H, 6.24; N, 12.38. Found: C, 53.12; H, 6.22; N, 12.37%.

A solution of 2-hydroxy-3-methoxybenzaldehyde O-(2-(aminooxy)ethyl) oxime (452.4 mg, 2 mmol) in ethanol (10 mL) was added dropwise to a solution of 2-hydroxy-3-aminoacetophenone (303.2 mg, 2 mmol) in ethanol (10 mL), and the mixture solution was heated at 55 – 60 °C for 24 h. After cooling to room temperature, brownish intermediate products (359.9 mg, 1 mmol) were collected on a suction filter. Yield, 50%. M.p. 123-124 °C. *Anal.* Calc. for $C_{18}H_{21}N_3O_5$: C, 60.16; H, 5.89; N, 11.69. Found: C, 60.27; H, 5.78; N, 11.54%.

A solution of above intermediate products (719.8 mg, 2 mmol) in ethanol (10 mL) was added to a solution of 2,3-dihydroxybenzaldehyde (276.2 mg, 2 mmol) in ethanol (10 mL),

and the mixture solution was heated at 50 – 55 °C for 4 h. Takeing advantage of heat filtration, red precipitates of H₄L (796.8 mg, 1.6 mmol) were collected on a suction filter. Yield, 80%. M.p. 136-137 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.37 (s, 3H, CH₃), 3.90 (s, 3H, CH₃), 4.52 (s, 4H, CH₂), 6.17 (s, 1H, ArH), 6.70 (m, 1H, ArH), 6.91 (m, 6H, ArH), 7.35 (dd, *J* = 8, 2H, ArH), 8.37 (s, 1H, CH=N), 8.65 (s, 1H, CH=N), 9.72 (s, 1H, OH), 11.89 (s, 1H, OH), 15.13 (s, 1H, OH). *Anal.* Calc. for C₂₅H₂₅N₃O₇ (H₄L): C, 62.62; H, 5.26; N, 8.76. Found: C, 62.75; H, 5.07; N, 8.65%.

2.3. Synthesis of the Cu(II) complex

A solution of copper(II) acetate monohydrate (1.99 mg, 0.01 mmol) in methanol (4 ml) was added to a solution of H₄L (2.50 mg, 0.005 mmol) in dichloromethane (2 ml) at room temperature. The color of the mixing solution turned to dark-green immediately, the mixture solution was filtered and the filtrate was allowed to stand at room temperature for about one week. The solvent was partially evaporated and dark-brown block-shaped single crystals suitable for X-ray crystallographic analysis were obtained (0.699 mg, 0.001 mmol). Yield, 20.6%. *Anal.* Calc. for $C_{55}H_{54}Cu_4N_6O_{19}$: C, 48.67; H, 4.01; N, 6.19; Cu, 18.73. Found: C, 48.68; H, 4.03; N, 6.17; Cu, 18.74%.

2.4. Synthesis of the Zn(II) complex

A solution of zinc(II) acetate dihydrate (2.19mg, 0.01mmol) in ethanol (6 ml) was added to a solution of H₄L (2.50 mg, 0.005 mmol) in dichloromethane (2 ml) at room temperature. The color of the mixing solution turned to yellow immediately, the mixture solution was filtered and the filtrate was allowed to stand at room temperature for about one week. The solvent was partially evaporated and several yellow block-shaped single crystals suitable for X-ray crystallographic analysis were obtained (0.837 mg, 0.001 mmol). Yield, 23.5%. *Anal*. Calc. for $C_{29}H_{31}Zn_2N_3O_{10}$: C, 48.90; H, 4.39; N, 5.90; Zn, 18.36. Found: C, 48.91; H, 4.38; N, 5.88; Zn, 18.39%.

2.5. Synthesis of the Cd(II) complex

A solution of cadmium(II) acetate dihydrate (2.66 mg, 0.01 mmol) in ethanol (3 ml) was added dropwise to a solution of H_4L (2.50 mg, 0.005 mmol) in chloroform (3 ml) at room temperature. The color of the mixing solution turned to yellow immediately, the mixture solution was filtered and the filtrate was allowed to stand at room temperature for

about several weeks. The solvent was partially evaporated and several yellow block-shaped single crystals suitable for X-ray crystallographic analysis were obtained (1.190 mg, 0.001 mmol). Yield, 25.7%. *Anal.* Calc. for $C_{60}H_{64}Cd_4Cl_6N_6O_{20}$: C, 38.92; H, 3.48; N, 4.54; Cd, 24.28. Found: C, 38.94; H, 3.49; N, 4.52; Cd, 24.26%.

2.6. X-ray Crystallography

X-ray diffraction data (Table 1) for the Cu(II), Zn(II) and Cd(II) complexes were collected on a Bruker Smart Apex CCD diffractometer at 293.42(10), 290.92(10) and 293.42(10) K, respectively. Using graphite monochromatized Mo K α radiation (λ = 0.071073 nm). Unit cell parameters were determined by least squares analysis. The LP factor and Semi-empirical absorption corrections were applied to the intensity data. The structure was solved by the direct methods (SHELXS-97) and subsequent difference-Fourier map revealed the positions of the remaining atoms, and all hydrogen atoms were added theoretically. All non-hydrogen atoms were refined anisotropically using a full-matrix least-squares procedure on F^2 with SHELXL-97.

 Table 1 X-ray crystallographic data collection, solution and refinement parameters for the Cu(II), Zn(II) and Cd(II) complexes.

3 Result and discussion

3.1 Crystal structures

3.1.1 The Cu(II) complex

The crystal structure and atom numbering of the Cu(II) complex is given in Fig. 1. Selected bond distances and angles of the Cu(II) complex are listed in Table 2.

X-ray crystallographic analysis of the Cu(II) complex reveals a rare dinuclear structure. The Cu(II) complex crystallizes in the triclinic system, space group *P*-1, and the unit cell contains two crystallographically independent but chemically identical dinuclear complexes (molecules 1 and 2, Fig. 1) consisting of two Cu(II) atoms, one $(HL)^{3-}$ unit and one coordinated acetate ion as expected from the analytical data. The Cu1 atom is penta-coordinated by two nitrogen atoms (N1, N2) and two oxygen atoms (O2, O5) of

(HL)³⁻ unit and one oxygen atom (O15) of coordinated acetate ion. And the phenolic oxygen atoms (O2 and O5) and the oxime nitrogen atoms (N1 and N2) of the (HL)³⁻ unit constitute together the basal plane (Cu1–O2, 1.919(4) Å; Cu1–O5, 1.944(5) Å; Cu1–N1, 1.944(6) Å and Cu1–N2, 2.024(5) Å), the oxygen atom (O15) of coordinated acetate ion is occupying the axial position (Cu1…O15, 2.178(5) Å), the coordination geometry around the Cu1 center can be regarded as a distorted square pyramidal geometry which is deduced by calculating the value of $\tau = 0.147$ [20]. The Cu2 atom is tetra-coordinated by one oxime nitrogen atom (Cu2–N3, 1.952(5) Å), two phenolic oxygen atoms (Cu2–O5, 1.959(4) Å; Cu2–O6, 1.890(4) Å) of (HL)³⁻ unit and one oxygen atom (Cu2–O16, 1.963(5) Å) of coordinated acetate ion, and has a slightly distorted square geometry. Therefore, two Cu(II) atoms of [{Cu(HL)(OAc)Cu}₂]·CH₃OH have two different coordination geometries.

In the Cu(II) complex, the Cu1 atom is displaced 0.2380(4) Å from the mean plane N_2O_2 . The coordination planes of O2–Cu1–N1 and O5–Cu1–N2 have a dihedral angle of 19.22(3)°, giving a nonplanar configuration. The Cu2 atom is displaced 0.1182(3) Å from the mean plane NO₃. The dihedral angle between the coordination planes of O6–Cu2–N3 and O5–Cu2–O16 is 12.83(3)°. In addition, the ethylenedioxime carbons C1 and C2 in the Cu(II) complex are buckled asymmetrically from the Cu1-N1-N2 plane, with the displacement for C1 being 1.311(4) Å toward the plane and for C2 being only 1.889(4) Å in the same direction.

Table 2. Selected bond distances (Å) and angles (°) for the Cu(II), Zn(II) and Cd(II) complexes.

Fig. 1. Molecular structure of the Cu(II) complex with the atom numbering. The hydrogen atoms are omitted for clarity.

In the crystal structure, the Cu(II) complex molecules 1 and 2 are linked by intermolecular hydrogen bond interactions. Three pairs of intermolecular hydrogen bonds, C17–H17…O8, C42–H42…O1 and C42–H42…O2 are formed (Fig. S1). One of the protons (C17–H17) of the benzene ring is hydrogen-bonded to the methoxy oxygen atom

(O8) of the $(HL)^{3-}$ unit. The other one (C42-H42) is hydrogen-bonded to one of the phenolic oxygen atoms (O2) and the methoxy oxygen atom (O1) of the $(HL)^{3-}$ unit, respectively (Table 2). Consequently, these hydrogen-bonding interactions have stabilized the Cu(II) complex molecules 1 and 2. The hydrogen bond data are summarized in Table 3.

As shown in Fig. S1, the Cu(II) complex molecules are interlinked by C9–H9B····Cg18 (C29-C34) interactions into a 1D chain structure along the *b* axis [21]. In addition, the adjacent chains along the *b* axis are held together to form an infinite 2D structure on the *ab* crystallographic plane by three pairs of intermolecular C23–H23····O11, C30–H30····O14 and C51–H51····O4 hydrogen bonds (Fig. S2), which are formed between the C23–H23 unit of the benzene ring, the C30–H30 unit of the benzene ring and the C51–H51 unit of the benzene ring and the oxygen atoms of oxime group (O11), phenolic oxygen (O14), acetic oxygen (O4) of each adjacent Cu(II) complex molecules, respectively [22, 23]. The planes are further interlinked by C39–H39C···O12 intermolecular hydrogen bond interaction to form an infinite 3D structure (Fig. S3) [24].

Thus, a self-assembled infinite 3D structure is formed by seven intermolecular hydrogen bonds and C-H··· π interaction of neighboring Cu(II) complex molecules.

Table 3. Hydrogen-bonding interactions [Å, °] for the Cu(II), Zn(II) and Cd(II) complexes.

3.1.2 The Zn(II) complex

The structural features of the Zn(II) complex are very similar to those of the Cu(II) complex mentioned above, the crystal structure and atom numbering of the Zn(II) complex is presented in Fig. 2 and selected bond distances and angles of the Zn(II) complex are shown in Table 2.

The Zn(II) complex crystallizes in the monoclinic space group P2(1)/c, which consists of two Zn(II) atoms, one (HL)³⁻ unit, one coordinated acetate ion and one coordinated ethanol molecule. Moreover, the Zn(II) complex also forms a novel 1:2 ((L)³⁻ : Zn(II)) dinuclear structure which is different from the structures of 1:1 [25,26], 2:3 [23], 2:4 [8], 4:8 [12] (L: Zn(II)) Salamo-type Zn(II) complexes reported earlier. The Zn1 atom is penta-coordinated by two nitrogen atoms (N1, N2) and two oxygen atoms (O1, O5) of

(HL)³⁻ unit and one oxygen atom (O8) of coordinated acetate ion. Moreover the phenolic oxygen atom (O1), the oxime nitrogen atom (N2) of the $(HL)^{3-}$ unit and the oxygen atom (O8) of coordinated acetate ion constitute together the basal plane (Zn1–O1, 1.972(3) Å; Zn1–O8, 2.020(3) Å and Zn1–N2, 2.059(3) Å), one phenolic oxygen atoms (O5) and one oxime nitrogen atoms (N1) are occupying the axial position (Zn1–O5, 2.016(3) Å; Zn1–N1, 2.136(3) Å). The Zn2 atom is also penta-coordinated by two phenolic oxygen atoms (O5, O6), one oxygen atom (O9) of coordinated acetate ion, one Schiff base nitrogen atom (N3) and one oxygen atom (O10) of coordinated ethanol molecule. Moreover the oxygen atom (O9) of coordinated acetate ion, the Schiff base nitrogen atom (N3) and the oxygen atom (O10) of coordinated ethanol molecule constitute together the basal plane (Zn2–O9, 1.979(3) Å; Zn2–O10, 2.034(3) Å and Zn2–N3, 2.029(3) Å), the two phenolic oxygen atoms (O5, O6) are occupying the axial position (Zn2–O5, 2.100(3) Å; Zn2–O6, 1.981(3) Å). As we know, the coordination number of Zn(II) is generally four or six and the coordination geometry around Zn(II) is tetrahedron or octahedron [25]. However, there are only a few reports of the five-coordinated Salamo-type Zn(II) complexes having distorted square-pyramidal or trigonal-bipyramidal configurations [12]. Here, this dinuclear Zn(II) complex obtained in which the Zn1 and Zn2 atoms are both five-coordinated with trigonal bipyramidal geometries which are deduced by calculating the values of $\tau_1 = 0.848$, $\tau_2 =$ 0.764, respectively [20].

The Zn(II) complex molecules form a dimer structure by π - π stacking interaction of neighboring benzene rings. As illustrated in Fig. S4, the Zn(II) complex molecules are interlinked by Cg7 (C12-C17)…Cg8 (C19-C24) π - π stacking interaction into a dimer. Consequently, two π - π stacking interactions of neighboring benzene rings have stabilized a pair of the Zn(II) complex molecules to form a dimer. As shown in Fig. S5, the dimers are interlinked by C14–H14…Cg6 (C1-C6) and C21–H21…Cg7 (C12-C17) interactions into a infinite 2D network structure along the *bc* axis, which are formed between the C14–H14 units of the benzene rings, the C21–H21 units of the benzene rings and the neighboring benzene rings of each adjacent dimers, respectively [18]. Thus, a self-assembled infinite 2D structure is formed by C–H… π interaction of neighboring dimmers in the solid state. It is interesting to note that there are strong intermolecular π - π stacking interactions between the

nearest parallel benzene rings. Two neighboring parallel benzene planes of the Zn(II) complex molecules form π - π stacking interaction at a distance of 3.808(4) Å.

Fig. 2. Molecular structure of the Zn(II) complex with the atom numbering. The hydrogen atoms are omitted for clarity.

3.1.3 The Cd(II) complex

The crystal structure and atom numbering of the Cd(II) complex are drawn in Fig. 3. The selected bond distances and bond angles are summed in Table 2.

The Cd(II) complex is composed of four Cd(II) atoms, two (HL)³⁻ units, two coordinated acetate ions and two coordinated ethanol molecules. Two Cd(II) atoms of $[{Cd(HL)(OAc)Cd(CH_3CH_2OH)}_2] \cdot 2CHCl_3$ have two different coordination geometries. The Cd2 atom is hexa-coordinated by two nitrogen atoms (N2, N3) and two oxygen atoms (O3, O6) of (HL)³⁻ unit and two oxygen atoms (O9, O10) of coordinated acetate ion. Meanwhile, the phenolic oxygen atom (O3), the oxime nitrogen atom (N3) and the oxygen atoms (O9, O10) of coordinated acetate ion constitute together the basal plane (Cd2-O3, 2.235(3) Å; Cd2-O9, 2.374(4) Å; Cd2-O10, 2.331(4) Å and Cd2-N3, 2.354(4) Å), the phenolic oxygen atom (O6) and the oxime nitrogen atom (N2) are occupying the axial position (Cd2–O6, 2.221(3) Å; Cd2–N2, 2.332(4) Å). The coordination geometry around the Cd2 center can be regarded as a distorted octahedral geometry. The Cd1 atom is hepta-coordinated by four phenolic oxygen atoms (O3, O6, O2, O2[#]), one oxygen atom (O7) of methoxy group of $(HL)^{3}$, one Schiff base nitrogen atom (N1) and one oxygen atom (O8) of coordinated ethanol molecule. Moreover, the oxygen atom (O7) of methoxy group of $(HL)^{3-}$, the Schiff base nitrogen atom (N1) and the phenolic oxygen atoms (O2, O3, O6) constitute together the basal plane (Cd1-O3, 2.348(3) Å; Cd1-O2, 2.250(3) Å; Cd1-O7, 2.559(3) Å; Cd1–O6, 2.254(3) Å and Cd1–N1, 2.318(4) Å), the phenolic oxygen atoms $(O2^{*})$ and the oxygen atom (O8) of coordinated ethanol molecule are occupying the axial position (Cd1–O8, 2.374(4) Å; Cd1–O2[#], 2.330(3) Å). The coordination geometry around the Cd1 center can be regarded as a distorted pentagonal bipyramidal geometry. This hepta-coordinated Cd(II) complex forms a novel 2:4 $((L)^{3-}$: Cd) tetranuclear structure

which is different from the structure of 1:1 (L : Cd) [25] reported earlier in the Salamo-type Cd(II) complexes.

The Cd(II) complex forms a infinite 1D structure by C–H··· π interaction of neighboring complex molecules. As shown in Fig. S6, the Cd(II) complex molecules are interlinked by C15–H15A···Cg5 (C8-C13) interaction into a infinite 1D chain structure along the *c* axis.

Fig. 3. Molecular structure of the Cd(II) complex with the atom numbering. The hydrogen atoms are omitted for clarity.

3.2 FT-IR spectral analysis

The FT-IR spectra of H₄L and its corresponding Cu(II), Zn(II) and Cd(II) complexes exhibit various bands in the 400–4000 cm⁻¹ region (Fig. 4). The most important FT-IR bands for H₄L and its Cu(II), Zn(II) and Cd(II) complexes are given in Table 4. The Cu(II), Zn(II) and Cd(II) complexes have similar FT-IR spectra which indicate that they have similar structures. The free ligand H₄L shows a broad characteristic band of the OH group at 2935-3065 cm⁻¹. This band is weakened in the FT-IR spectra of the Cu(II), Zn(II) and Cd(II) complexes, which is indicative of the fact that the phenolic OH groups of H₄L have been deprotonized and coordinated to the Cu(II), Zn(II) and Cd(II) atoms [27]. For the Cu(II), Zn(II) and Cd(II) complexes, these bands weakened are expected due to the substitution of hydrogen atoms for the Cu(II), Zn(II) and Cd(II) atoms upon coordination [28].

 Table 4. The most important FT-IR bands for the ligand and its Cu(II), Zn(II) and Cd(II)

 complexes (cm⁻¹).

The free ligand H₄L exhibits characteristic C=N stretching band at 1613 cm⁻¹, while the C=N stretching bands of the Cu(II), Zn(II) and Cd(II) complexes are observed in the 1605 cm⁻¹, 1605 cm⁻¹ and 1598 cm⁻¹, respectively. The C=N stretching frequencies are shifted to lower frequencies by *ca*. 8, 8 and 15 cm⁻¹ upon complexation, indicating that the Cu(II),

Zn(II) and Cd(II) atoms are coordinated by N_2O_2 donor atoms of $(HL)^{3-}$ units. Thus, it provides evidence for the coordination of H₄L with Cu(II), Zn(II) and Cd(II) atoms. In the 1438-1466 cm⁻¹ region, the observed bands are attributed to aromatic C=C vibration. Upon coordination these bands shift to lower frequencies for the Cu(II), Zn(II) and Cd(II) complexes [29].

The Ar–O stretching frequency appears at 1257 cm⁻¹ for the ligand H₄L, while the Ar–O stretching frequencies of the Cu(II), Zn(II) and Cd(II) complexes are observed in the 1244, 1244 and 1240 cm⁻¹, respectively. The Ar–O stretching frequencies are shifted to a lower frequencies, indicating that the Cu-O or Zn–O or Cd–O bonds are formed between the Cu(II), Zn(II) and Cd(II) ions and oxygen atoms of phenolic groups [30].

The far-infrared spectra of the Cu(II), Zn(II) and Cd(II) complexes were also obtained in the region 550-100 cm⁻¹ in order to identify frequencies due to the M-O and M-N bonds. The bands at 422 cm⁻¹ in the Cu(II) and Zn(II) complexes are assigned to v_{Cu-O} and v_{Zn-O} , while the bands at 526 cm⁻¹ are assigned to v_{Cu-N} and v_{Zn-N} , respectively. The FT-IR spectrum of the Cd(II) complex shows v_{Cd-O} at 413 cm⁻¹, and v_{Cd-N} is very weak, so it isn't marked out in the spectrum of Cd(II) complex. These new bands are observed for the Cu(II), Zn(II) and Cd(II) complexes and are not present in the spectrum of the free ligand H₄L. As pointed out by Percy and Thornton [31], the metal–oxygen and metal–nitrogen frequency assignments are at times very difficult.

3.3 UV-vis absorption spectral study

The UV-vis absorption spectra of H₄L and its Cu(II), Zn(II) and Cd(II) complexes were determined in chloroform solution ($c = 1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$), are shown in Fig. 5. The absorption peaks of the Cu(II), Zn(II) and Cd(II) complexes are obviously different from those of the ligand.

UV-Vis spectrum of the free ligand H₄L exhibits two absorption bands at 271 and 364 nm. The former absorption band at 271 nm can be assigned to the π - π * transition of the benzene rings and the latter one at 364 nm can be attributed to the π - π * transition of the oxime groups [32]. Upon coordination of the ligand, the absorption bands of the Zn(II) and

Cd(II) complexes appear at *ca*. 269 nm, and absorption intensities are weakened compared with the free ligand H₄L, which indicate that the oxime nitrogen atoms are involved in coordination to the Zn(II) or Cd(II) atoms. Upon coordination of the ligand, the intraligand π - π * transition of the benzene ring of salicylaldehyde is disappeared in the Cu(II) complex [33]. Moreover, the new bands are observed at 387, 407 and 368 nm in the Cu(II), Zn(II) and Cd(II) complexes respectively, which is assigned to the n– π * charge transfer transition from the filled p π orbital of the bridging phenolic oxygen to the vacant d-orbital of the metal(II) ions [34].

3.4 Fluorescence spectral study

The fluorescent properties of H₄L and its corresponding Cu(II), Zn(II) and Cd(II) complexes were measured at room temperature (Fig. 6). The Cu(II), Zn(II) and Cd(II) complexes display enhanced emission intensities compared to the corresponding ligand (H₄L) when excited with the some amount of energy. Enhancement of fluorescence through complexation is of much interest as it creates the opportunity for photochemical applications of these complexes [35, 36].

The fluorescence of the free ligand is probably quenched by the occurrence of a photoinduced electron transfer process due to the presence of a lone pair of nitrogen atoms. Such the process is prevented by the complexation of the ligand with metal atoms. Thus the fluorescence intensity may be effectively enhanced by the coordination of Cu(II), Zn(II) and Cd(II) atoms [37].

The free ligand exhibits a weak emission peak at 443 nm upon excitation at 407 nm. The Cu(II) complex shows an intense photoluminescence with maximum emission at 444 nm upon excitation at 407 nm (Fig. 6). Since the emission peak position of the Cu(II) complex is similar to that of the free ligand, the emission peak of the Cu(II) complex may also arise from the intraligand transition.

The emission spectra shows that the emission spectral shape of the Zn(II) complex closely resemble that of the Cd(II) complex. In comparison with the corresponding H₄L with the maximum emission wavelength at 443 nm when excited with 407 nm, the Zn(II) and Cd(II) complexes exhibits red-shift with the maximum emission at 533 and 537 nm

when excited with 407 nm, which could be assigned to ligand-to-metal charge transfer (LMCT) [38].

Conclusions

According to the data and discussion above, three new complexes with the chemical formulae $[{Cu(HL)(OAc)Cu}_2] \cdot CH_3OH,$ $[Zn(HL)(OAc)Zn(CH_3CH_2OH)]$ and $[{Cd(HL)(OAc)Cd(CH_3CH_2OH)}_2] \cdot 2CHCl_3$, have been synthesized and structurally characterized. The Cu(II) complex forms a dimer unit by intermolecular hydrogen bonds. In addition, a self-assembled infinite 1D, 2D, 3D structure are formed by intermolecular hydrogen bonds and C-H··· π interaction of neighboring dimmers in the solid state. The Zn(II) complex molecules form a dimer structure by π - π stacking of neighboring benzene rings. In addition, a self-assembled infinite 2D structure is formed by C-H $\cdots \pi$ interaction of neighboring dimmers in the solid state. The Cd(II) complex forms a infinite 1D structure by C-H··· π interaction of the neighboring complex molecules. In the FT-IR spectra of the Cu(II), Zn(II) and Cd(II) complexes, the v(M-O) and v(M-N) vibrational absorption frequencies have been observed. Meanwhile, the Cu(II), Zn(II) and Cd(II) complexes exhibit blue emission with the maximum emission wavelength at 444, 533, 537 nm when excited with 407 nm,

Acknowledgements

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CCDC deposit number ⁺	1424749	1424750	1424748
Empirical formula	$C_{55}H_{54}Cu_4N_6O_{19}$	$C_{29}H_{31}Zn_2N_3O_{10}$	$C_{60}H_{64}Cd_4Cl_6N_6O_{20}$
Formula weight	1357.20	712.31	1851.46
Crystal size (mm)	$0.25 \times 0.30 \times 0.32$	$0.22\times0.26\times0.28$	$0.25 \times 0.31 \times 0.32$
Crystal system	triclinic	monoclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> -1
<i>a</i> (Å)	9.8721(4)	14.8512(5)	9.6876(10)
<i>b</i> (Å)	15.5004(8)	13.4320(7)	12.9281(10)
<i>c</i> (Å)	19.2091(8)	15.7579(7)	14.2601(10)
α (°)	95.063(4)	90	104.768(6)
β (°)	97.008(4)	111.368(5)	94.128(7)
γ (°)	94.171(4)	90	93.940(7)
Ζ	2	4	1
Cell volume ($Å^3$)	2895.7(2)	2927.3(2)	1715.4(3)
Density calculated $(g \text{ cm}^{-3})$	1.557	1.616	1.792
$\mu (\mathrm{mm}^{-1})$ /	1.528	1.702	1.532
Collected reflections	20620	11588	11994
	11315	5760	6744
Unique reflections (K_{int})	$[R_{\rm int} = 0.046]$	$[R_{\rm int} = 0.054]$	$[R_{\rm int} = 0.033]$
Data/restraints/parameters	11315/0/767	5760/3/405	6744/0/442
Goodness-of-fit on F ²	1.044	1.042	1.072
	$R_1 = 0.0713,$	$R_1 = 0.0531,$	$R_1 = 0.0426,$
Final K_1 Indices $[I > 2\sigma(I)]$	$wR_2 = 0.1838$	$wR_2 = 0.0797$	$wR_2 = 0.0843$
	$R_1 = 0.1033,$	$R_1 = 0.0982,$	$R_1 = 0.0657,$
k indices (all data)	$wR_2 = 0.2141$	$wR_2 = 0.1024$	$wR_2 = 0.1023$
Residuals peak/hole ($e / \text{\AA}^3$)	4.36 and -0.57	0.61 and -0.47	0.94 and -0.87

Table 1 X-ray crystallographic data collection, solution and

refinement parameters for the Cu(II), Zn(II) and Cd(II) complexes.

Data for these compounds can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

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		complex	kes.		
Cu(II) complex					
Cu1-N1	1.944(6)	Cu1-O2	1.919(4)	Cu1-O5	1.944(5)
Cu1-N2	2.024(5)	Cu1-O15	2.178(5)	Cu2-O5	1.959(4)
Cu2-O6	1.890(4)	Cu2-O16	1.963(5)	Cu2-N3	1.952(5)
N1-Cu1-O15	102.3(2)	O2-Cu1-O15	91.54(19)	O5-Cu1-N1	170.2(2)
N1-Cu1-N2	95.2(2)	O2-Cu1-N1	91.0(2)	O5-Cu1-N2	83.9(2)
N2-Cu1-O15	104.2(2)	O2-Cu1-N2	161.4(2)	N1-Cu1-O15	102.3(2)
O2-Cu1-O5	87.04(18)	O5-Cu1-O15	87.39(19)	N1-Cu1-N2	95.2(2)
N3-Cu2-O16	167.0(2)	O5-Cu2-O16	95.09(19)	O6-Cu2-O5	176.46(19)
O6-Cu2-O16	88.4(2)	O6-Cu2-N3	93.7(2)	N3-Cu2-O5	82.75(19)
Zn(II) complex			\sim		
Zn1-O1	1.972(3)	Zn1-O5	2.016(3)	Zn1-N1	2.136(3)
Zn1-O8	2.020(3)	Zn2-N3	2.029(3)	Zn1-N2	2.059(3)
Zn2-O5	2.100(3)	Zn2-O6	1.981(3)	Zn2-O9	1.979(3)
Zn2-O10	2.034(3)				
O1-Zn1-O5	94.07(12)	O1-Zn1-O8	111.93(13)	O1-Zn1-N1	87.45(14)
O1-Zn1-N2	122.06(14)	O5-Zn1-O8	95.34(12)	O5-Zn1-N1	176.75(13)
O5-Zn1-N2	85.15(12)	08-Zn1-N1	86.73(13)	O8-Zn1-N2	125.86(15)
N2-Zn1-N1	91.61(14)	06-Zn2-O5	170.69(11)	O6-Zn2-O10	93.90(13)
O6-Zn2-N3	92.69(13)	O9-Zn2-O5	94.46(12)	O9-Zn2-O6	93.44(13)
O9-Zn2-O10	109.65(13)	O9-Zn2-N3	124.46(14)	O10-Zn2-O5	88.07(12)
N3-Zn2-O5	78.77(12)	N3-Zn2-O10	124.87(14)		
Cd(II) complex					
Cd1-O2	2.250(3)	Cd1-O3	2.348(3)	Cd1-O6	2.254(3)
Cd1-07	2.559(3)	Cd1-O8	2.374(4)	Cd1-N1	2.318(4)
Cd1-O2#	2.330(3)	Cd2-O6	2.221(3)	Cd2-O9	2.374(4)
Cd2-O10	2.331(4)	Cd2-N2	2.332(4)	Cd2-N3	2.354(4)
Cd2-C28	2.690(6)	Cd2-O3	2.235(3)		
O2-Cd1-O3	144.49(12)	O2-Cd1-O6	139.28(11)	O2-Cd1-O7	78.50(11)
O2-Cd1-O8	106.14(14)	O2-Cd1-N1	79.56(13)	O3-Cd1-O7	136.72(11)
O3-Cd1-O8	86.78(14)	O6-Cd1-O3	72.76(11)	O6-Cd1-O7	64.89(11)
O6-Cd1-O8	86.91(14)	O6-Cd1-N1	141.15(13)	O8-Cd1-O7	82.55(15)
N1-Cd1-O2	106.20(12)	N1-Cd1-O3	69.96(13)	N1-Cd1-O7	147.23(13)
N1-Cd1-O8	80.52(15)	O3-Cd2-O9	88.78(13)	O3-Cd2-O10	143.36(14)

Table 2. Selected bond distances (Å) and angles (°) for the $Cu(II),\,Zn(II)$ and Cd(II)

O3-Cd2-N2	76.49(14)	O3-Cd2-N3	122.56(13)	O3-Cd2-C28	116.79(17)
O6-Cd2-O3	75.56(11)	O6-Cd2-O9	91.99(13)	O6-Cd2-O10	107.54(15)
O6-Cd2-N2	147.50(14)	O6-Cd2-N3	76.96(13)	O6-Cd2-C28	99.64(15)
O9-Cd2-C28	28.04(16)	O10-Cd2-O9	54.97(15)	O10-Cd2-N2	104.76(16)
O10-Cd2-N3	92.95(15)	O10-Cd2-C28	27.00(16)	N2-Cd2-O9	103.68(15)
N2-Cd2-N3	105.05(16)	N2-Cd2-C28	107.58(16)	N3-Cd2-O9	141.49(16)
N3-Cd2-C28	116.90(18)				
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D-H	d(D-H)	$d(H \cdots A)$	$d(D \cdots A)$	∠D-H···A	А	Symmetry code
Cu(II) complex						
C17-H17	0.930	2.480	3.313(5)	150	08	
C42-H42	0.930	2.540	3.316(7)	141	01	
C42-H42	0.930	2.570	3.366(4)	144	O2	
C23-H23	0.930	2.410	3.322(2)	168.00	011	[2-x, 1-y, 1-z]
C30-H30	0.930	2.560	3.484(6)	170.00	014	[-x, 1-y, -z]
C51-H51	0.930	2.560	3.426(7)	155.00	O4	[-x, -y, -z]
C39-H39C	0.960	2.520	3.454(8)	165.00	012	[1-x, 1-y, 1-z]
C9-H9B	0.970	2.680	3.477(8)	140.00	Cg18	[x, y-1, z]
Zn(II) complex						
C14-H14	0.930	2.910	3.748(5)	150.00	Cg6	[1-x, -1/2+y, 1/2-z]
C21-H21	0.930	2.990	3.336(6)	104.00	Cg7	[x, 1/2-y, 1/2+z]
Cd(II) complex						
C15-H15A	0.960	2.960	3.786(7)	145.00	Cg5	[-x, -y, 1-z]
	\frown	*				

Table 3. Hydrogen-bonding interactions [Å, °] for the Cu(II), Zn(II) and Cd(II) complexes.

Compound H ₄ L Cu(II) comple Zn(II) comple Cd(II) comple	v _{C=N} 1613 x 1605 x 1605 x 1598	v _{Ar-0} 1257 1244 1244 1240	v _{M-N} 526 526	v _{M-0} 422 422 413	<u>v_{0-H}</u> 3065 — —	v _{C=C} 1466 1448 1448 1438
H ₄ L Cu(II) comple Zn(II) comple Cd(II) comple	1613 x 1605 x 1605 x 1598	1257 1244 1244 1240			3065	1466 1448 1448 1438
Cu(II) comple Zn(II) comple Cd(II) comple	x 1605 x 1605 <u>x 1598</u>	1244 1244 1240	526 526	422 422 413		1448 1448 1438
Zn(II) comple Cd(II) comple	x 1605 x 1598	1244 1240	526	422 413	_	1448 1438
<u>Cd(II) comple</u>	x 1598	1240	D	413	5	1438
			D		0	5
		4				

Table 4. The most important FT-IR bands for the ligand and its Cu(II), Zn(II) and Cd(II)

Figures legends:

Scheme 1. Synthetic route to H₄L.

Fig. 1. Molecular structure of the Cu(II) complex with the atom numbering. The hydrogen atoms are omitted for clarity.

Fig. 2. Molecular structure of the Zn(II) complex with the atom numbering. The hydrogen atoms are omitted for clarity.

Fig. 3. Molecular structure of the Cd(II) complex with the atom numbering. The hydrogen atoms are omitted for clarity.

Fig. 4. Infrared absorption spectra of H₄L and its Cu(II), Zn(II) and Cd(II) complexes.

Fig. 5. UV-vis absorption spectra of H₄L and its Cu(II), Zn(II) and Cd(II) complexes in chloroform solution ($c = 1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$).

Fig. 6. Emission spectra of H₄L and its Cu(II), Zn(II) and Cd(II) complexes in chloroform solution (c = $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$).

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Graphical Abstract-pictogram:

Wen-kui Dong et al. **Graphical Abstract**

An novel asymmetric Salamo-type ligand H_4L and its three novel supramolecular multinuclear Cu(II), Zn(II) and Cd(II)complexes have been synthesized and characterized by FT-IR, UV-vis spectra and X-ray crystallography. The obtained crystal structures are very interesting. In addition, the photophysical properties of the Cu(II), Zn(II) and Cd(II) complexes have also been discussed.





Highlights:

- 1. A new asymmetric Salamo-type ligand H₄L has been synthesized firstly;
- 2. Three novel Cu(II), Zn(II) and Cd(II) complexes have been synthesized and characterized structurally;
- 3. The photophysical properties of the Cu(II), Zn(II) and Cd(II) complexes have also