

## Syntheses and photoluminescence properties of new Zn(II) and Cd(II) coordination polymers prepared from 5-sulfoisophthalate ligand

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**Abstract:** New coordination polymers, formulated as  $\{[\text{Zn}(\mu\text{-sipH})(\mu\text{-apim})] \cdot 3\text{H}_2\text{O}\}_n$  (**1**) and  $\{[\text{Cd}(\mu\text{-sip})(\text{H}_2\text{O})_2(\text{apimH})] \cdot 3\text{H}_2\text{O}\}_n$  (**2**) were synthesized based on the 1-(3-aminopropyl)imidazole (apim) along with 5-sulfoisophthalate (sip) ligands. The complexes were synthesized under mild hydrothermal conditions. All the complexes were characterized by elemental analysis, FT-IR spectroscopy, and single-crystal X-ray diffraction studies. The X-ray crystallographic studies of **1** and **2** reveal Zn(II) and Cd(II) ions are  $\mu$ -bridged by dianionic sipH and trianionic sip ligands in bis(monodentate) and bis(bidentate) coordination mode, respectively, to generate 1D polymer chains. In complex **1**, the adjacent chains are linked by two apim ligands to form a 1D nanotubular structure. Complex **2** is the first example of a protonated apimH ligand. In the complexes the adjacent 1D chains extend into a 3D supramolecular network by hydrogen bonds. The thermal decomposition behavior and photoluminescent property of the complexes are also discussed herein.

**Key words:** 5-Sulfoisophthalate complexes, coordination polymer, photoluminescence, thermal analysis, crystal structure

### 1. Introduction

The synthesis of new coordination polymers is attracting interest, due to their intriguing structural diversities and potential applications in gas adsorption and separation, their catalytic activities, and for sensor technology.<sup>1–5</sup> Photoluminescent Zn(II) and Cd(II) coordination polymers have recently attracted attention because of their potential as photoactive materials.<sup>6</sup> Investigations of the photoluminescent properties of coordination polymers with  $d^{10}$  metal ions reveal that their behaviors are associated with the metal ions and the organic ligands coordinated with them.<sup>7,8</sup> In addition, photoluminescent  $d^{10}$  metal complexes have much more benefits such as higher thermal stability and emitting intensity over organic ligands.<sup>9</sup> These coordination polymers can be synthesized depending on the combination of metal ions, polycarboxylate, and N-donor connecting ligands. In the synthesis of coordination polymers, conventional synthesis, solvothermal/hydrothermal, microwave-assisted, sonochemical, electrochemical, and mechanochemical methods have been applied.<sup>10</sup> Among these methods, solvothermal/hydrothermal synthesis is the most important and common tool to obtain new, highly robust, and extended coordination polymers in single crystal form.<sup>11,12</sup>

5-Sulfoisophthalic acid (sipH<sub>3</sub>) is one such interesting ligand and has two functional groups,  $-\text{SO}_3\text{H}$  and  $-\text{COOH}$ . Partly or fully deprotonated sipH<sup>2-</sup> and sip<sup>3-</sup> are useful building blocks for constructing coordination polymers and act as a versatility ligand and coordinate to metal ions as bridging ligand.<sup>13–16</sup> On the other

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hand, to obtain coordination polymers with interesting structures a useful strategy is to use flexible imidazole-containing ligands.<sup>17,18</sup> It was reported that 1-(3-aminopropyl)imidazole (apim) as a flexible bridging ligand that possesses two different types of nitrogen donor, that is imidazole and amine groups, was used to construct coordination polymers. To date, few examples are reported concerning apim ligands though corresponding studies are attractive.<sup>19–22</sup>

Keeping these facts in mind we used here 5-sulfoisophthalate, which have two carboxylate and sulfo groups, as a primary ligand and 1-(3-aminopropyl)imidazole as secondary ligand to form coordination polymers with Zn(II) and Cd(II) ions. Their structures were determined by single crystal X-ray diffraction analyses. The crystal structures of these complexes, along with the effect of the 1-(3-aminopropyl)imidazole, 5-sulfoisophthalate, and the metal ions on the structure of coordination polymers are discussed herein. In addition, the thermal analysis and luminescent property of complexes were also investigated.

## 2. Results and discussion

### 2.1. Spectral characterization

The complexes were investigated by FT-IR spectroscopy (Figure 1). The presence of water molecules in the complexes gave rise to broad absorption bands at 3406 and 3418  $\text{cm}^{-1}$ , respectively. The weak bands observed in the 3132–2963  $\text{cm}^{-1}$  region are due to aromatic and aliphatic C–H stretching vibrations. The absence of strong absorption bands around 1720  $\text{cm}^{-1}$  indicates the full deprotonation of carboxylate groups of the NasipH<sub>2</sub> ligand. The most characteristic FT-IR bands of the complexes correspond to the carboxyl group stretching vibrations. Thus,  $\nu_{asym}(\text{OCO})$  are observed at 1622 and 1568  $\text{cm}^{-1}$  for **1** and 1607 and 1553  $\text{cm}^{-1}$  for **2**, and  $\nu_{sym}(\text{OCO})$  are seen at 1356  $\text{cm}^{-1}$  for **1** and 1437  $\text{cm}^{-1}$  for **2**; FT-IR analysis of 5-sulfoisophthalic acid sodium salt was reported<sup>23</sup> By comparisons of the characteristic carboxylate stretching vibrations of the free ligands and the synthesized complexes, the characteristic carboxylate stretching vibrations have been replaced. The separation  $\Delta\nu$ , defined as  $\nu_{asym}(\text{OCO}) - \nu_{sym}(\text{OCO})$ , provides practical information on the bonding fashion of the carboxylate groups. The separation of  $\Delta\nu$  was calculated as 266  $\text{cm}^{-1}$  for **1** and 170  $\text{cm}^{-1}$  for **2**. The frequency separations between the asymmetric and symmetric carboxylate stretching vibrations of complex **1** are higher than 240  $\text{cm}^{-1}$  but those of **2** are lower, which suggests that the carboxylate groups in **1** adopt monodentate mode whereas those in **2** adopt bidentate mode to coordinate to metal centers in accordance with the single crystal structure determination of the complexes.<sup>24</sup> The bands at 1268–1128  $\text{cm}^{-1}$  are due to  $\nu(\text{S-O})$  stretching vibrations stemming from sulfonate groups.

Luminescent Zn(II) and Cd(II) complexes have been developing rapidly and attracting a lot of attention over the past few years<sup>25</sup> Owing to the luminescent properties of d<sup>10</sup> complexes, the emission spectra of complex **1** and **2** and its ligand (NasipH<sub>2</sub>) in the solid state were investigated at room temperature (Figure 2).

NasipH<sub>2</sub> shows luminescence with an emission band maximum at 323 nm upon excitation at 280 nm, which is attributed to the  $\pi^* \rightarrow n$  transition. Complexes **1** and **2** exhibit intense fluorescent emission bands at 451 nm and 431 nm upon excitation at 339 nm and 344 nm. Therefore, the emission of complexes may be attributed to ligand centered luminescence emission. A similar emission band at 439 nm for  $\{[\text{Zn}(2,3\text{-pymaH})(\text{sip})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$  (2,3-pyma = 2,3'-(Iminodimethanediyl)dipyridine),<sup>26</sup> 425 nm for  $[\text{Cd}(\text{sip})(\text{Hpip})(\text{H}_2\text{O})_2]$  (pip = piperazine),<sup>27</sup> and 437 nm for  $\{[\text{Cd}_{1.5}(\text{btrp})(\text{sip})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$  (btrp = 1,3-bis(1,2,4-triazol-1-yl)propane) have been recently observed.

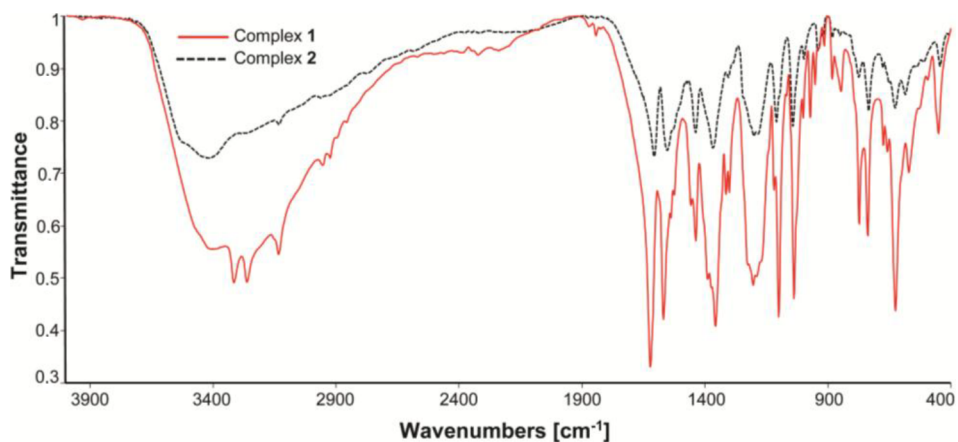


Figure 1. FT-IR spectra of 1 and 2.

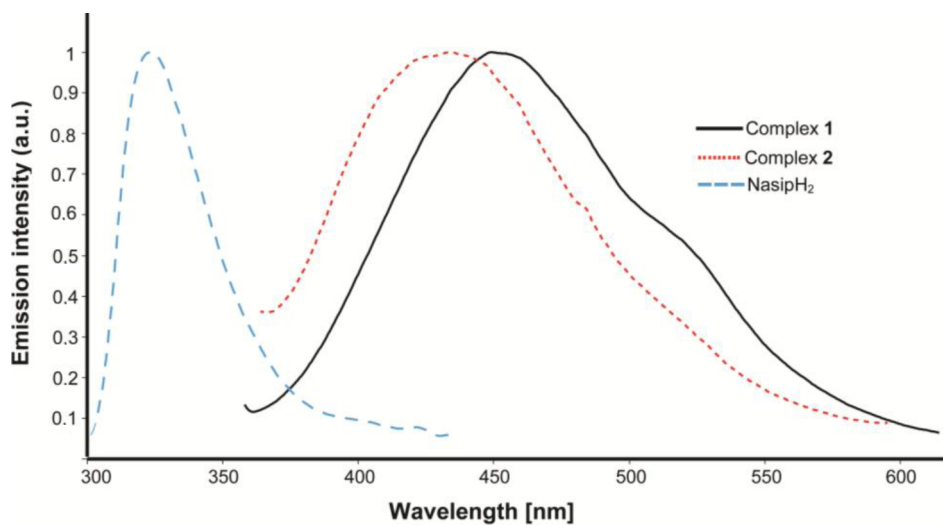


Figure 2. Solid-state emission spectra of NasipH<sub>2</sub>, 1, and 2 at room temperature.

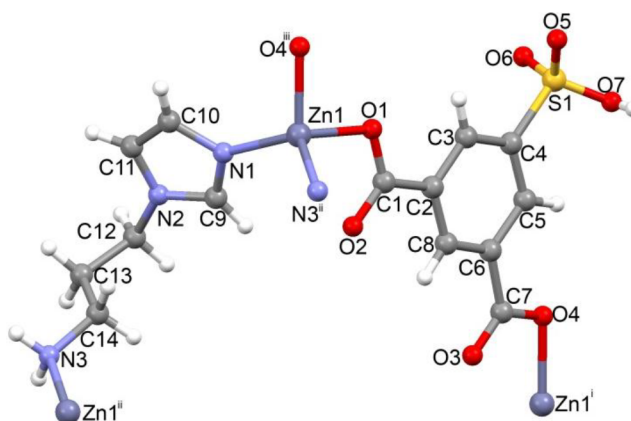


Figure 3. The molecular structure of 1 showing the atom numbering scheme. [(i)  $-x, 1-y, -z$ ; (ii)  $-1+x, y, z$ ; (iii)  $1+x, y, z$ ].

## 2.2. Crystal structures

The relevant crystal data and experimental conditions with the final parameters are summarized in Table 1. Details of these interaction distances are given in Tables 2 and 3.

**Table 1.** Crystal data and structure refinement parameters for complexes **1** and **2**.

Crystal data	<b>1</b>	<b>2</b>
Empirical formula	C <sub>14</sub> H <sub>21</sub> N <sub>3</sub> O <sub>10</sub> SZn	C <sub>14</sub> H <sub>25</sub> CdN <sub>3</sub> O <sub>12</sub> S
Formula weight	488.72	571.83
Crystal system	Monoclinic	Triclinic
Space group	P2 <sub>1</sub> /c	P-1
<i>a</i> (Å)	10.154(3)	10.072(7)
<i>b</i> (Å)	17.007(3)	10.128(8)
<i>c</i> (Å)	11.223(3)	12.637(9)
$\alpha$ (°)	90.00(2)	68.978 (2)
$\beta$ (°)	93.76(2)	81.360 (2)
$\gamma$ (°)	90.00	64.029 (2)
<i>V</i> (Å <sup>3</sup> )	1934.00	1081.84 (14)
<i>Z</i>	4	2
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.493	1.755
$\mu$ (mm <sup>-1</sup> )	1.42	1.17
$\theta$ range (°)	3.0–28.4	3.3–28.4
Measured refls.	35,074	63,555
Independent refls.	4821	5401
<i>R<sub>int</sub></i>	0.204	0.057
<i>S</i>	1.07	1.05
R1/wR2	0.120/0.335	0.035/0.082
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (eÅ <sup>-3</sup> )	2.63/–0.99	1.01/–0.51

**Table 2.** Selected bond distances (Å) and angles (°), hydrogen-bond parameters, and  $\pi \cdots \pi$  interactions distances for **1**.

Bond lengths (Å)			
Zn1—N3	2.002 (8)	Zn1—O1	2.004 (6)
Zn1—O4	2.007 (6)	Zn1—N1	2.015 (8)
Angles (°)			
N3—Zn1—O4	113.1 (3)	O4—Zn1—N1	109.7 (3)
N3—Zn1—O1	108.7 (3)	O1—Zn1—O4	95.2 (3)
N3—Zn1—N1	116.9 (3)	O1—Zn1—N1	111.2 (3)
D—H $\cdots$ A	H $\cdots$ A (Å)	D $\cdots$ A (Å)	D—H $\cdots$ A (°)
N3—H3A $\cdots$ O4	2.45	3.062	125
N3—H3B $\cdots$ O1	2.23	3.069	155
C12—H12B $\cdots$ O1	2.47	3.424	168
C10—H10 $\cdots$ O6	2.86	3.770	165
$\pi \cdots \pi$ interactions distances for complexes for <b>1</b> (Å)			
Cg(I)	Cg(J)	Cg—Cg	
Cg(5) <sup>i</sup>	Cg(5)	4.1202	
Symmetry codes: i = 2 - x, -y, 1 - z; Cg(5) = C(2)—C(3)—C(4)—C(5)—C(6)—C(8)			

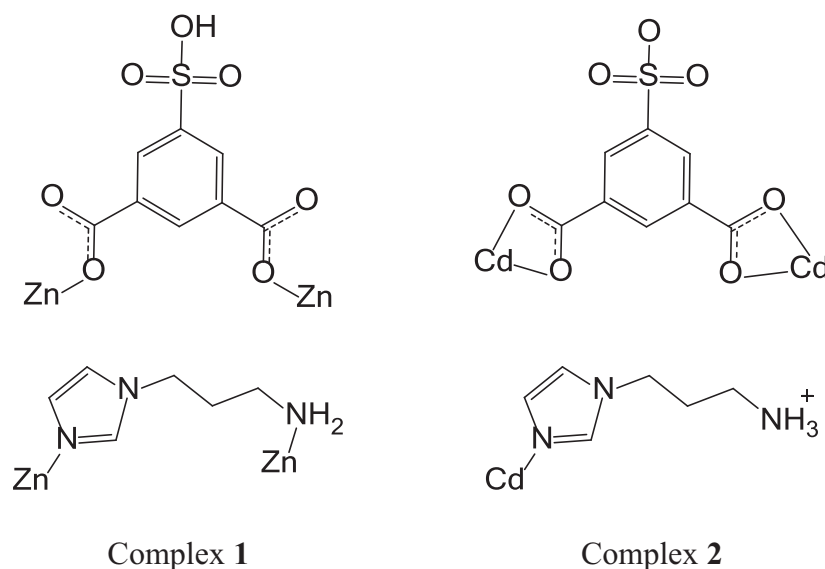
**Table 3.** Selected bond distances (Å) and angles (°), hydrogen-bond parameters, and  $\pi \cdots \pi$  interactions distances for **2**.

Bond lengths (Å)			
O4—Cd1 <sup>i</sup>	2.433 (2)	O8—Cd1	2.348 (3)
O3—Cd1 <sup>i</sup>	2.418 (2)	O9—Cd1	2.331 (3)
O1—Cd1	2.277 (2)	N1—Cd1	2.244 (2)
Angles (°)			
O3 <sup>ii</sup> —Cd1—O4 <sup>ii</sup>	53.72 (6)	O8—Cd1—O3 <sup>ii</sup>	97.57 (9)
O1—Cd1—O4 <sup>ii</sup>	80.00 (7)	O9—Cd1—O4 <sup>ii</sup>	84.72 (9)
O1—Cd1—O3 <sup>ii</sup>	132.59 (7)	O9—Cd1—O3 <sup>ii</sup>	83.11 (9)
O1—Cd1—O8	92.15 (9)	O9—Cd1—O8	173.82 (9)
O1—Cd1—O9	82.96 (9)	N1—Cd1—O4 <sup>ii</sup>	141.09 (8)
O8—Cd1—O4 <sup>ii</sup>	90.72 (9)	N1—Cd1—O1	138.91 (8)
N1—Cd1—O3 <sup>ii</sup>	87.88 (8)	N1—Cd1—O8	88.24 (9)
N1—Cd1—O9	97.93 (10)		
D—H $\cdots$ A	H $\cdots$ A (Å)	D $\cdots$ A (Å)	D—H $\cdots$ A (°)
N3—H3A $\cdots$ O12	1.90(3)	2.765(5)	163(2)
N3—H3B $\cdots$ O8	2.41(3)	3.262(3)	161(2)
N3—H3C $\cdots$ O11	2.47(3)	3.2131(3)	141(2)
N3—H3C $\cdots$ O9	2.55(3)	3.2771(3)	139(2)
O8—H8B $\cdots$ O10	1.91(4)	2.7152(2)	167(2)
O8—H8A $\cdots$ O4 <sup>i</sup>	1.88(4)	2.750(3)	178(2)
O12—H12C $\cdots$ O0AA <sup>ii</sup>	1.96(3)	2.798(4)	167(2)
O12—H12D $\cdots$ O5 <sup>iii</sup>	2.04(3)	2.864(4)	164(2)
O11—H11A $\cdots$ O7 <sup>iv</sup>	2.09(3)	2.889(5)	156 (4)
O11—H11B $\cdots$ O2 <sup>v</sup>	1.87(3)	2.720(3)	172(4)
O9—H9A $\cdots$ O11	1.99(4)	2.751(4)	173(4)
O9—H9B $\cdots$ O3 <sup>v</sup>	1.89(5)	2.701(3)	162(4)
O10—H10A $\cdots$ O5 <sup>vi</sup>	2.02(7)	2.786(5)	173(7)
O10—H10B $\cdots$ O7	2.10(6)	2.797(5)	167(7)
C9—H9 $\cdots$ O0AA	2.55(3)	3.3582(3)	152(3)
$\pi \cdots \pi$ interactions distances for complexes for <b>2</b> (Å)			
Cg(I)	Cg(J)	Cg-Cg	
Cg1(vii)	Cg2	4.1672(3)	
Cg2(iii)	Cg2	3.5992(3)	
Symmetry codes: (i) x, y + 1, z; (ii) x, y - 1, z (iii) -x + 2, -y + 1, -z + 1; (iv) x - 1, y, z - 1; (v) -x + 1, -y, -z + 1; (vi) x - 1, y, z; (vii) -x + 1, -y + 1, -z + 1; (viii) -x + 2, -y + 1, -z + 2; Cg1 = N1—C9—N2—C11—C10; Cg2 = C2—C3—C4—C5—C6—C8.			

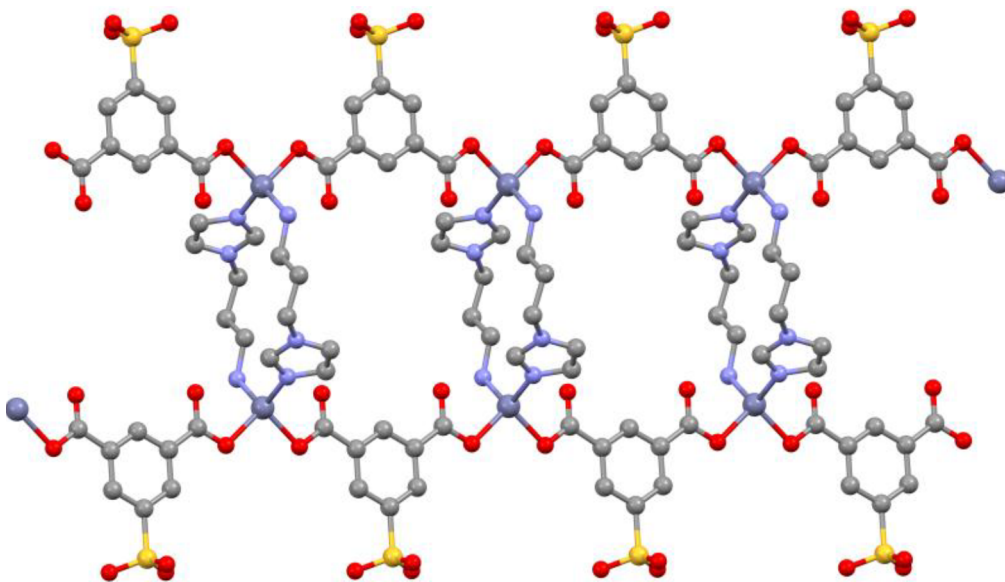
**2.2.1. {[Zn( $\mu$ -sipH)( $\mu$ -apim)] $\cdot$ 3H<sub>2</sub>O} <sub>n</sub> (**1**)**

The X-ray crystal structure analysis revealed that the complex crystallizes in the monoclinic system, P2<sub>1</sub>/c space group. The asymmetric unit of {[Zn( $\mu$ -sipH)( $\mu$ -apim)] $\cdot$ 3H<sub>2</sub>O} <sub>n</sub> (**1**) consists of a Zn(II) ion, one sipH ligand, and one apim ligand (Figure 3). The Zn(II) ion is located on a symmetry center and is coordinated by two oxygen atoms [O1 and O4<sup>i</sup>] from two sipH ligands and two nitrogen atoms [N1 and N3<sup>ii</sup>] from two apim ligands[(i) = -1 + x, y, z; (ii) = 1 - x, -y, -z](Scheme). The coordination geometry around the Zn(II) ion can be described as a slightly distorted tetrahedral. The average Zn–N bond length is 2.008 Å, the Zn–O bond length is 2.005 Å, and the bond angles around Zn(II) fall in the range of 95.2 (3)–116.9 (3)° (Table 3).

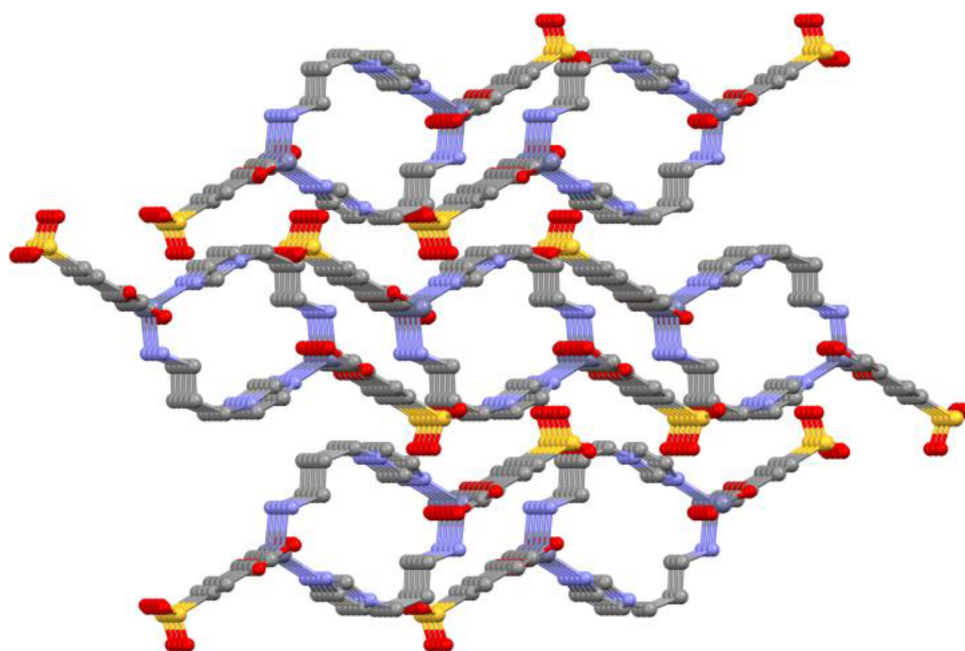
With the coordination of sip ligand by Zn(II) ions the electron density on the benzene ring of the sip ligand decreases. For this reason, the acidic feature of the sip ligand reduces and the sip ligand is protonated. The Zn(II) ions are  $\mu$ -bridged by sipH ligands with carboxylate oxygens to generate the 1D polymer chain structure of **1** (Figure 4). The adjacent Zn(II) ions are linked by two apim ligands to form the 1D nanotubular structure of **1**. The Zn1  $\cdots$  Zn1<sup>ii</sup> separation is 7.454 Å, similar to those found in [Zn(SCN)<sub>2</sub>(apim)<sub>2</sub>]<sub>n</sub> (Å)<sup>22</sup> and {[Cu(apim)<sub>2</sub>(H<sub>2</sub>O)]·(ClO<sub>4</sub>)<sub>2</sub>·CH<sub>3</sub>CN}<sub>n</sub>.<sup>19</sup> Moreover, the 1D nanotubular structures are connected together through C–H $\cdots$ O, N–H $\cdots$ O hydrogen bonds and  $\pi$  $\cdots$  $\pi$  interactions to form a 3D supramolecular structure (Figure 5).



**Scheme.** Coordination modes for the sip and apim ligands in **1** and **2**.



**Figure 4.** 1D chain structure with tubular cavities in **1**.

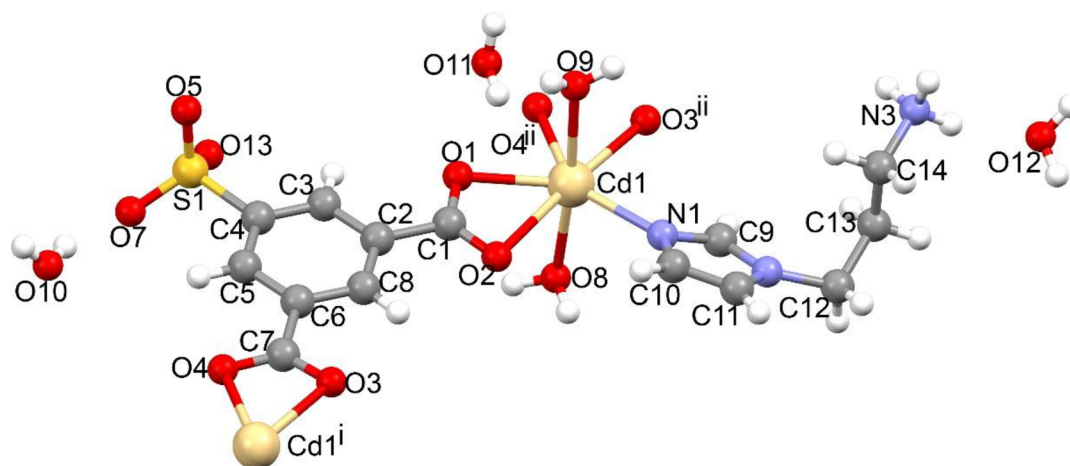


**Figure 5.** A view of 3D supramolecular structure with tubular channels of **1**.

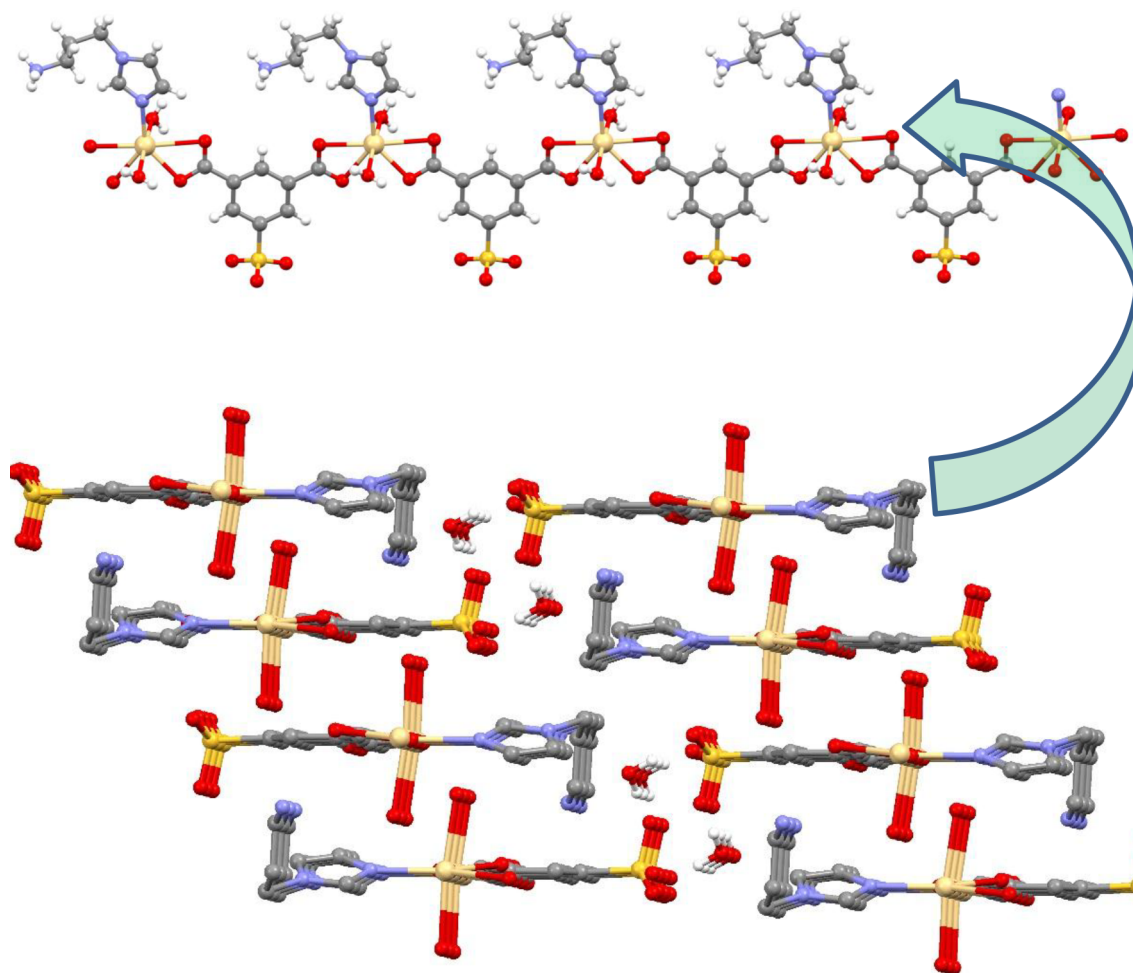
### 2.2.2. $\{[\text{Cd}(\mu\text{-sip})(\text{H}_2\text{O})_2(\text{apimH})] \cdot 3\text{H}_2\text{O}\}_n$ (**2**)

The X-ray crystallographic analysis shows that **2** crystallizes in the triclinic space group P-1 and has an infinite 1D structure. As shown in Figure 6, a crystallographically independent Cd(II) ion is surrounded by a distorted pentagonal bipyramidal geometry with four oxygen atoms [O1, O2, O3<sup>i</sup>, and O4<sup>i</sup>] from two different sip ligands, one nitrogen [N1] atom from apim ligands, and two oxygens [O8 and O9] from aqua ligands [(i) = x, -1 + y, z] (Scheme). Coordination polymers containing seven-coordinated Cd(II) are rarely seen in the literature.<sup>28–31</sup> The average Cd–O bond length is 2.361 Å, the Cd–N bond length is 2.244 (2) Å, and the bond angles around Cd(II) fall in the range of 53.72 (3)–173.82 (9)° (Table 3). The equatorial plane of the pentagonal bipyramidal geometry is provided by one nitrogen atom from apim and four oxygen atoms from two different sip ligands. The axial position is occupied by two oxygen atoms from aqua ligands. The sip ligand is coordinated to two Cd(II) ions in a bis(bidentate) mode with its four oxygen atoms of the carboxylate groups to form a 1D coordination polymer chain. The Cd1 ⋯ Cd1<sup>ii</sup> separation is 5.803 Å [(ii) = 1 - x, -y, 1 - z]. The crystal structure of **2** showed the apim ligand charged to apimH by proton transfer from the carboxylic acid group of the NasipH<sub>2</sub> during the complexation reaction. The structural properties of metal complexes having protonated cation ligands have rarely been reported.<sup>32,33</sup> This work is the first example of a sip coordination polymer having a protonated 1-(3-aminopropyl)imidazolium (apimH) ligand that is coordinated Cd(II) ion in a monodentate manner.

The crystal packing of the complex is a composite of  $\pi \cdots \pi$  and hydrogen bonding interactions. The adjacent 1D chains extend into a 3D supramolecular network by N–H⋯O and O–H⋯O hydrogen bonds (Figures 7 and 8a). Furthermore, there are interchain  $\pi \cdots \pi$  interactions between aromatic rings of two sip ligands. Sulfate groups attract attention for their interaction with water owing to its high charge density<sup>34</sup> In **2**, the adjacent chains interact with each other through water–sulfate bridges by strong hydrogen bonds to form a 2D layer [O10–H10A⋯O5<sup>vi</sup> = 1.96(3), O10–H10B⋯O7 = 2.04(3), O12–H12C⋯O0AA<sup>ii</sup> = 2.02(7)



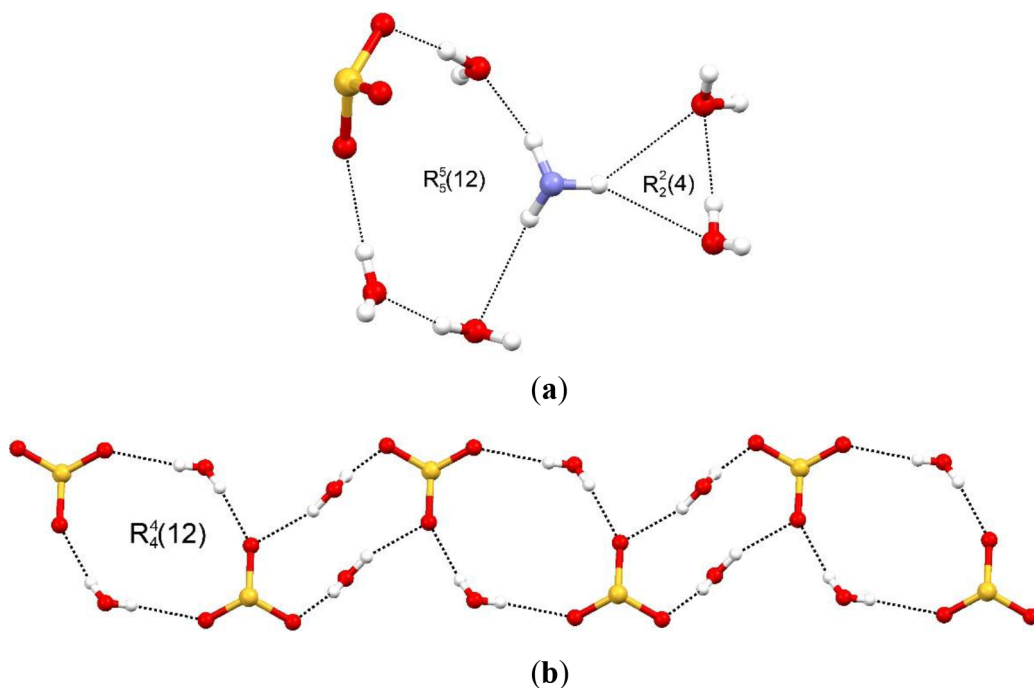
**Figure 6.** The molecular structure of **2** showing the atom numbering scheme. [(i)  $-x, 1-y, -z$ ; (ii)  $-1+x, y, z$ ; (iii)  $1+x, y, z$ ].



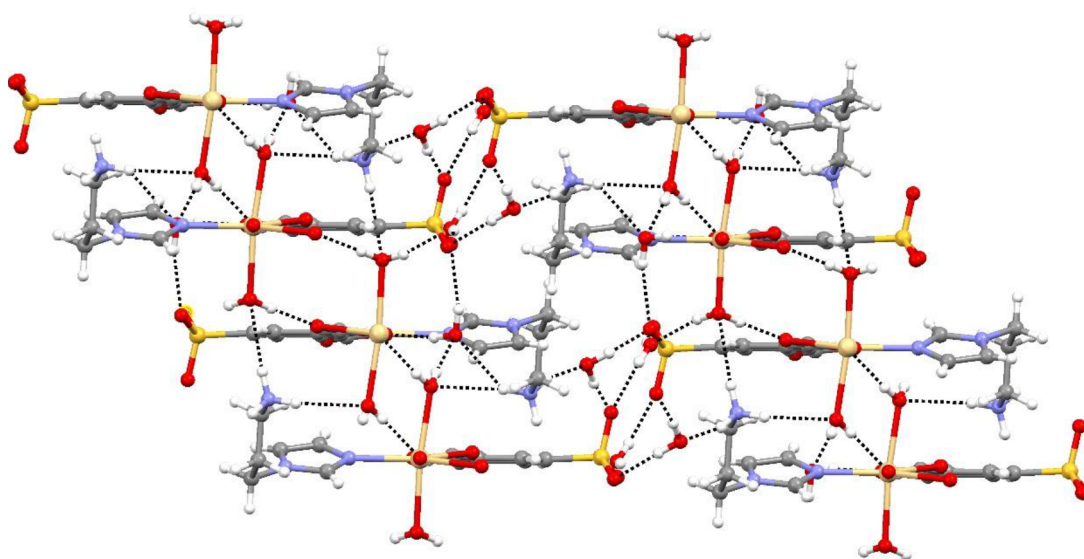
**Figure 7.** A view of 1D structure of **2**.



and  $O12-H12D \cdots O5^{iii} = 2.10(6)$ ; (ii)  $x, y - 1, z$  (iii)  $-x + 2, -y + 1, -z + 1$ ; (iv)  $x - 1, y, z - 1$ ] (Figures 8a and 8b). The 2D layers are connected together by apimH cations through  $N-H \cdots O$  interactions [ $N3-H3A \cdots O12 = 1.90(3)$ ,  $N3-H3B \cdots O8 = 2.41(3)$ ,  $N3-H3C \cdots O11 = 2.47(3)$ , and  $N3-H3C \cdots O9 = 2.55(3)$ ] resulting in the 3D supramolecular network (Figure 9). Furthermore, there are also  $C-H \cdots O$  and  $\pi \cdots \pi$  interactions between both imidazole ring (Cg1) and sip ligand (Cg2), and benzene rings of sip ligands (Cg1) [(Cg1 =  $N1-C9-N2-C11-C10$  and Cg2 =  $C2-C3-C4-C5-C6-C8$ ; Cg1<sup>vii</sup>  $\cdots$  Cg2 =  $4.1672(3)$ ; Cg2<sup>iii</sup>  $\cdots$  Cg2 =  $3.5992(3)$ ], resulting in a 3D supramolecular network (Figure 9).



**Figure 8.** Hydrogen bonding motifs in **2** showing the ring patterns (a)  $R_2^2(4)$ ,  $R_5^5(12)$  and (b)  $R_4^4(12)$ .



**Figure 9.** A view of the hydrogen bonded 2D network of **2**.

### 2.3. Thermal analysis

The synthesized complexes are stable in ambient conditions, and thermogravimetric experiments (TG, DTG, and DTA) were performed to examine their thermal stability. The thermal decomposition of complex **1** occurs in three stages (Figure 10). The first stage between 122 °C and 214 °C for **1** corresponds to the endothermic elimination of three water molecules with an experimental mass loss of 10.36% (calcd. mass loss 11.03%,  $DTG_{max} = 182.58$  °C). There is no weight loss between 214 and 311 °C. The second stage between 311 and 448 °C is related to the elimination of one apim ligand ( $DTG_{max} = 396.92$  °C, found 25.39%, calcd. 25.61%). The last stage between 448 and 574 °C is related to the decomposition of sip ligand with exothermic effect ( $DTG_{max} = 544.83$  °C, found 39.84%, calcd. 38.50%). The total mass loss at 574 °C is 75.59% (calc. 75.14%), which is consistent with the ZnO and ZnSO<sub>4</sub> mixture as the end product for **1**<sup>35,36</sup>. The thermal decomposition of complex **2** occurs in two stages (Figure 11). The weight loss in the temperature range 30–126 °C corresponds to the loss of five water molecules ( $DTG_{max} = 74.49$  °C, weight loss of 17.92%, calcd. 15.75%). There is no weight loss between 126 and 270 °C. The weight loss of 59.53% in the region of 270–583 °C corresponds to the elimination of one apimH and one sip for **2** (calculated: 61.79% and  $DTG_{max} = 364.22$  and  $572.73$  °C for **2**). The total mass loss at 583 °C is 77.45% (calc. 77.54%), which is consistent with CdO as the end product for **2**.

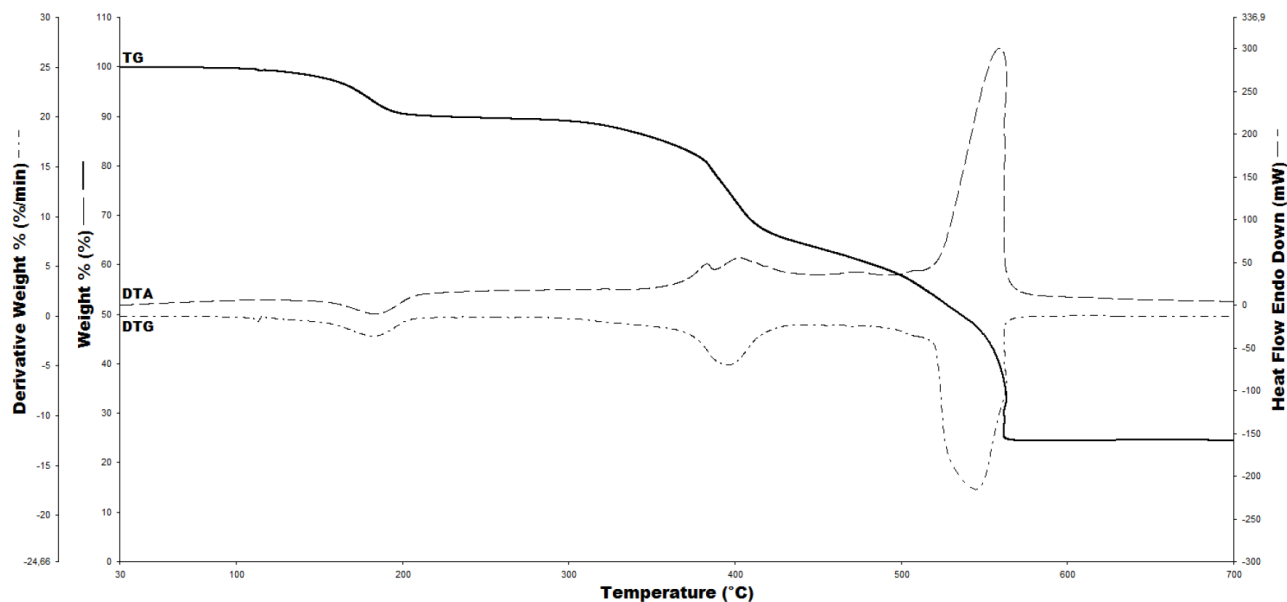


Figure 10. TG, DTG, and DTA curves of complex **1**.

In conclusion, two new coordination polymers were hydrothermally synthesized by utilizing the 1-(3-aminopropyl)imidazole (apim) and 5-sulfoisophthalate (sip) ligands. The complexes were characterized by elemental analysis, FT-IR spectroscopy, photoluminescent spectroscopy, and thermal analysis. Their structures were determined by single crystal X-ray diffraction technique. In **1**, the coordination geometry around the Zn(II) ion can be described as a distorted tetrahedral, while in **2**, the seven-coordinated Cd(II) ion can be defined as a distorted pentagonal bipyramidal. The Zn(II) centers are linked by sipH ligands to form the 1D polymer chain structure of **1**. The adjacent Zn(II) ions are connected by two apim ligands to form the 1D nanotubular structure of **1**. The Cd(II) ions are bridged by sip ligands to generate 1D coordination polymer in

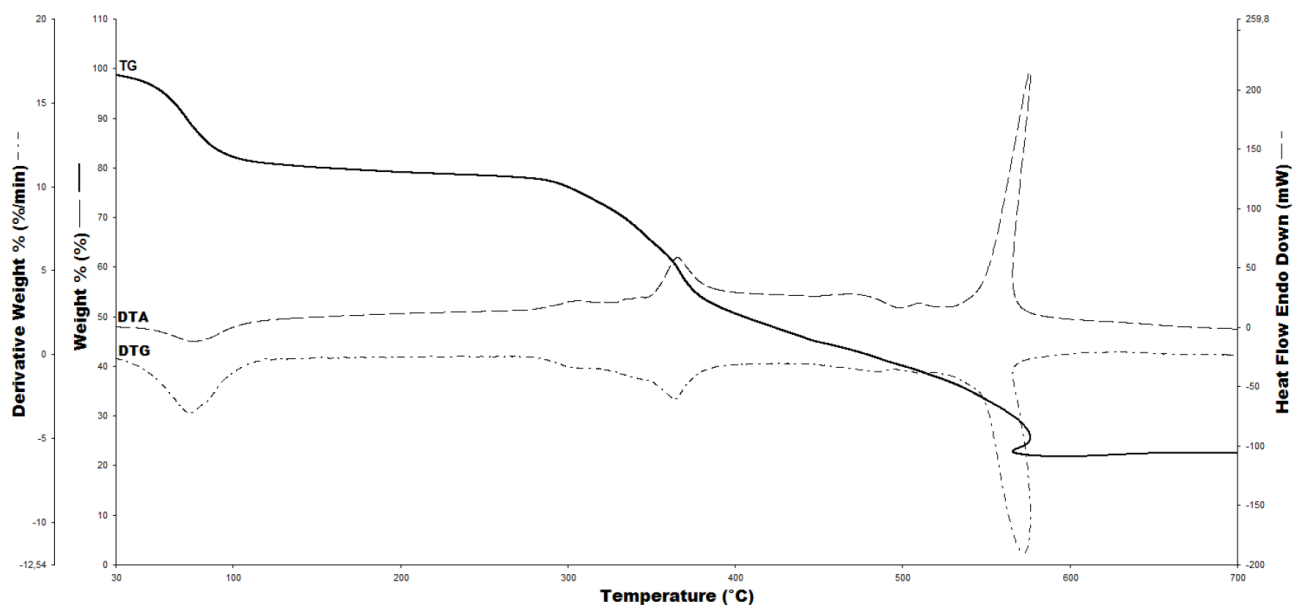


Figure 11. TG, DTG, and DTA curves of complex **2**.

**2**. Rarely observed water–sulfate bridges play an important role in the supramolecular structure of **2**. In the complex **2**, the  $\text{NH}_2^-$  group of apim ligand is protonated because it is not coordinated to the Cd(II) center; when it comes to complex **1** the  $\text{NH}_2^-$  group of apim ligand is coordinated by Zn(II) and therefore the free  $\text{SO}_3^-$  group of sipa ligand is protonated. Moreover, complex **2** is the first example of a sip coordination polymer having protonated 1-(3-aminopropyl)imidazolium (apimH) ligands.

### 3. Experimental

#### 3.1. Synthesis of complexes

##### 3.1.1. $\{[\text{Zn}(\mu\text{-sipH})(\mu\text{-apim})] \cdot 3\text{H}_2\text{O}\}_n$ (**1**)

A mixture of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (0.20 g; 0.91 mmol),  $\text{NasipH}_2$  (0.25 g, 0.93 mmol), apim (0.35 g; 2.80 mmol), ethanol (10 mL), and water (20 mL) was stirred at 50 °C for half an hour. Then the mixture was sealed in a 50-mL Schott Duran brand glass bottle with a PBT screw cap and heated at 100 °C for 2 days; then it was cooled to room temperature at the rate of 10 °C/h. Pale yellow crystals of **1** were obtained (yield: 0.25 g, 57% based on  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ). Anal. Calcd for  $\text{C}_{14}\text{H}_{21}\text{N}_3\text{O}_{10}\text{SZn}$ : C, 34.40; H, 4.33; N, 8.60%. Found: C, 33.43; H, 4.21; N, 9.03%. IR data (KBr,  $\text{cm}^{-1}$ ): 3406m, 3315s, 3261s, 3132m, 1622vs, 1568s, 1437w, 1356vs, 1203s, 1099s, 1038s, 771m, 737m, 625s.

##### 3.1.2. $\{[\text{Cd}(\mu\text{-sip})(\text{H}_2\text{O})_2(\text{apimH})] \cdot 3\text{H}_2\text{O}\}_n$ (**2**)

A mixture of  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (0.25 g; 0.94 mmol),  $\text{NasipH}_2$  (0.25 g, 0.93 mmol), apim (0.24 g; 1.92 mmol), ethanol (10 mL), and water (20 mL) was stirred at 50 °C for half an hour. Then the mixture was sealed in a 50-mL Schott Duran brand glass bottle with a PBT screw cap and heated at 100 °C for 2 days; then it was cooled to room temperature at the rate of 10 °C/h. Colorless crystals of **2** were obtained (yield: 0.25 g, 57% based on  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ). Anal. Calcd for  $\text{C}_{14}\text{H}_{25}\text{CdN}_3\text{O}_{12}\text{S}$ : C, 29.41; H, 4.41; N, 7.35%. Found: C,

30.27; H, 4.66; N, 7.43%. IR data (KBr,  $\text{cm}^{-1}$ ):  $\nu$  3418m, 3265s, 3130m, 2963w, 1607vs, 1553s, 1437w, 1367vs, 1202s, 1109m, 1042s, 773w, 733m, 627m.

### 3.2. Materials and measurements

All chemicals were commercially available and used without further purification. Elemental analyses (C, H, and N) were performed on a PerkinElmer 2400C Elemental Analyzer. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer using KBr pellets in the range of 400–4000  $\text{cm}^{-1}$ . Thermal analyses (TG, DTG, and DTA) were carried out with a PerkinElmer Diamond TG/DTA Thermal Analyzer in static air atmosphere with a heating rate of 10  $^{\circ}\text{C}/\text{min}$  in the temperature range of 30–700  $^{\circ}\text{C}$ . The photoluminescence (excitation and emission) spectrum for the solid complexes sample was determined with a PerkinElmer LS-55 Fluorescence spectrometer.

### 3.3. Crystallographic analyses

Suitable crystals of **1** and **2** were selected for data collections, which were performed on a Bruker D8-QUEST diffractometer equipped with graphite-monochromatic Mo- $K\alpha$  radiation at 296 K. The structures were solved by direct methods using the programs OLEX2<sup>37</sup> and SHELXS-97<sup>38</sup> with anisotropic thermal parameters for all nonhydrogen atoms. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares methods in SHELXL-97.<sup>38</sup> In complex **1**, a reasonable structural method could not be found for determination of three noncoordinating water molecules and so the data were corrected by applying the “solvent mask” in OLEX2<sup>37</sup>. Molecular drawings were obtained using MERCURY.<sup>39</sup>

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**Appendix A. Supplementary data**

CCDC 1463769 and 1463768 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).