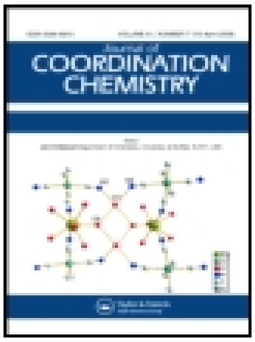

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Three multinuclear Co(II), Zn(II) and Cd(II) complexes based on a single-armed salamo-type bisoxime: Syntheses, structural characterizations and fluorescent properties

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Three multinuclear complexes, $[Co(L)(OAc)Co(CH_3CH_2OH)_2]\cdot H_2O$, $[Zn(L)(OAc)Zn(CH_3OH)]$ and $[\{Cd(L)(OAc)Cd(CH_3OH)\}_2]$, containing a single-armed salamo-type bisoxime H_3L have been synthesized and characterized structurally. The Co(II) complex forms a dimeric unit by intermolecular hydrogen bond interactions of neighboring dimeric molecules. The Zn(II) complex also forms a dimeric unit by intermolecular hydrogen bond interactions. Interesting features of the crystal structure include O···O short contacts. Meanwhile, self-assembling infinite 1D, 2D and 3D supramolecular structures are formed by intermolecular hydrogen bond and C–H···π interactions. The Cd(II) complex forms an infinite 2D supramolecular structure by intermolecular hydrogen bond interactions. The photophysical properties of the Co(II), Zn(II) and Cd(II) complexes have also been discussed.

Keywords: Single-armed salamo-type bisoxime; Multinuclear complex; Synthesis; Crystal structure; Fluorescent property

1. Introduction

Transition metal complexes with Salen-type ligands have been extensively studied for many decades [1-7] and have attracted much interest due to their catalytic activities [8], especially in the area of asymmetric catalysis [9], biological activity, such as anticancer [10], fluorescent characteristics [11, 3c, 4b] and magnetic properties [3b, 3d]. Photoluminescence has been one of the highlights in modern coordination chemistry owing to its potential applications in

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*Corresponding author. Email: dongwk@126.com luminescent devices, which also have been observed for Salen-type compounds and their transition metal complexes [12]. Noticeably, several excellent works have been devoted to synthesizing and characterizing mononuclear, homo- or heteropolynuclear transition metal complexes bearing a salamo-type ligand or its derivatives [13].

Compared with symmetric salamo-type ligands, the asymmetric configuration would afford opportunities for a greater structural variation and infinite coordination polymers, which would be expected to lead to novel characteristics [1b]. Selective synthesis of asymmetrical salamo-type ligands is important because the 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 [7b]. In order to study the structural features and fluorescent characteristics of transition metal complexes with asymmetric salamo-type ligands, herein we designed and synthesized a single-armed salamo-type bisoxime, H_3L (6-[2-nitrilomethylidyne(4,6-dibromobenzene)]-6′-methoxy-2,2′-[1,1′-(ethylenedioxy(nitrilomethylidyne)(nitriloethylidyne)]triphenol), which has the capability to coordinate with metal ions to form multinuclear complexes. The syntheses, crystal structures and fluorescent properties of the Co(II), Zn(II) and Cd(II) complexes have been fully investigated.

2. Experimental

2.1. *Materials and instruments*

3,5-Dibromosalicylaldehyde, 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.

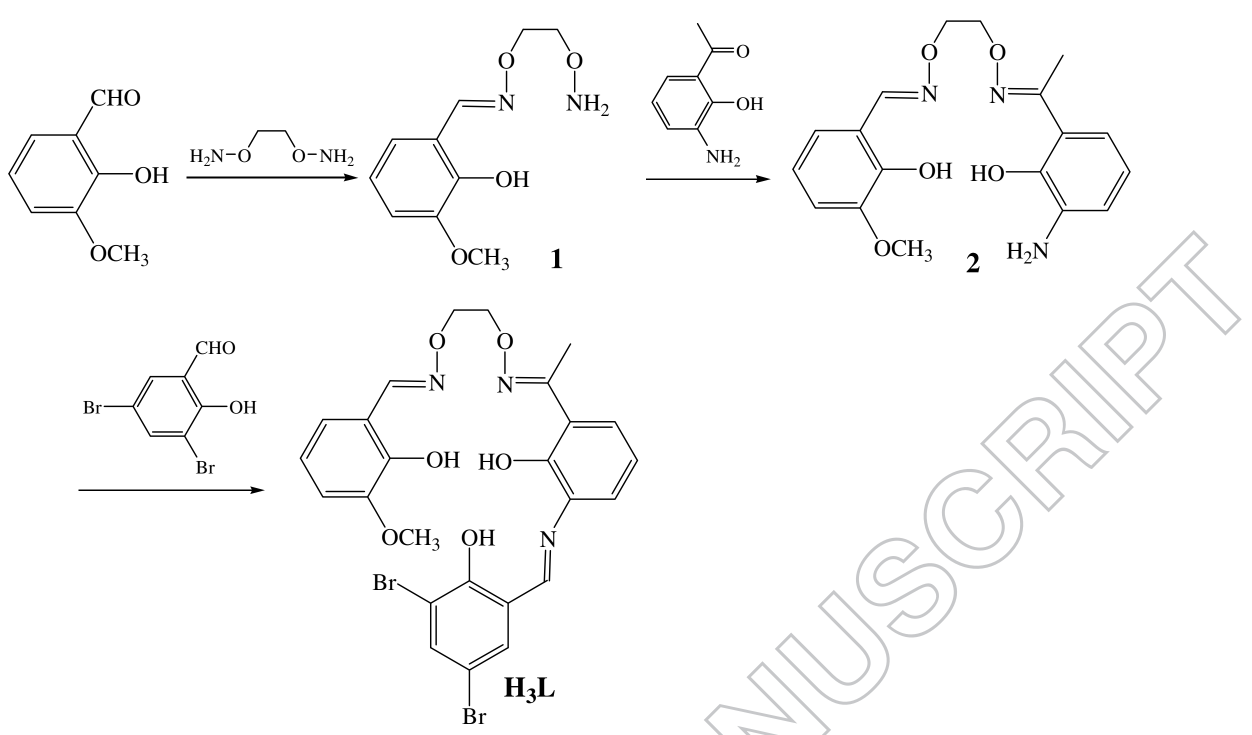
C, H, and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. Elemental analyses for Co(II), Zn(II) and Cd(II) ions were measured using an IRIS ER/S·WP–1 ICP atomic emission spectrometer. FT-IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with 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. ^{1}H NMR spectra were determined using a Bruker AVANCE DRX-400 spectrometer. Melting points were obtained by use of an X_4 microscopic melting point apparatus made by 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 6-[2-nitrilomethylidyne(4,6-dibromobenzene)]-6'-methoxy-2,2'-[1,1'-(ethylenedioxy(nitrilomethylidyne)(nitriloethylidyne)]triphenol (H_3L)***

1,2-Bis(phthalimidoxy)ethane was synthesized according to the literature [1c, 13c]. 1,2-Bis(aminooxy)ethane was prepared according to an analogous method reported earlier [1b, 13c].

The single-armed salamo-type bisoxime H_3L was synthesized by a modified method reported in the earlier literature (scheme 1) [4e, 4f].



Scheme 1. Synthetic route to H_3L.

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 solution was heated at 50–55 °C for 6 h. The solution was concentrated *in vacuo* and the residue was purified by column chromatography (SiO_2, chloroform/ethyl acetate, 10:1) to afford a colorless flocculent crystalline solid of 2-[*O*-(1-ethyloxyamide)]oxime-6-methoxyphenol (**1**). Yield, 48% (163.6 mg). M.p. 91-92 °C. Anal. Calc. for $C_{10}H_{14}N_2O_4$ (%): C, 53.09; H, 6.24; N, 12.38. Found (%): C, 53.12; H, 6.22; N, 12.37.

A solution of **1** (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 solution was heated at 55–60 °C for 24 h. After cooling to room temperature, the brownish intermediate product 6-amino-6′-methoxy-2,2′-[1,1′-(ethylenedioxy(nitrilomethylidyne)(nitriloethylidyne)]-bisphenol (**2**) was collected via suction filtration. Yield, 25% (179.7 mg). 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 **2** (719.8 mg, 2 mmol) in ethanol (10 mL) was added to a solution of 3,5-dibromosalicylaldehyde (560.0 mg, 2 mmol) in ethanol (10 mL), and the solution was heated at 50–55 °C for 4 h. Taking advantage of a hot filtration, the orange precipitate of H_3L was collected via suction filtration. Yield, 43% (532.4 mg). M.p. 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.13 (s, 1H), 11.89 (s, 1H), 9.72 (s, 1H), 8.65 (s, 1H), 8.37 (s, 1H), 6.82 – 6.96 (m, 6H), 6.69 (d, J = 7.8 Hz, 1H), 6.17 (s, 1H), 4.52 (s, 4H), 3.90 (s, 3H), 2.37 (s, 3H). IR (KBr, cm^{-1}) 3065(w), 1625(s), 1446(s), 1255(s), 1014(m), 725(s). Anal. Calc. for $C_{25}H_{23}Br_2N_3O_6$ (%): C, 48.33; H, 3.73; N, 6.76. Found (%): C, 48.46; H, 3.65; N, 6.70.

2.3. *Synthesis of diethanol(μ-acetato){6-[2-Nitrilomethylidyne(4,6-dibromobenzene)]-6′-methoxy-2,2′-[1,1′-(ethylenedioxy(nitrilomethylidyne)(nitriloethylidyne)]triphenolato)dicobalt(II)} (1)*

A solution of cobalt(II) acetate tetrahydrate (2.49 mg, 0.01 mmol) in ethanol (2 ml) was added to a solution of H_3L (3.11 mg, 0.005 mmol) in acetone (4 ml) at room temperature. The color of the mixing solution turned dark-red immediately. The mixture was filtered, and the filtrate was allowed to stand at room temperature for about one week. The solvent was partially evaporated, and dark-red block-shaped single crystals suitable for X-ray crystallographic analysis were obtained. Yield, 46% (404.6 mg). IR (KBr, cm^{-1}) 3053(w), 1598(s), 1440(s), 1242(m), 1076(m), 734(m), 534(w), 433(w). Anal. Calc. for $C_{31}H_{37}Br_2Co_2N_3O_{11}$ (%): C, 41.13; H, 4.12; N, 4.64; Co, 13.02. Found (%): C, 41.35; H, 4.07; N, 4.70; Co, 13.11.

2.4. *Synthesis of methanol(μ-acetato){6-[2-Nitrilomethylidyne(4,6-dibromobenzene)]-6′-methoxy-2,2′-[1,1′-(ethylenedioxy(nitrilomethylidyne)(nitriloethylidyne)]triphenolato)dizinc(II)} (2)*

A solution of zinc(II) acetate dihydrate (2.19mg, 0.01mmol) in methanol (4 ml) was added to a solution of H_3L (3.11 mg, 0.005 mmol) in acetone (2 ml) at room temperature. The color of the mixing solution immediately turned to yellow. The mixture was filtered, and the filtrate was allowed to stand at room temperature for about one week. After the solvent was partially evaporated, several yellow block-shaped single crystals separated out which were suitable for X-ray crystallographic analysis. Yield, 48% (399.1 mg). IR (KBr, cm^{-1}) 3047(w), 1602(s), 1442(s), 1251(w), 1076(w), 740(m), 533(w), 445(w). Anal. Calc. for $C_{28}H_{27}Br_2Zn_2N_3O_9$ (%): C, 40.03; H, 3.24; N, 5.00; Zn, 15.57. Found (%): C, 40.08; H, 3.27; N, 5.04; Zn, 15.51.

2.5. ***Synthesis of di{methanol(µ-acetato){6-[2-Nitrilomethylidyne(4,6-dibromobenzene)]-6'-methoxy-2,2'-[1,1'-(ethylenedioxy(nitrilomethylidyne)(nitriloethylidyne)]triphenolato)dicadmium(II)}} (3)***

A solution of cadmium(II) acetate dihydrate (2.66 mg, 0.01 mmol) in methanol (4 ml) was added dropwise to a solution of H_3L (3.11 mg, 0.005 mmol) in acetone (2 ml) at room temperature. The color of the mixing solution turned yellow immediately, then it was allowed to volatilize at room temperature. After several weeks, the solvent had partially evaporated and several yellow block-shaped single crystals were obtained, which were suitable for X-ray crystallographic analysis. Yield, 51% (947.2 mg). IR (KBr, cm^{-1}) 3059(w), 1608(s), 1438(s), 1240(m), 1043(w), 742(m), 521(w), 443(w). Anal. Calc. for $C_{56}H_{54}Br_4Cd_4N_6O_{18}$ (%): C, 36.00; H, 2.91; N, 4.50; Cd, 24.07. Found (%): C, 36.05; H, 2.93; N, 4.56; Cd, 24.02.

2.6. ***X-ray crystallography***

X-ray diffraction data for the Co(II), Zn(II) and Cd(II) complexes were collected on a Bruker Smart Apex CCD diffractometer at 293.42(10), 293.01(2) and 173.42(10) K, respectively, using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection and reduction were performed using SMART and SAINT software [14]. The structures were solved using the direct method and refined by full-matrix least-squares on F^2 using the SHELXL-97 program package [15]. All non-hydrogen atoms were refined anistropically and hydrogens were added in calculated positions and refined using a riding model. The X-ray crystallographic data collection, solution and refinement parameters for the Co(II), Zn(II) and Cd(II) complexes are summarized in table 1.

3. Results and discussion

3.1. *X-ray crystal structures*

3.1.1. The Co(II) complex. The crystal structure and atom numbering of the Co(II) complex are given in figure 1. Selected bond distances and angles of the Co(II) complex are listed in table 2.

The Co(II) complex crystallizes in the monoclinic system, space group *C*2/*c*, which consists of two Co(II) ions, one $(L)^{3-}$ unit, one coordinated acetate ion, two coordinated ethanol molecules and one crystallized water molecule. Moreover, the Co(II) complex forms a novel 1:2 ($(L)^{3-}$: Co(II)) dinuclear structure which is less common in the reported salamo-type complexes [1, 13]. The Co1 ion is six-coordinate by one nitrogen (N1) and two oxygens (O1, O2) of the $(L)^{3-}$ unit, one oxygen (O9) of the coordinated acetate ion and two oxygens (O7 and O8) of coordinated ethanol molecules. Moreover the phenolic oxygens (O1 and O2), the oxime nitrogen (N1) of the $(L)^{3-}$ unit and the oxygen (O9) of the coordinated acetate ion together constitute the basal plane; two oxygens (O7 and O8) of coordinated ethanol molecules occupy the axial positions. The Co2 ion is five-coordinate by two phenolic oxygens (O2 and O5), one oxygen (O10) of the coordinated acetate ion and two oxime nitrogens (N2 and N3). Moreover the oxygen (O10) of the coordinated acetate ion, the oxime nitrogen (N2) and the phenolic oxygen (O5) together constitute the basal plane; the oxime nitrogen (N3) and the phenolic oxygen (O2) occupy the axial positions. Here, we have synthesized a dinuclear Co(II) complex in which the Co1 ion is six-coordinate with a slightly distorted octahedral geometry and the Co2 ion is five-coordinate with a trigonal bipyramidal geometry which is deduced by calculating the value of $\tau = 0.838$ [16]. The non-coordinated water molecule in the structure of the Co(II) complex is disordered unequally over three different positions. This was allowed for during refinement and their total occupancy is 1.0 with the O1W, O2W and O3W atoms occupancies refined to 0.4, 0.3 and 0.3, respectively.

The Co(II) complex molecules form a dimeric structure via intramolecular and intermolecular hydrogen bond interactions. As illustrated in figure 2, three pairs of intramolecular hydrogen bonds, O7-H7A···O5, C15-H15A···O3 and C17 –H17···O10, are formed. The adjacent Co(II) complex molecules are interlinked into a dimer via intermolecular hydrogen bond interactions O8-H8···O9 between the O8–H8 units of the coordinated ethanol molecules and the O9 atom of the μ_2-acetate ion from the adjacent Co(II) complex molecule [1, 5-7]. The hydrogen bond data for the Co(II) complex are summarized in table 3.

3.1.2. The Zn(II) complex. The structural features of the Zn(II) complex are very similar to those of the Co(II) complex. The crystal structure and atom numbering of the Zn(II) complex are presented in figure 3 and selected bond distances and angles of the Zn(II) complex are shown in table 2.

The Zn(II) complex crystallizes in the triclinic system, space group *P*-1, and the unit cell contains two crystallographically independent, but chemically identical, dinuclear complexes (figure 3) consisting of two Zn(II) atoms, one $(L)^{3-}$ unit, one coordinated acetate ion and and one coordinated methanol molecule as expected from the analytical data. Moreover, the Zn(II) complex forms a novel 1:2 ($(L)^{3-}$: Zn(II)) dinuclear structure which is different from the structures of 1:1 [1d, 1h], 2:3 [13g], 2:4 [1c], 4:8 [13d] (L: Zn(II)) salamo-type Zn(II) complexes reported earlier. The Zn1 ion is five-coordinate by two nitrogens (N1 and N2) and two oxygens (O1 and O5) of the $(L)^{3-}$ unit and one oxygen (O7) of the coordinated acetate ion in a μ_2-fashion. Moreover the phenolic oxygen (O1), the oxime nitrogen (N2) of the $(L)^{3-}$ unit and the oxygen (O7) of the coordinated acetate ion together constitute the basal plane, while one phenolic oxygen (O5) and one oxime nitrogen (N1) occupy the axial positions. The Zn2 ion is five-coordinate by two phenolic oxygens (O5 and O6), one oxygen (O8) of the coordinated acetate ion also in a μ_2-fashion, one oxime nitrogen (N3) and one oxygen (O9) of the coordinated methanol molecule. Moreover the oxygen (O8) of the coordinated acetate ion, the oxime nitrogen (N3) and the oxygen (O9) of the coordinated methanol molecule together constitute the basal plane; the two phenolic oxygens (O5 and O6) occupy the axial positions. As we know, the coordination number of Zn(II) is generally four or six and the coordination geometry around Zn(II) atom is tetrahedral or octahedral [1d]. However, there are only a few reports of five-coordinate salamo-type Zn(II) complexes having distorted square–pyramidal or trigonal–bipyramidal configurations [1e]. Here, we have designed and synthesized a dinuclear Zn(II) complex in which the Zn1 and Zn2 ions are both five-coordinate with distorted trigonal bipyramidal geometries which are deduced by calculating the values of $\tau_1 = 0.875$, $\tau_2 = 0.600$, respectively [16].

In the crystal structure, the Zn(II) complex molecules form a dimeric structure via two pairs of intermolecular C24–H24···O2 and C18–H18···O9 hydrogen bond interactions [17]. Meanwhile, an interesting feature of the crystal structure are two pairs of short O1···O9 contacts [18] (figure 4). The hydrogen bond data are summarized in table 3.

As shown in figure 4, the dimers are interlinked by C7–H7···Cg3 (C41-C46) interactions into a 1D chain structure along the *b* axis [1f]. In addition, the adjacent chains along the *b* axis are held together to form an infinite 2D network structure on the *ab* crystallographic plane by C37–H37A···Cg2 (C19-C24) interactions (figure 5) [1g, 13h]. The planes are interlinked further by C40–H40B···Cg1 (C1-C6) interactions to form an infinite 3D structure [19]. Thus, a self-assembled infinite 3D supramolecular structure is formed by abundant intermolecular hydrogen bonds, three pairs of C–H···π interactions of neighboring dimers (table 3).

3.1.3. The Cd(II) complex. The crystal structure and atom numberings of the Cd(II) complex are drawn in figure 6. The selected bond distances and angles are summed in table 2.

Previously, the mononuclear salamo-type Cd(II) complex, [Cd(Br$_4$salamo)(H$_2$O)$_2$], was reported [1d]. Here, the Cd(II) complex is composed of four Cd(II) ions, two $(L)^{3-}$ units, two coordinated acetate ions and methanol molecules. The Cd(II) complex crystallizes in the orthorhombic system, space group *Pbca*, is a symmetric tetranuclear structure, and is a dimer of the {Cd(L)(OAc)Cd(CH_3OH)} unit. The Cd(II) complex has a “stepped” conformation as observed in the dimers of [Cu(salamo)] [13a]. Two Cd(II) ions (Cd1 and Cd2) have two different coordination geometries. The Cd1 ion is six-coordinate by two nitrogens (N2 and N3) and two oxygens (O2 and O5) of the $(L)^{3-}$ unit and two oxygens (O7 and O8) of one chelating acetate ion. Meanwhile, the phenolic oxygen (O2), the phenolic oxygen (O5) and one oxygen (O8) of the chelate acetate ion together constitute one triangular plane, while the oxime nitrogens (N2 and N3) and one oxygen (O7) of the chelating acetate ion together constitute another triangular plane. The coordination geometry around the Cd1 center can be regarded as a distorted triangular prism. The Cd2 atom is uncommon as it is seven-coordinate, bonded by four phenolic oxygens (O1, O2, O5 and $O1^{\#}$), one oxygen (O6) of a methoxy group of an $(L)^{3-}$ unit, one oxime nitrogen (N1) and one oxygen (O9) of a coordinated methanol molecule. Moreover, the oxygen (O6) of a methoxy group of the $(L)^{3-}$ unit, the oxime nitrogen (N1) and the phenolic oxygens (O1, O2 and O5) together constitute the basal plane, while the phenolic oxygens ($O1^{\#}$) and the oxygen (O9) of coordinated methanol molecule occupy the axial positions. The coordination geometry around the Cd2 center can be described as slightly distorted pentagonal bipyramidal geometry [20]. As far as we know, this is the first time a seven-coordinate salamo-type Cd(II) complex has been reported. Thus, this novel 2:4 ($(L)^{3-}$: Cd) tetranuclear structure is different from that of 1:1 (L : Cd(II)) reported earlier in a salamo-type Cd(II) complex [1d]. In addition, the dihedral angle between the coordination plane of N2-Cd1-O2 and that of N3-Cd1-O5 is 52.51(3)°; the two planes are bent asymmetrically making angles of 23.09(3)° and 21.88(3)°, respectively, with respect to the plane of O1-Cd2-N1, indicating the salamo moiety and the single-armed salicylaldehyde unit have good coplanarity. The dimer is bridged through O1 across the crystallographic center of symmetry ($Cd2\cdots O1^{\#}$ = 2.344(3) Å, $Cd2\cdots Cd2^{\#}$ = 3.593(4) Å,

∠Cd2···O1···Cd2$^{\#}$ = 100.79(10)° and ∠O1···Cd2···O1$^{\#}$ = 79.21(10)).

As shown in figure 7, the Cd(II) complex molecules are interlinked by intermolecular hydrogen bonds C15–H15C···O3, O9–H9X···O8, C16–H16···O7 and C17–H17A···N2 to form an infinite 2D network structure on the *ab* crystallographic plane (table 3) [21]. Synchronously, this linkage is further stabilized by short intermolecular Br1···Br1 contacts between the bromine atoms coming from the bromo-substituted salicylaldehyde of one Cd complex unit and that of another Cd complex unit, to form a 1D supramolecular chain-like structure [22].

3.2. *IR spectra*

The FT-IR spectra of H_3L and its corresponding Co(II), Zn(II) and Cd(II) complexes exhibit various bands from 400–4000 cm^{-1} (figure S1). The Co(II), Zn(II) and Cd(II) complexes have similar FT-IR spectra which indicate that they have similar structures. The free ligand H_3L shows a broad characteristic band of the OH group at 3065 cm^{-1}. This band disappeared in the FT-IR spectra of the Co(II), Zn(II) and Cd(II) complexes, which is indicative of the fact that the phenolic OH groups of H_3L have been deprotonated and coordinated to the Co(II), Zn(II) and Cd(II) atoms [23].

The free ligand H_3L exhibits a characteristic C=N stretching band at 1625 cm^{-1}, while the C=N stretching bands of the Co(II), Zn(II) and Cd(II) complexes are observed at 1598, 1602 and 1608 cm^{-1}, respectively. The C=N stretching frequencies are shifted to lower frequencies by *ca*. 27, 23 and 17 cm^{-1} upon complexation, indicating that the Co(II), Zn(II) and Cd(II) atoms are coordinated by N_2O_2 donor atoms of $(L)^{3-}$ units. Thus, it provides evidence for the coordination of H_3L with Co(II), Zn(II) and Cd(II) atoms. In the 1438-1446 cm^{-1} region, the observed bands are attributed to aromatic C=C vibration. Upon coordination these bands shift to lower frequencies for the Co(II), Zn(II) and Cd(II) complexes.

The Ar–O stretching frequency appears at 1255 cm^{-1} for H_3L, while the Ar–O stretching frequencies of the Co(II), Zn(II) and Cd(II) complexes are observed at 1242, 1251 and 1240 cm^{-1}, respectively. The Ar–O stretching frequencies are shifted to lower frequencies, indicating that the Co–O, Zn–O and Cd–O bonds are formed between the Co(II), Zn(II) and Cd(II) atoms and oxygen atoms of phenolic groups [1h]. In addition, there is a broad absorption centered on 3053, 3047 and 3059 cm^{-1} in the Co(II), Zn(II) and Cd(II) complexes, respectively, which may be assigned to the O-H stretching vibration of CH_3OH or CH_3CH_2OH molecules.

The far-infrared spectra of the Co(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 433, 445 and 443 cm^{-1} in the Co(II), Zn(II) and Cd(II) complexes are assigned to $\nu_{Co–O}$, $\nu_{Zn–O}$ and $\nu_{Cd–O}$, while the bands at 534, 533 and 521 cm^{-1} are assigned to $\nu_{Co–N}$, $\nu_{Zn–N}$ and $\nu_{Cd–N}$, respectively.

3.3. *UV–vis absorption spectra*

The UV-vis absorption spectra of the free ligand H_3L and its Co(II), Zn(II) and Cd(II) complexes were determined in chloroform solution (c = 1×10^{-5} mol·L^{-1}) and are shown in figure S2. The absorption peaks of the Co(II), Zn(II) and Cd(II) complexes are obviously different from those of H_3L.

The UV-vis spectrum of H_3L exhibits three absorption bands at 263, 270 and 447 nm. The former absorption band at 263 nm can be assigned to the *π–π** transition of the benzene rings, the second can be attributed to the *π–π** transition of the oxime groups [24], and the latter one at 447 nm which is ascribed to the quinoid form of H_2Salen. It is of note that this band cannot be seen sometimes in the corresponding salen derivatives [25]. Upon coordination of the ligand, the absorption band at 263 nm for the Co(II), Zn(II) and Cd(II) complexes is hypochromically shifted to *ca*. 240, 239 and 241 nm, respectively, and the band at 270 nm is bathochromically shifted to 282, 282 and 280 nm, respectively, which indicate that the phenolic oxygen and oxime nitrogens are involved in coordination to the Co(II), Zn(II) or Cd(II) atoms. In addition, new bands are observed at 457, 443 and **432(372)** ***[au: is this correct?]*** nm in the Co(II), Zn(II) and Cd(II) complexes, respectively, which are assigned to the *n–π** charge transfer transition from a nonbonding electron pair of the bridging phenolic oxygen to the vacant d-orbital of the metal(II) ions [1].

3.4. *Fluorescence properties*

The fluorescent properties of H_3L and its corresponding Co(II), Zn(II) and Cd(II) complexes were measured at room temperature (figure S3). The Zn(II) and Cd(II) complexes display enhanced emission intensities compared to the corresponding ligand (H_3L) when excited at 452 nm. Enhancement of fluorescence through complexation is of much interest as it creates the opportunity for photochemical applications of these complexes [26, 27]. The fluorescence of the free ligand is quenched by the occurrence of a photoinduced electron transfer process, probably due to the presence of lone pairs on the nitrogen atoms, and as such, the process is prevented by the complexation of the free ligand with metal atoms. Thus the fluorescence intensity may be effectively enhanced by the coordination of Zn(II) and Cd(II) atoms [28].

The free ligand exhibits a weak emission peak at 548 nm upon excitation at 452 nm. The Co(II) complex shows a lower photoluminescence upon excitation at 452 nm (figure S3). Since the emission peak position of the Co(II) complex is similar to that of the free ligand, the emission peak of the Co(II) complex may also arise from the intraligand transition. Compared with the free ligand, the Co(II) complex's emission intensity is reduced significantly which indicates that the Co(II) ions have the property of fluorescent quenching. The emission spectrum shows that the emission spectral shape of the Zn(II) complex closely resembles that of the Cd(II) complex. In comparison with the corresponding H_3L with the maximum emission wavelength at 548 nm when excited at 452 nm, the Zn(II) and Cd(II) complexes exhibit blue-shifts with the maximum emission at 510 and 502 nm when excited at 452 nm, which could be assigned to ligand-to-metal charge transfer (LMCT) [29].

4. Conclusion

Three new complexes with the chemical formulas $[Co(L)(OAc)Co(CH_3CH_2OH)_2]\cdot H_2O$,

$[Zn(L)(OAc)Zn(CH_3OH)]$ and $[\{Cd(L)(OAc)Cd(CH_3OH)\}_2]$ have been synthesized and structurally characterized. There is good coplanarity between the salamo moiety and the single-armed salicylaldehyde unit in the Cd(II) complex, while that of the Co(II) or Zn(II) complex is poor. The Co(II) complex forms a dimeric unit by intermolecular hydrogen bond interactions of neighboring dimeric molecules. The Zn(II) complex also forms a dimeric unit by intermolecular hydrogen bond interactions. Self-assembling infinite 1D, 2D and 3D supramolecular structures are formed by intermolecular hydrogen bond and C–H···*π* interactions. Also, the Cd(II) complex forms an infinite 2D supramolecular structure via intermolecular hydrogen bond interactions. In the FT-IR spectra of the Co(II), Zn(II) and Cd(II) complexes, the ν(M-O) and ν(M-N) vibrational absorption frequencies have been observed. Meanwhile, the Zn(II) and Cd(II) complexes exhibit blue emission with the maximum emission wavelength at 510 and 502 nm when excited at 452 nm.

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 depository number CCDC Nos. 1534113, 1484600 and 1534112 for the Co(II), Zn(II) and Cd(II) complexes, respectively.

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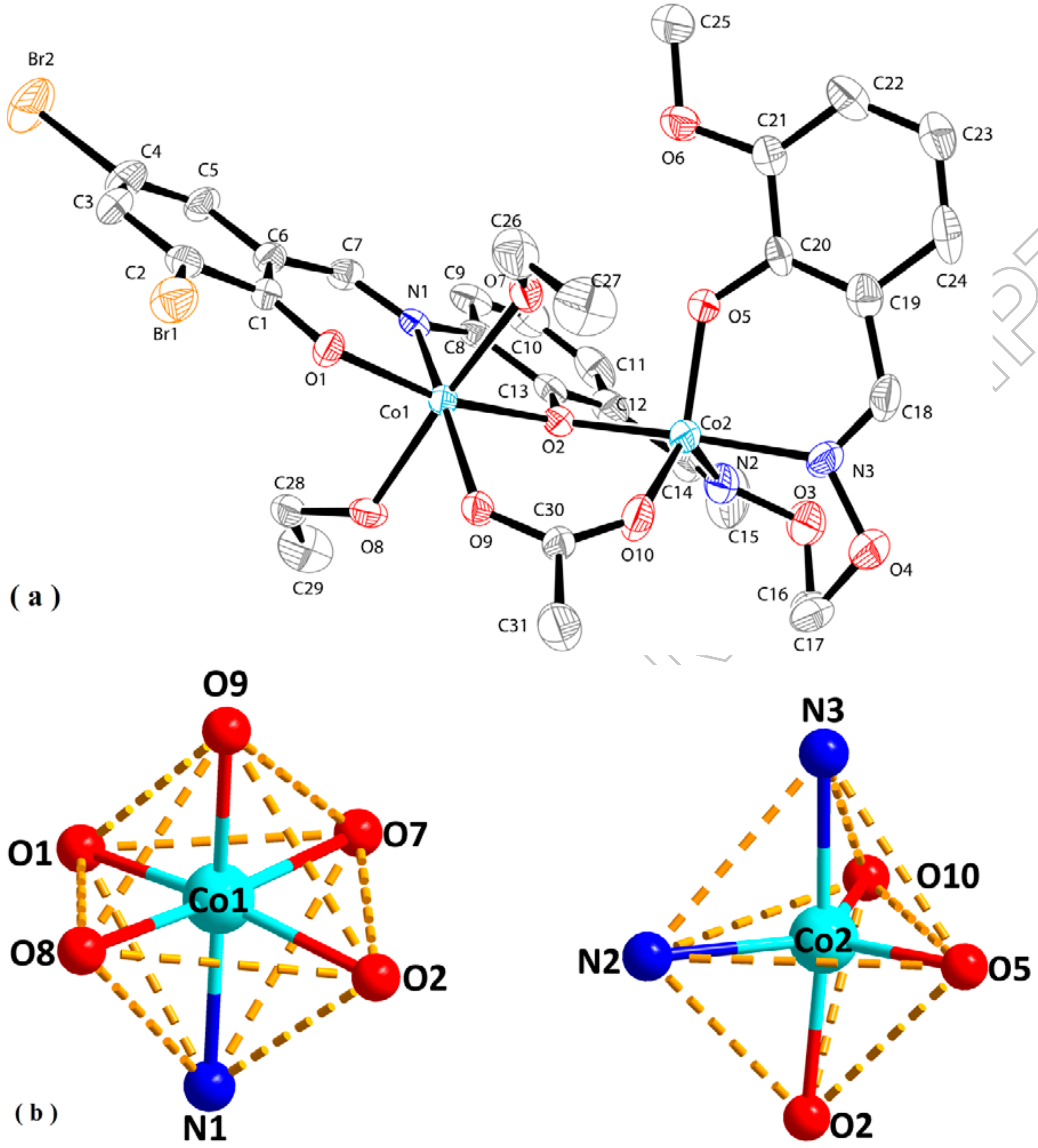

Figure 1. (a) Molecular structure of the Co(II) complex with the atom numbering (hydrogens omitted for clarity); (b) Coordination polyhedra for Co(II) atoms of the Co(II) complex.

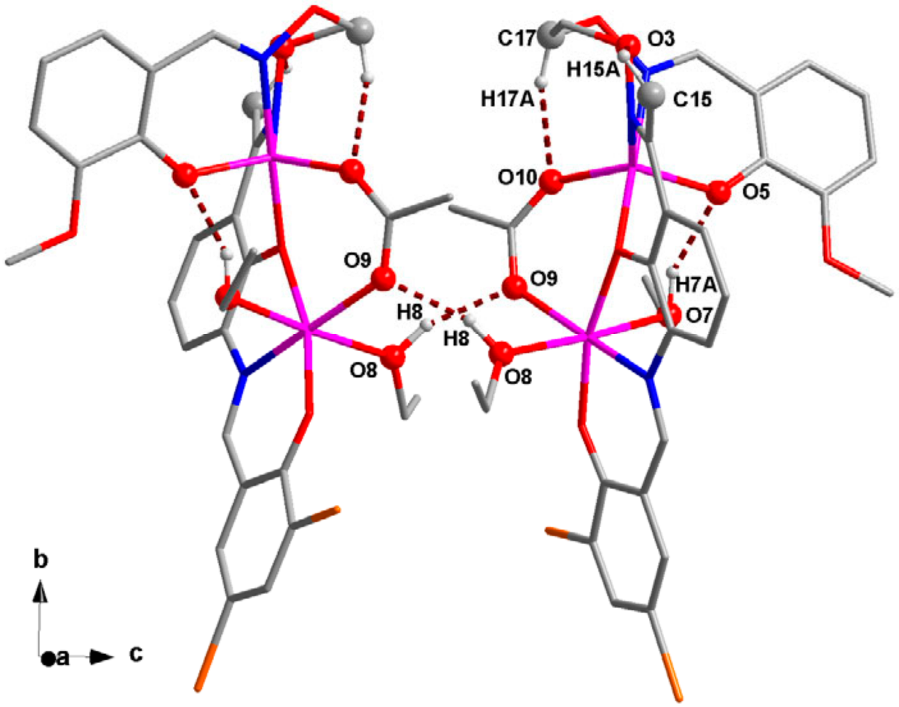

Figure 2. A dimeric unit of the Co(II) complex formed by intramolecular and intermolecular hydrogen bonds.

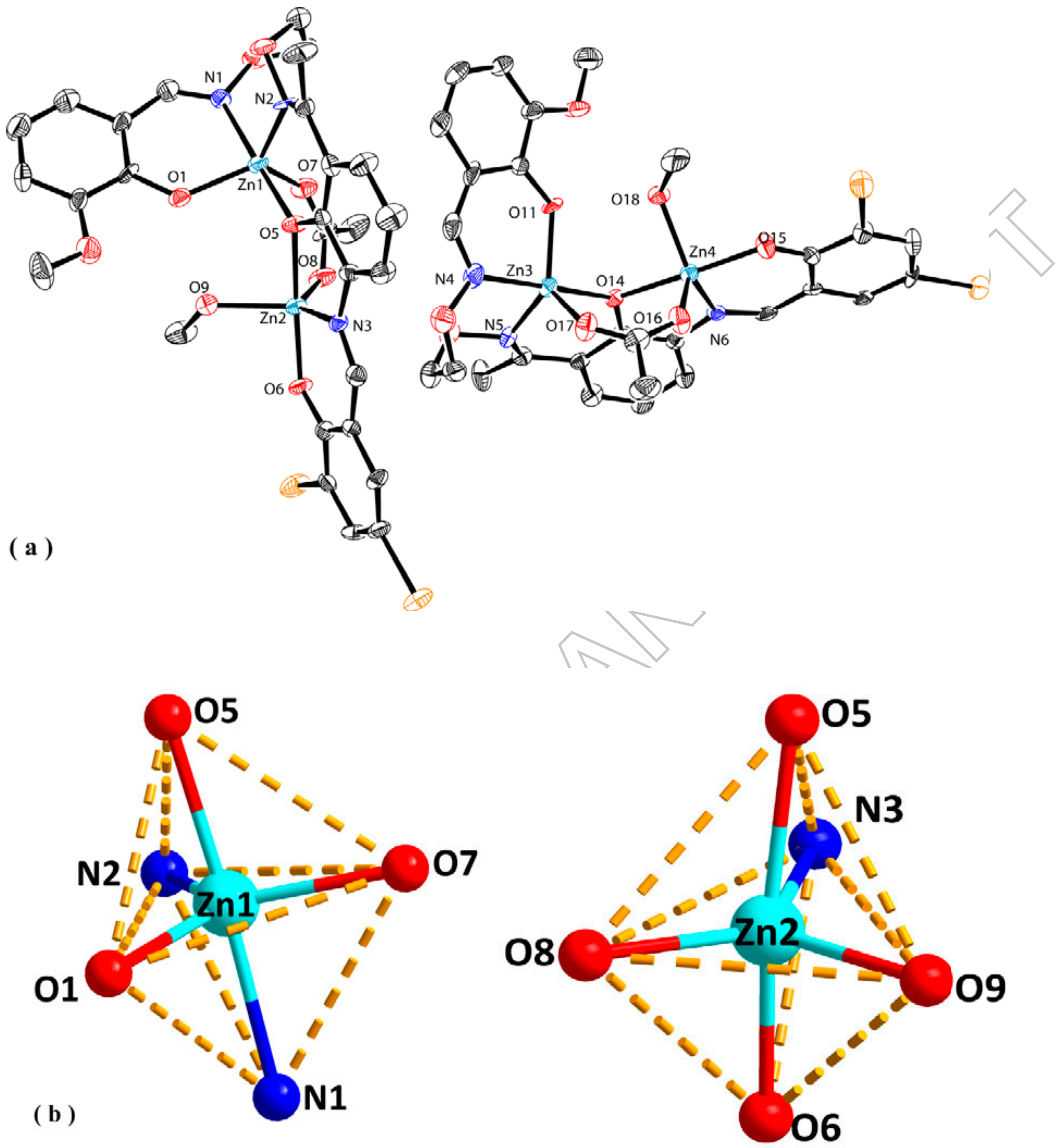

Figure 3. (a) Molecular structure of the Zn(II) complex with the atom numbering (hydrogens omitted for clarity); (b) Coordination polyhedra for Zn(II) atoms of the Zn(II) complex.

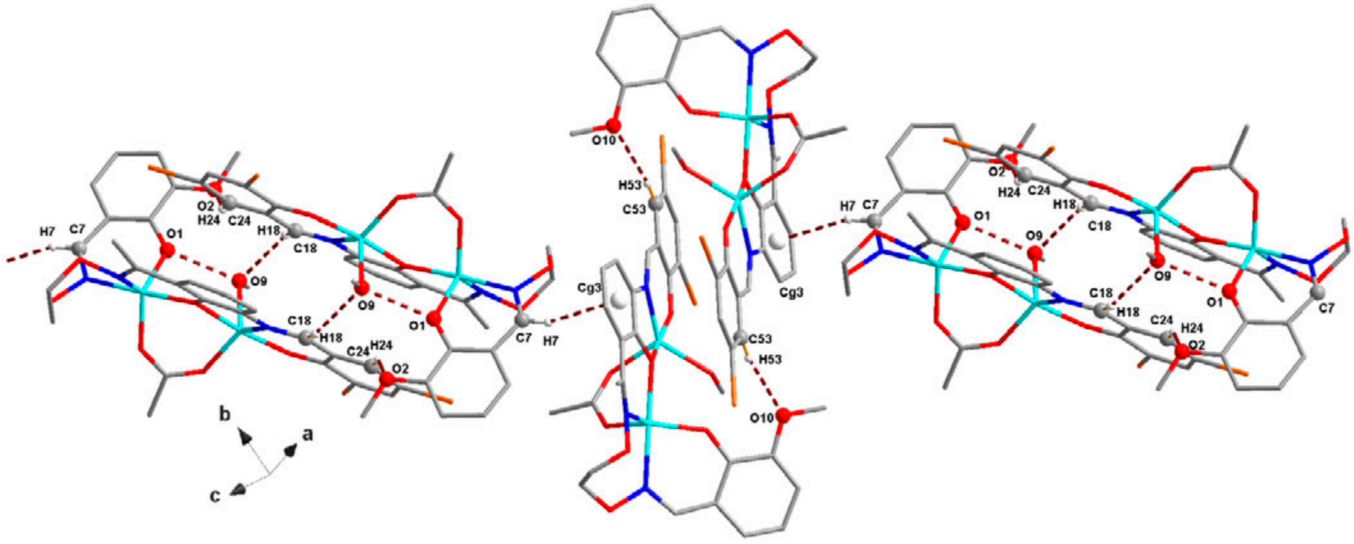

Figure 4. View of an infinite 1D chain motif of the Zn(II) complex along the *b* axis.

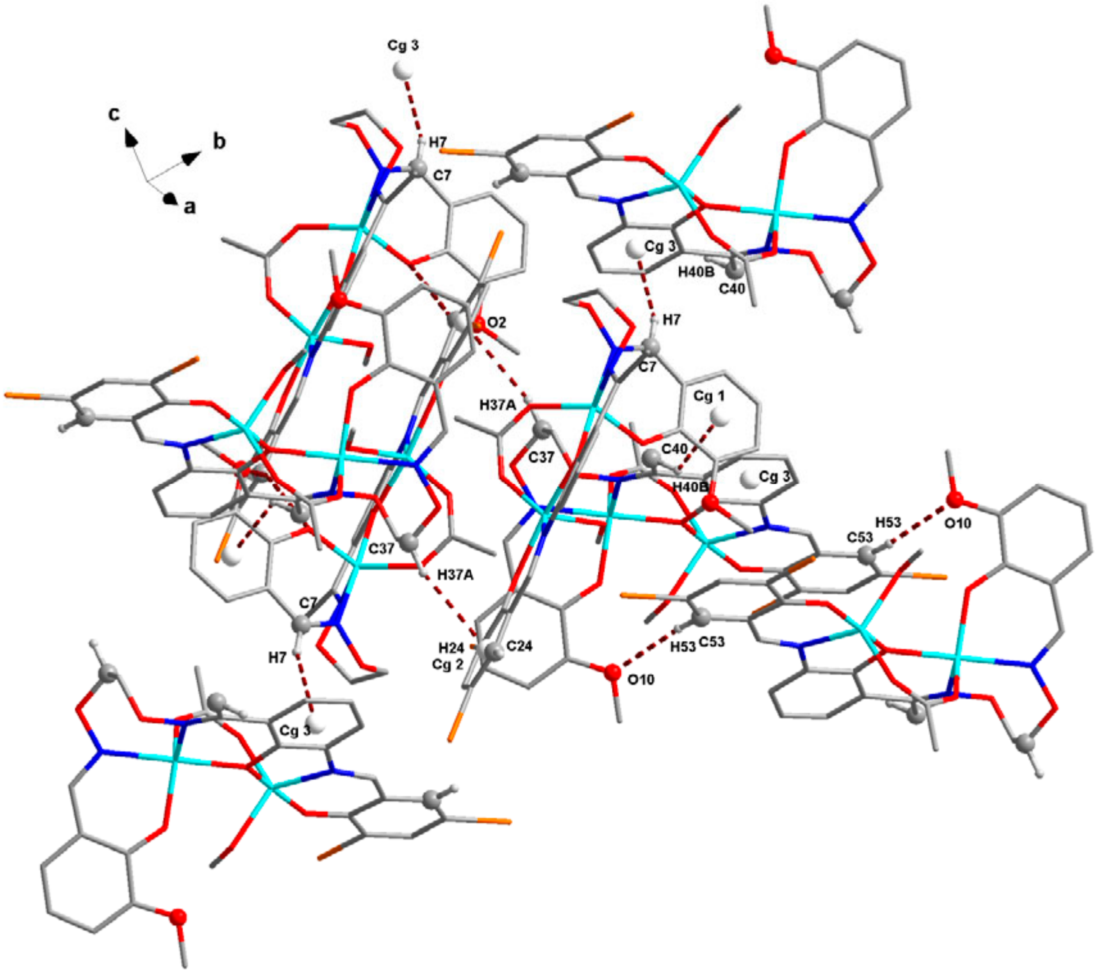

Figure 5. View of an infinite 2D network of the Zn(II) complex on the *ab* plane.

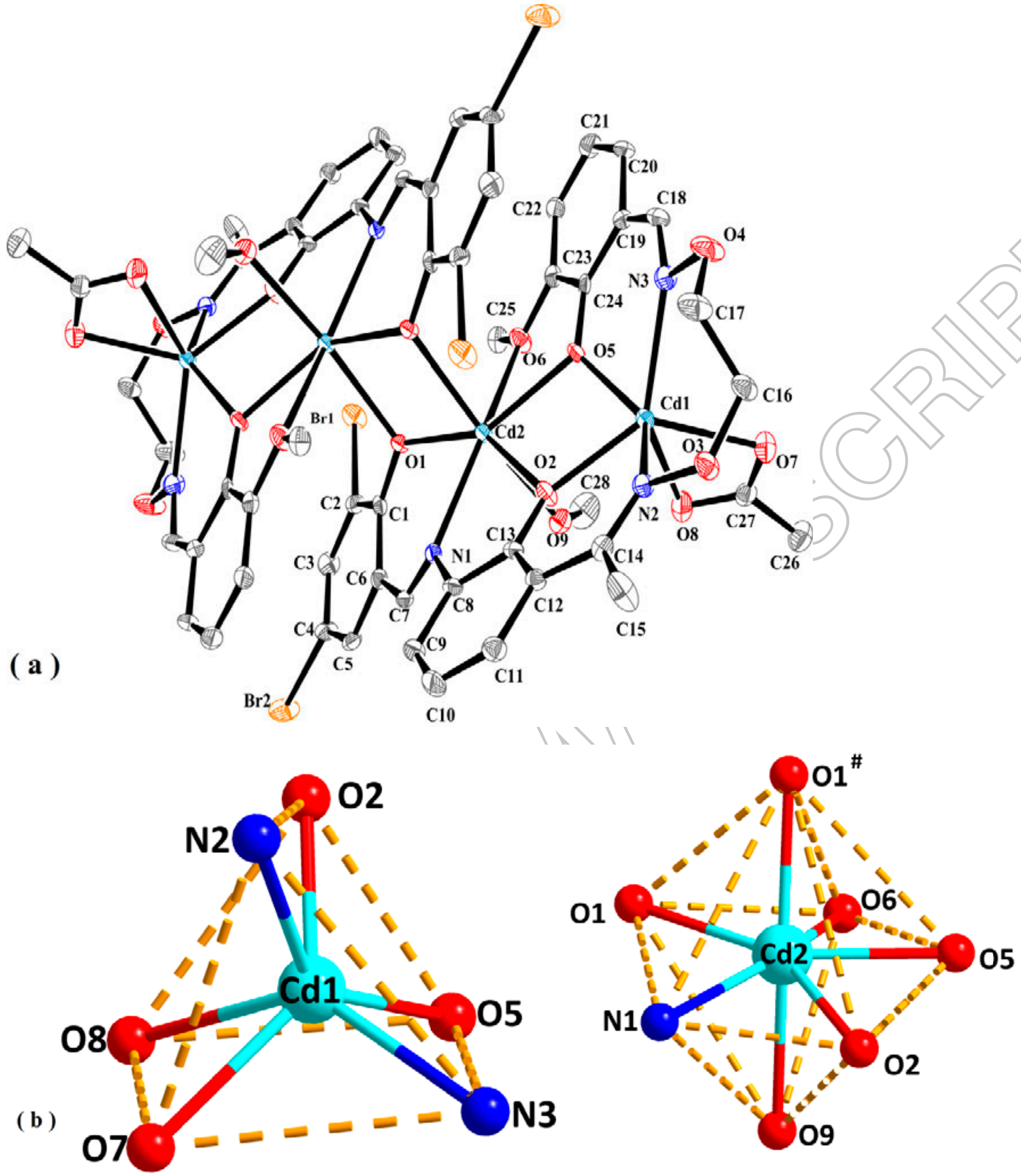

Figure 6. (a) Molecular structure of the Cd(II) complex with the atom numbering (hydrogens omitted for clarity); (b) Coordination polyhedra for Cd(II) atoms of the Cd(II) complex.

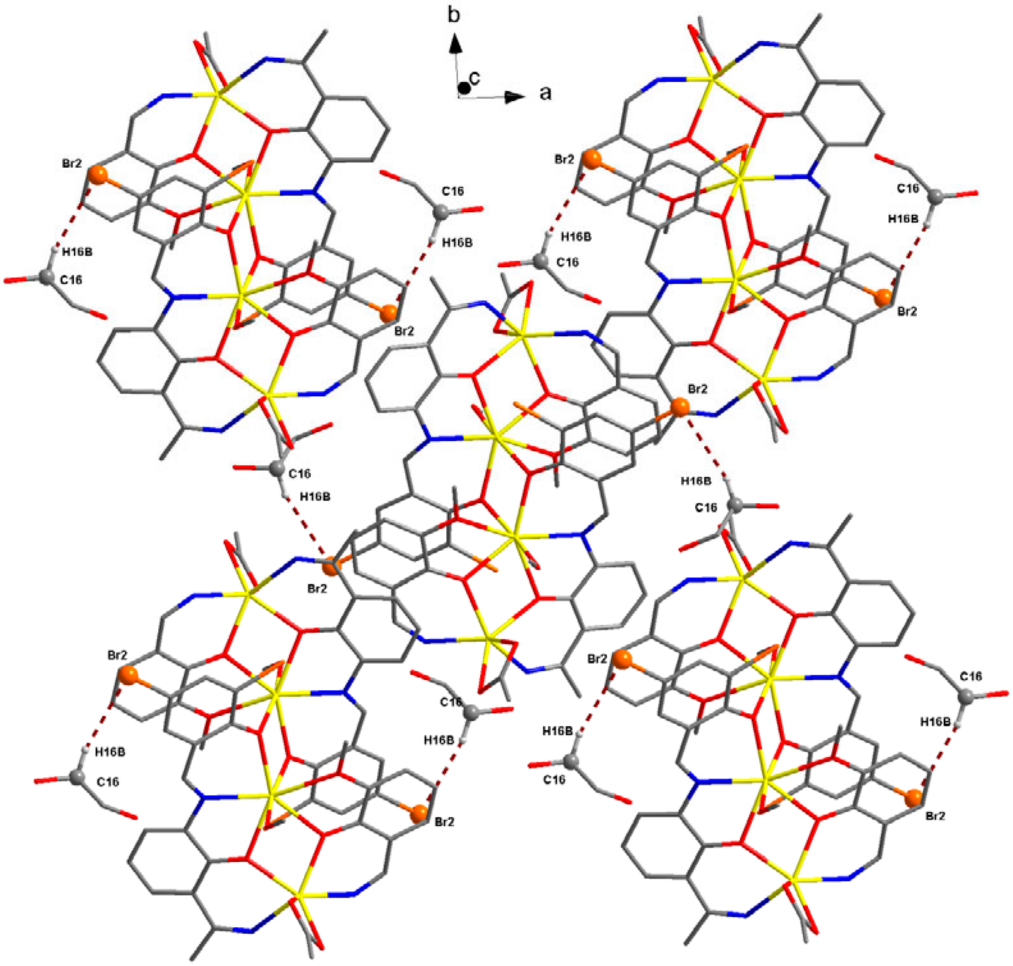

Figure 7. View of an infinite 2D network of the Cd(II) complex on the *ab* plane.

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

Empirical formula	$C_{31}H_{37}Br_2Co_2N_3O_{11}$	$C_{28}H_{27}Br_2Zn_2N_3O_9$	$C_{56}H_{54}Br_4Cd_4N_6O_{18}$
Formula weight	905.31	840.09	1868.29
Temperature (K)	293.42(10)	293.01(2)	173.42(10)
Wavelength (Å)	MoKα, 0.71073	MoKα, 0.71073	MoKα, 0.71073
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	*C*2/*c*	*P*-1	*Pbca*
a (Å)	10.0471(13)	14.2905(13)	16.9945(6)
b (Å)	31.7717(18)	15.1159(16)	17.4212(5)
c (Å)	24.9332(14)	15.6405(13)	19.9811(5)
α (º)	90	93.113(8)	90
β (º)	92.652(3)	93.401(7)	90
γ (º)	90	93.276(8)	90
Z	8	4	4
Volume ($Å^3$)	7950.5(12)	3361.4(5)	5915.7(3)
D_c ($Mg\ m^{-3}$)	1.513	1.660	2.098
μ (mm^{-1})	2.900	3.857	4.199
F (0 0 0)	3648	1672	3632
Crystal size (mm)	0.26 × 0.24 × 0.22	0.28 × 0.26 × 0.25	0.24 × 0.22 × 0.20
θ range (°)	2.05–25.12	3.39–26.02	1.96–25.997
Index ranges	$-12 \le h \le 12$, $0 \le k \le 39$, $0 \le l \le 30$	$-17 \le h \le 16$, $-18 \le k \le 18$, $-19 \le l \le 19$	$-20 \le h \le 10$, $-12 \le k \le 21$, $-22 \le l \le 24$
Reflections collected	17831	24793	15856
Independent reflections	7830	13167	5813
R_{int}	0.0202	0.102	0.0223
Completeness to θ	100% ($\theta = 26.00$)	99.4% ($\theta = 26.02$)	100% ($\theta = 25.997$)
Data / restraints / parameters	7830 / 3 / 465	13167 / 6 / 807	5813 / 0 / 401
GOF	1.024	0.916	1.082
R_1, wR_2 [$I>2\sigma(I)$]	0.0349, 0.0808	0.0739, 0.1402	0.0299, 0.0935
R_1, wR_2 (all data)	0.0512, 0.0847	0.1331, 0.1740	0.0405, 0.0986
$\Delta\rho_{max,min}$ (e / $Å^3$)	0.913 and -0.331	1.22 and -1.12	0.847 and -0.712

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

Co(II) complex		Zn(II) complex		Cd(II) complex	
Co1-O1	1.9765(17)	Zn1-O1	1.977(5)	Cd1-O2	2.194(3)
Co1-O8	2.1802(19)	Zn1-N1	2.131(6)	Cd1-O5	2.227(3)
Co2-O2	2.026(2)	Zn2-O6	1.962(6)	Cd1-O7	2.332(3)
Co2-N2	2.039(3)	Zn2-N3	2.026(6)	Cd1-N3	2.371(4)
Co1-O2	2.0820(19)	Zn1-O5	2.047(5)	Cd1-N2	2.392(4)
Co1-O9	2.0764(19)	Zn1-N2	2.062(7)	Cd1-O8	2.424(3)
Co2-O5	1.9339(18)	Zn2-O8	1.972(6)	Cd2-O5	2.274(3)
Co2-N3	2.123(3)	Zn1-O7	1.992(6)	Cd2-O1	2.318(3)
Co1-O7	2.1827(18)	Zn2-O5	2.105(5)	Cd2-N1	2.322(4)
Co1-N1	2.071(2)	Zn2-O9	2.066(5)	Cd2-O1$^{\#}$	2.344(3)
Co2-O10	2.012(2)	O1-Zn1-O5	93.5(2)	Cd2-O2	2.375(3)
O1-Co1-O2	166.24(8)	O1-Zn1-N2	120.8(3)	Cd2-O9	2.398(4)
O1-Co1- O9	98.93(7)	O7-Zn1-O5	93.6(2)	Cd2-O6	2.580(3)
O2-Co1- O8	94.10(7)	N2-Zn1-N1	91.5(3)	O2-Cd1-O5	76.64(10)
O7-Co1- O8	175.57(7)	O6-Zn2-O9	93.0(2)	O2-Cd1-O7	131.96(12)
N1-Co1- O7	95.79(7)	O8-Zn2-O9	105.4(2)	O5-Cd1-O7	120.26(12)
O2-Co2-N3	175.21(10)	N3-Zn2-O5	77.5(2)	O2-Cd1-N3	132.60(12)
O5-Co2-N2	119.09(10)	O1-Zn1-O7	116.1(2)	O5-Cd1-N3	76.37(11)
O10-Co2-N2	125.04(10)	O5-Zn1-N1	175.6(3)	O7-Cd1-N3	95.34(13)
N2-Co2-N3	89.23(11)	O7-Zn1-N1	90.2(3)	O2-Cd1-N2	77.07(11)
O1-Co1- O7	87.02(7)	O6-Zn2-O5	168.5(2)	O5-Cd1-N2	141.54(11)
O1-Co1-N1	89.70(8)	O6-Zn2-N3	91.5(2)	O7-Cd1-N2	98.20(11)
O2-Co1- O9	93.15(8)	O8-Zn2-N3	132.5(2)	N3-Cd1-N2	102.27(13)
O9-Co1- O7	94.56(7)	N3-Zn2-O9	121.3(2)	O2-Cd1-O8	82.67(11)
N1-Co1-O8	88.45(7)	O1-Zn1-N1	86.9(2)	O5-Cd1-O8	89.83(11)
O5-Co2-O2	95.91(8)	O5-Zn1-N2	84.5(2)	O7-Cd1-O8	55.25(11)
O5-Co2-N3	86.95(9)	O7-Zn1-N2	123.1(3)	N3-Cd1-O8	135.08(12)
O10-Co2-N3	88.72(9)	O6-Zn2-O8	94.6(3)	N2-Cd1-O8	113.99(12)
O1-Co1-O8	94.27(7)	O8-Zn2-O5	95.5(2)	O2-Cd1-C27	107.50(13)
O2-Co1- O7	85.46(7)	O9-Zn2-O5	89.7(2)	O5-Cd1-C27	106.81(14)
O2-Co1-N1	79.62(8)			O7-Cd1-C27	27.69(14)
O9-Co1- O8	81.07(7)			N3-Cd1-C27	117.27(14)
N1-Co1- O9	166.85(8)			N2-Cd1-C27	107.58(14)
O5-Co2-O10	93.49(8)			O8-Cd1-C27	27.57(14)
O10-Co2-O2	93.49(8)			O5-Cd2-O1	139.53(10)
N2-Co2-O2	86.02(9)			O5-Cd2-N1	140.68(11)

		O1-Cd2-N1	79.47(10)
		O5-Cd2-O1#	88.44(10)
		O1#-Cd2-O1	79.21(10)
		N1-Cd2-O1#	108.57(10)
		O5-Cd2-O2	72.23(10)
		O1-Cd2-O2	147.82(10)
		N1-Cd2-O2	68.50(10)
		O2-Cd2-O1#	113.32(10)
		O5-Cd2-O9	88.58(13)
		O1-Cd2-O9	94.70(11)
		N1-Cd2-O9	81.74(14)
		O9-Cd2-O1#	166.56(13)
		O2-Cd2-O9	78.13(12)
		O5-Cd2-O6	64.25(10)
		O1-Cd2-O6	76.23(10)
		N1-Cd2-O6	149.58(11)
		O6-Cd2-O1#	84.62(10)
		O2-Cd2-O6	132.37(10)
		O9-Cd2-O6	82.28(13)

Symmetry transformations used to generate equivalent atoms: #, 1-x, 1-y, 1-z for the Cd(II) complex.

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

D-H···A	d(D-H) (α)	d(H···A) (DCC)	d(D···A) (CgI-perp)	∠D-H···A (CgJ-perp)	Symmetry code
Co(II) complex					
O7-H7A···O5	0.85	1.93	2.695(3)	150	[x, y, z]
O8-H8···O9	0.93	1.91	2.798(3)	158	[-x, y, 1/2-z]
C15-H15A···O3	0.96	2.23	2.605(4)	102	[x, y, z]
C17 –H17···O10	0.97	2.26	3.153(4)	152	[x, y, z]
Zn(II) complex					
O9-H9···O1	0.86	2.18	2.577(8)	108	[x, y, z]
O9 -H9···O2	0.86	2.30	3.110(9)	157	[x, y, z]
O18-H18A···O10	0.86	2.30	3.033(8)	143	[x, y, z]
O18-H18A···O11	0.86	1.88	2.567(7)	136	[x, y, z]
C8-H8B···O7	0.97	2.51	3.297(11)	138	[x, y, z]
C10-H10C···O4	0.96	2.19	2.599(12)	104	[x, y, z]
C18–H18···O9	0.93	2.66	3.474(4)	147	[x, y, z]
C24-H24···O2	0.93	2.47	3.321(11)	152	[1-x, 1-y, 1-z]
C37-H37B···O17	0.97	2.47	3.286(11)	141	[x, y, z]
C40-H40C···O13	0.96	2.29	2.651(12)	101	[x, y, z]
C53-H53···O10	0.93	2.55	3.469(10)	168	[2-x, 2-y, -z]
C7-H7···Cg3		2.87	3.754(10)	158	[x, -1+y, z]
C37-H37A···Cg2		2.89	3.803(11)	157	[x, y, z]
C40-H40B···Cg1		2.95	3.539(11)	121	[2-x, 1-y, 1-z]
Cd(II) complex					
C16-H16B···Br2	0.99	2.92	3.873(6)	163	[-1/2+x,1/2-y,1-z]
O9-H9X···O8	0.85	2.12	2.680(5)	123	[x, y, z]
C15-H15C···O3	0.98	2.03	2.535(6)	110	[x, y, z]
C16-H16A···O7	0.99	2.35	3.308(7)	163	[x, y, z]
C17-H17A···N2	0.99	2.56	2.955(6)	104	[x, y, z]

DCC = distance between ring centroids; α = dihedral angle between planes I and J; CgI-perp = perpendicular distance of Cg(I) from ring J; CgJ-perp = perpendicular distance of Cg(J) from ring I. Zn(II) complex Cg1 = C_1-C_6; Cg2 = C_{19}-C_{24}; Cg3 = C_{41}-C_{46}.

Graphical abstract