



Different geometrical arrangements in carboxylate coordination polymers of flexible dicarboxylic acid

Himangshu Deka^a, Rupam Sarma^a, Satchi Kumari^b, Alike Khare^b, Jubaraj B. Baruah^{a,*}

^a Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781 039, Assam, India

^b Department of Physics, Indian Institute of Technology Guwahati, Guwahati 781 039, Assam, India

ARTICLE INFO

Article history:

Received 25 November 2010

Received in revised form

19 April 2011

Accepted 1 May 2011

Available online 14 May 2011

Keywords:

Coordination polymers

Flexible carboxylic acids

Structural study

Self-assembly

Fluorescence

Nonlinear optics

ABSTRACT

Dicarboxylate coordination polymers (**1–5**) of Mn(II), Ni(II), Cu(II), Zn(II) and Cd(II), respectively, derived from (7-carboxymethoxy-naphthalen-2-yloxy)-acetic acid (**L₁H₂**) are synthesized and characterized. Depending on the coordination sites around the metal centers and coordination mode of the ligand, dimensionality of these polymers varies. The dicarboxylates adopt three spatial orientations: in-plane linear coordination, out-of-plane *cis* coordination and out-of-plane *trans* coordination mode. Both the *cis* and *trans* out-of-plane coordination modes are found to exist only if the ancillary ligand pyridine is coordinated to the metal ion. When the aquoligand coordinates the in-plane linear coordination mode of **L₁** predominates. The coordination polymers **4** and **5** show photoluminescence in solution. The dicarboxylate of (5-carboxymethoxy-naphthalen-1-yloxy)-acetic acid (**L₂H₂**) does not form coordination polymer under ambient conditions, but prefers to remain as uncoordinated anion providing hydrophobic confinement to hexa-aquametal(II) cation. Compound **3** crystallizes in *P*2₁ space group and it shows broadband ultra-violet fluorescence centered at 352.9 nm on focusing 632.8 nm He:Ne laser.

© 2011 Elsevier Inc. All rights reserved.

1. Introduction

Coordination polymers [1–8] are extensively studied in the recent years for gas storage, [9–12] sensing, [13] molecular recognition, [14] molecular magnetism, [15–17] catalysis [18–19] and as nonlinear optical material [20]. Carboxylate coordination polymers, in this respect, are of special interest for their diverse structural features [21–30]. Carboxylate ligands possess several binding modes in different metal carboxylate complexes [31–35]. Metal complex/coordination polymers with flexible carboxylate arm such as malonate and other carboxylate ligands are also studied with great interest to understand their structures under variety of conditions [36–42]. However, there are the scopes for much work in this area to understand the control over structural topology as the reaction condition and complexity arising from supramolecular features that are associated with directional properties can guide such structures. Much research has been carried out using hydrothermal conditions [43] and we here demonstrate how room temperature reactions can lead to coordination polymers and their structure vary with the metal ions, the coordinating mode of anionic ligand and the ancillary ligands. We show here three types of geometries adopted by the di-anion of (7-carboxymethoxy-naphthalen-2-yloxy)-acetic acid (**L₁**)

with different transition metal ions (Fig. 1). These three different geometrical patterns arise from orientation of the dicarboxylate groups of the flexible arms of the carboxylate ligand (**L₁**). These orientations lead to cyclic or open chain polymeric structures with metal ions.

2. Experimental section

The ligands (7-carboxymethoxy-naphthalen-2-yloxy)-acetic acid **L₁H₂** and (5-carboxymethoxy-naphthalen-1-yloxy)-acetic acid **L₂H₂** were prepared as described earlier [44]. The X-ray structure of each coordination polymer is determined; corresponding CIF files were used to simulate the powder X-ray pattern and the experimentally determined X-ray powder pattern are compared with these (supplementary materials). The fluorescence spectra were measured from solutions of coordination polymer (10^{-4} M in desired solvent) followed by excitation at 260 nm.

2.1. Synthesis of complex $[MnL_1(H_2O)_3]_n$ **1**

The ligand (7-carboxymethoxy-naphthalen-2-yloxy)-acetic acid (0.028 g, 0.1 mmol) along with NaOH (0.008 g, 0.2 mmol) was dissolved in water (20 mL). To this solution $MnCl_2 \cdot 4H_2O$ (0.0197 g, 0.1 mmol) was added with constant stirring at room temperature. Precipitation occurred in the reaction mixture.

* Corresponding author.

E-mail address: juba@iitg.ernet.in (J.B. Baruah).

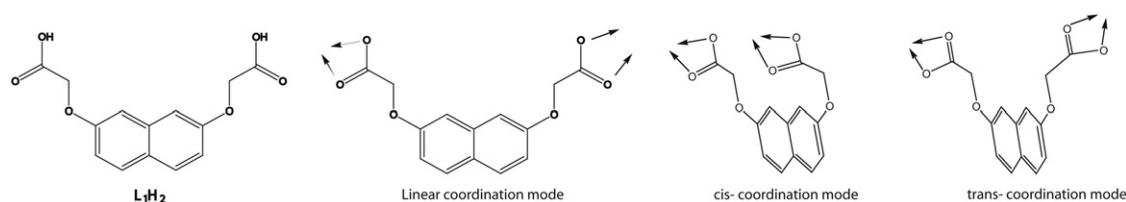


Fig. 1. Structure of L_1H_2 and possible coordination modes of the ligand L_1 .

The precipitate was dissolved in pyridine (10 mL). A small amount of dimethylformamide (3 mL) was added. The reaction mixture was stirred for half an hour. The resulting solution was filtered to discard any insoluble material and the filtrate was kept for crystallization. After 6 days diffraction quality crystals were collected and dried in air. Yield of the pure crystalline complex 60% (with respect to Mn). IR (KBr, cm^{-1}): 3478 (w), 3390 (w), 1608 (w), 1568 (s), 1515 (w), 1474 (w), 1427 (m), 1385 (m), 1331 (w), 1323 (w), 1253 (w), 1212 (s), 1171 (m), 1062 (w), 1052 (w), 844 (m) and 834 (m). Thermogravimetry: weight loss 80–140 °C 13.2% (calcd. 12.5% for loss of three water molecules); residue due to formation of MnO_2 at 575 °C (calcd. 22.7%, experimental 23.63%).

2.2. Synthesis of complex $[Ni(L_1)(Py)_3(H_2O)] \cdot H_2O$ **2**

Complex **2** was synthesized in a similar procedure as in **1** but with $NiCl_2 \cdot 6H_2O$ (0.0237 g, 0.1 mmol) as the metal source. Green colored diffraction quality crystals were collected after a week and dried in air. Yield of the pure crystalline complex 84% (with respect to Ni). IR (KBr, cm^{-1}): 3477 (w), 1614 (s), 1514 (w), 1461 (w), 1434 (w), 1381 (w), 1328 (w), 1210 (s), 1177 (m), 1062 (s), 846(s) and 713(m). Thermogravimetry: 55.98% weight loss 90–325 °C (calcd. 58.62% for loss of three pyridines along with two water molecules); residue due to formation of NiO at 450 °C (calcd. 12.24%, experimental 11.34%).

2.3. Synthesis of complex $[CuL_1(H_2O)(Py)_2]_n$ **3**

Complex **3** was synthesized in a similar procedure as in **1** but with $CuCl_2 \cdot 2H_2O$ (0.017 g, 0.1 mmol) at room temperature. After 1 week blue colored needle shaped crystals were collected and dried in air. Yield of the pure crystalline complex: 67% (with respect to Cu). IR (KBr, cm^{-1}): 3387 (w), 1629 (s), 1604 (s), 1511 (w), 1447 (w), 1408 (m), 1266 (m), 1203 (s), 1165 (w), 1054 (w), 832 (w), 764 (w) and 699 (m). Thermogravimetry: 30.0% weight loss 125–190 °C (calcd. 33.65% for loss of two pyridines along with a water molecule); residue due to formation of CuO at 500 °C (calcd. 15.5%, experimental 16.0%).

2.4. Synthesis of complex $[ZnL_1(H_2O)_2]_n$ **4**

Complex **4** was synthesized in a similar procedure as in **1** but with $ZnCl_2$ (0.0136 g, 0.1 mmol) as the metal source. Colorless crystals were collected a week after and dried in air. Yield of the pure crystalline complex 85% (with respect to zinc). IR (KBr, cm^{-1}): 3477(w), 1614(s), 1514(w), 1461(w), 1434(w), 1381(w), 1328(w), 1210(s), 1177(m), 1062(s), 846(s) and 713(m). 1H NMR (400MHz, DMSO- d_6 , ppm): 4.539 (s, 4H, $-CH_2-$), 6.97(d, 2H, aromatic, $^3J=8.8$ Hz), 7.06(s, 2H, aromatic), 7.70 (d, 2H, aromatic, $^3J=8.8$ Hz). Thermogravimetry: 8.9% weight loss 35–110 °C (calcd. 8.5% for loss of two water molecules); residue at 525 °C for $Zn(O_2CCH_3)_2$ (calcd. 48.45%, experimental 42.85%).

2.5. Synthesis of the complex $[CdL_1(H_2O)_3] \cdot H_2O$ **5**

Complex **5** was synthesized in a similar procedure as in **1** but with $CdCl_2 \cdot H_2O$ (0.02 g, 0.1 mmol) as the metal source. Colorless crystals were collected after 1 week. Yield of the pure crystalline complex: 55% (with respect to Cd). IR (KBr, cm^{-1}): 3463 (bw), 1614 (s), 1518(w), 1476 (w), 1422 (w), 1391 (w), 1339 (w), 1252 (w), 1213 (s), 1174 (w), 1052 (w), 841 (m), 709(w). 1HNMR (400 MHz, DMSO- d_6 , ppm): 4.49 (s, 4H, $-CH_2-$), 6.94 (m, 4H, aromatic), 7.64 (d, 2H, aromatic, $^3J=9.2$ Hz). Thermogravimetry: 14.58% weight loss 75–110 °C (calcd. 14.07% for loss of four water molecules); residue at 525 °C for $CdCO_3$ (calcd. 45.83%, experimental 47.92%).

2.6. Synthesis of complex $[Cd(H_2O)_6] \cdot L_2 \cdot (H_2O)_2$ **6**

Complex **6** was synthesized in a similar procedure as in **5** but using (5-carboxymethoxy-naphthalen-1-yloxy)-acetic acid as ligand. Yield of the pure crystalline complex 71% (with respect to Cd). IR (KBr, cm^{-1}): 3444 (bs), 1596 (s), 1574 (s), 1435 (w), 1412 (s), 1337 (m), 1271 (s), 1088 (w), 1069 (w), 788 (w). Thermogravimetry: residue 31.25% at 550 °C from continuous weight loss in the temperature range 225–550 °C (calcd. 31.27% for formation of $CdCO_3$).

3. X-ray crystallography

The X-ray crystallographic data were collected at 296 K with $MoK\alpha$ radiation ($\lambda=0.71073$ Å) using a Bruker Nonius SMART CCD diffractometer equipped with graphite monochromator. The SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software [45].

All the non-H atoms were refined in the anisotropic approximation against F^2 of all reflections. The H atoms attached to O and crystallized water molecule were located from the difference Fourier synthesis map and refined with isotropic displacement coefficients. It was necessary to apply restraints to optimize the distances of some hydrogen atoms of water molecules. Crystal parameters and details of the final refinement parameters are shown in Table 1.

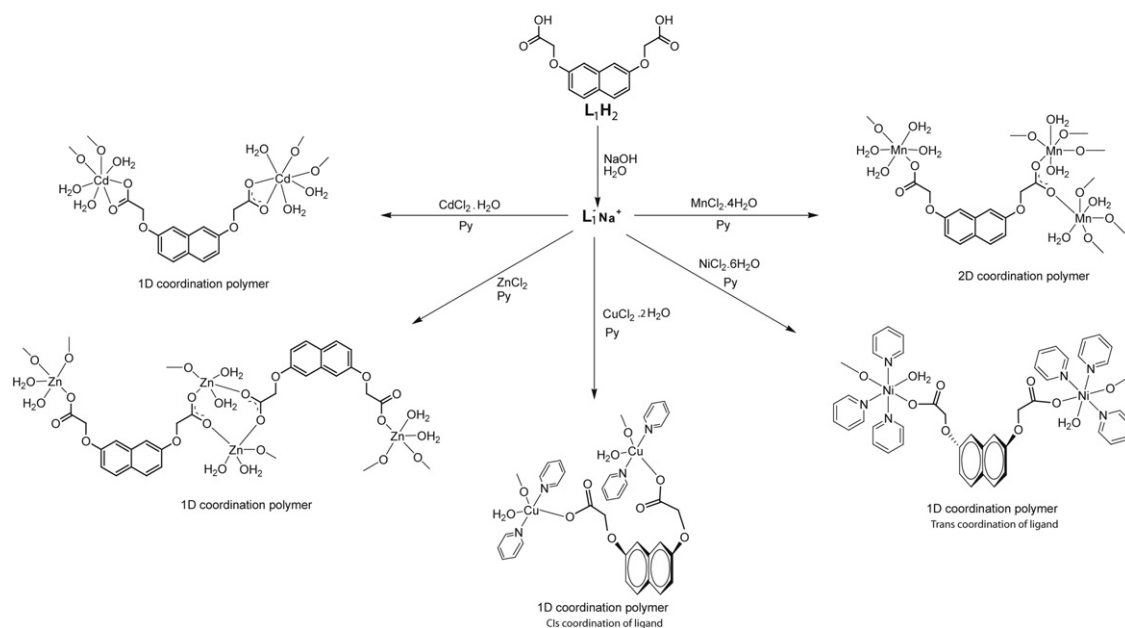
4. Results and discussion

The reactions of (7-carboxymethoxy-naphthalen-2-yloxy)-acetic acid in the presence of sodium hydroxide with transition metal salts of manganese(II), nickel(II), copper(II), zinc(II) and cadmium(II) lead to coordination polymers with varying compositions as well as dimensionalities. The reactions carried out are shown in Scheme 1.

Stoichiometric amount of $MnCl_2 \cdot 4H_2O$, L_1H_2 and NaOH in water react to form a two dimensional coordination polymer **1**

Table 1
Crystallographic parameters of complexes 1–6.

Compound no.	1	2	3	4	5	6
Formulae	C ₁₄ H ₁₆ Mn O ₉	C ₂₉ H ₂₇ N ₃ Ni O ₈	C ₂₄ H ₂₂ Cu N ₂ O ₇	C ₁₄ H ₁₄ O ₈ Zn	C ₁₄ H ₁₄ Cd O ₁₀	C ₁₄ H ₂₆ Cd O ₁₄
Formula wt.	383.21	604.25	513.98	375.62	454.65	530.75
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> –1	<i>P</i> –1	<i>P</i> ₂ ₁	<i>P</i> –1	<i>P</i> –1	<i>P</i> –1
<i>a</i> (Å)	4.7577(2)	9.0066(8)	13.3081(14)	7.3001(4)	6.8256(6)	6.3129(4)
<i>b</i> (Å)	5.8248(3)	10.7658(10)	6.8904(7)	7.6324(4)	8.6984(8)	6.5100(4)
<i>c</i> (Å)	26.9737(13)	15.4196(15)	13.4554(13)	12.8284(7)	14.9548(13)	13.4751(7)
α (deg)	87.754(3)	90.299(6)	90.00	91.089(4)	102.797(4)	93.300(3)
β (deg)	89.692(3)	94.313(6)	110.873(7)	97.389(4)	97.981(4)	100.110(3)
γ (deg)	84.740(3)	103.408(5)	90.00	95.697(4)	92.445(4)	113.129(2)
<i>V</i> (Å ³)	743.79(6)	1449.9(2)	1152.9(2)	704.96(7)	854.97(13)	496.45(5)
<i>Z</i>	2	2	2	2	2	1
Density (mgm ^{–3})	1.711	1.384	1.481	1.770	1.766	1.775
Abs. coeff. (mm ^{–1})	0.937	0.723	0.995	1.784	1.327	1.171
<i>F</i> (000)	394	628	530	384	452	270
Total no. of reflections	7186	8123	9774	5430	11,104	5524
Reflections, <i>I</i> > 2 σ (<i>I</i>)	2686	4632	3426	2424	3106	1645
Max. θ (deg)	25.50	25.00	23.98	25.00	25.50	25.00
Completeness to 2 θ (%)	97.2	90.4	97.0	97.5	97.8	93.6
Data/restraints/parameters	2686/0/235	4632/2/378	3426/1/312	2424/0/210	3106/8/231	1645/6/141
Goof (<i>F</i> ²)	1.245	1.028	1.033	1.047	1.090	1.193
<i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0433	0.0826	0.0427	0.0448	0.0881	0.0505
<i>R</i> indices (all data)	0.0466	0.1574	0.0519	0.0521	0.0920	0.0508



Scheme 1. Synthesis of coordination polymers.

having a composition $[\text{Mn}(\text{L}_1)(\text{H}_2\text{O})_3]_n$. The aquo group of the complex shows a broad IR absorption at 3478 cm^{-1} . The asymmetric and symmetric stretching of the carboxylate ligand appears at $1608\text{--}1385\text{ cm}^{-1}$, respectively. The coordination polymer **1** crystallizes in the triclinic space group *P*–1. All the manganese(II) centers in **1** adopt octahedral geometries. However, there are two different coordination environments for manganese(II) centers in the structure. Mn1 center is coordinated to two carboxylate ligands and two aquoligands while Mn2 is coordinated by two carboxylate oxygens and four aquoligands there by completing the hexa-coordination. The carboxylate ligand is coordinated to the metal centers with both bridging and monodentate binding mode there by linking three manganese(II) centers. This binding mode exhibiting by the ligand **L**₁ in **1** can be assigned as $\mu^3\text{--}\eta^2\text{:}\eta^1$ and is found to exhibit in

carboxylate coordination polymers [46]. The Mn1 centers are connected to a nearby Mn1 center by the μ^2 bidentate bridging mode of the ligand through O4 and O5 coordination. This bridging elongates the molecule along *a* crystallographic axis. There is no bridging between any two Mn2 centers. Mn2 center is coordinated by the ligand in a monodentate fashion and is connected to the Mn1 center through the coordination by the other end of the spacer ligand **L**₁. This bridging extends the molecule along the *c* crystallographic axis thereby providing it a two dimensional architecture as shown in Fig. 2a. Further to this, the two dimensional sheets of the coordination polymer **1** are connected to each other through $\text{O3--H3a}\cdots\text{O5}$, $\text{O3--H3}\cdots\text{O6}$ and $\text{O9--H9}\cdots\text{O2}$ interactions. These short range interactions holds the nearby 2D sheets together and impart the molecule a three dimensional hydrogen bonded network structure. The weak interactions

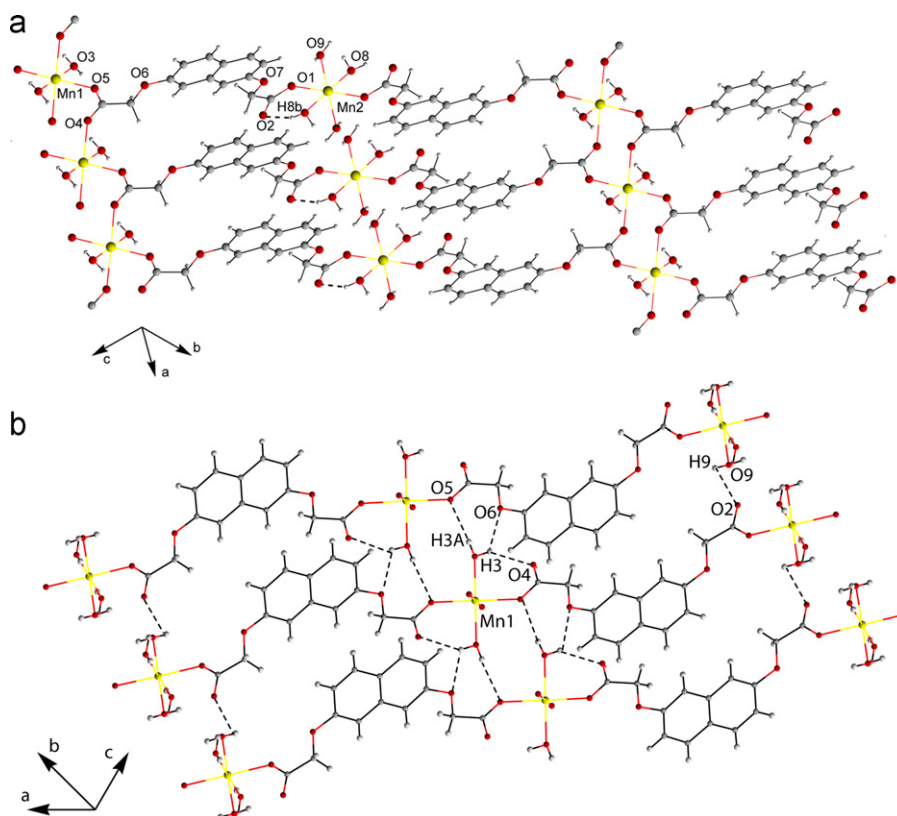


Fig. 2. (a) Two dimensional sheet of the coordination polymer **1** and (b) hydrogen bonded network formed by the coordination polymer **1**.

among the 2D sheets are shown in Fig. 2b and the interactions are tabulated in supplementary table 1s.

The reaction between $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and L_1H_2 in presence of sodium hydroxide in water/pyridine results in the formation of an one dimensional coordination polymer having composition $[\{\text{Ni}(\text{L}_1)(\text{Py})_3(\text{H}_2\text{O})\} \cdot \text{H}_2\text{O}]_n$ (**2**). The compound exhibits characteristic IR stretching frequencies for the coordinated carboxylate ligands at 1614 and 1381 cm^{-1} as well as for the pyridine ligands at 846 cm^{-1} . The single crystal X-ray analysis shows that the coordination polymer **2** crystallizes in the triclinic space group $P\bar{1}$. All the nickel(II) centers in the structure adopt a near octahedral geometry; the hexa-coordination around the metal center is satisfied by two carboxylate, three pyridine and one aquo groups. The $\text{Ni}-\text{O}_{\text{aquo}}$ bond ($\text{Ni}-\text{O}8$, 2.07 \AA) is longer than the $\text{Ni}-\text{O}_{\text{L}}$ bond ($\text{Ni}-\text{O}1$, 2.03 \AA and $\text{Ni}-\text{O}4$, 2.05 \AA). The $\text{Ni}-\text{N}$ bonds are even much longer lying in the range of $2.09\text{--}2.12\text{ \AA}$. However, these distances are common for octahedral nickel(II) complexes [47,48]. The carboxylate ligand L_1 here connects the nearby metal centers with a $\text{trans } \mu^2-\eta^1:\eta^1$ binding mode. In other words both the carboxylate ligating sites are coordinated to the metal center in a monodentate fashion, thereby nullifying the possibility of the coordination polymer of being a two dimensional like in the case of **1**. The bridging between the nearest nickel(II) centers are provided by the $\text{trans } \mu^2-\eta^1:\eta^1$ binding mode of the ligand L_1 that elongate the polymer along the b crystallographic axis. The coordinated aquo groups are involved in both intramolecular and intermolecular hydrogen bond formation viz. $\text{O}8-\text{H}8a \cdots \text{O}3$ and $\text{O}8-\text{H}8b \cdots \text{O}3$, respectively. These interactions hold one chain to another and thereby forms a two dimensional hydrogen bonded sheets as shown in Fig. 3b. It is noteworthy that the coordination polymer holds one water molecule of crystallization per nickel atom. These water molecules remain hydrogen bonded to the one dimensional chain forming a water channel in between two

polymeric chains. This channel is shown in Fig. 3(c). Helical structure is held by a layer of water structures in ordered manner.

The reaction of copper(II) chloride monohydrate and (7-carboxymethoxy-naphthalen-2-yloxy)-acetic acid (L_1H_2) in presence of sodium hydroxide in water/pyridine leads to the formation of a one dimensional coordination polymer having the composition $[\text{CuL}_1(\text{H}_2\text{O})(\text{Py})_2]_n$ (**3**). For this complex the IR stretching frequencies for the coordinated carboxylate ligands appear at 1629 and 1408 cm^{-1} and for the coordinated pyridine ligands appear at 832 cm^{-1} . The single crystal X-ray analysis shows that the coordination polymer **3** crystallizes in the monoclinic $P2_1$ space group. The crystal structure of **3** is shown in Fig. 4 and it is interesting to observe that the ligand coordinate the metal centers in *cis* fashion (Fig. 1). The copper (II) centers adopt a slightly distorted ($\tau=0.18$) square pyramidal geometry with both pyridines and the ligand L_1 occupying two coordination sites and the fifth coordination site is occupied by a water molecule. This index τ is zero for a perfectly square-pyramidal and a unity for perfectly trigonal-bipyramidal geometry (calculated as a difference between two largest angles divided by 60) [49]. The $\text{Cu}-\text{O}_{\text{L}}$ bond distances are $\text{Cu}-\text{O}1$, 1.97 \AA and $\text{Cu}-\text{O}5$, 1.98 \AA while the $\text{Cu}-\text{O}_{\text{aquo}}$ bond distance is 2.22 \AA . The nearest Cu1 centers are connected by the ligand with a $\mu^2-\eta^1:\eta^1$ binding mode. This bridging, in fact, results in the 1D coordination polymeric structures of **3** extending along the b crystallographic axis (Fig. 4b).

The ligand L_1 reacts with anhydrous zinc(II) chloride to result in the formation of another one dimensional coordination polymer **4** $[\text{ZnL}_1(\text{H}_2\text{O})_2]_n$. The compound crystallizes in the triclinic $P\bar{1}$ space group. The carboxylate ligand is coordinated to the metal centers with a similar binding mode as in the coordination polymer **1**. Each of the ligand L_1 adopts the $\mu^3-\eta^2:\eta^1$ binding mode thereby linking three zinc(II) centers. However the difference with **1** arises in that all the zinc(II) centers are penta

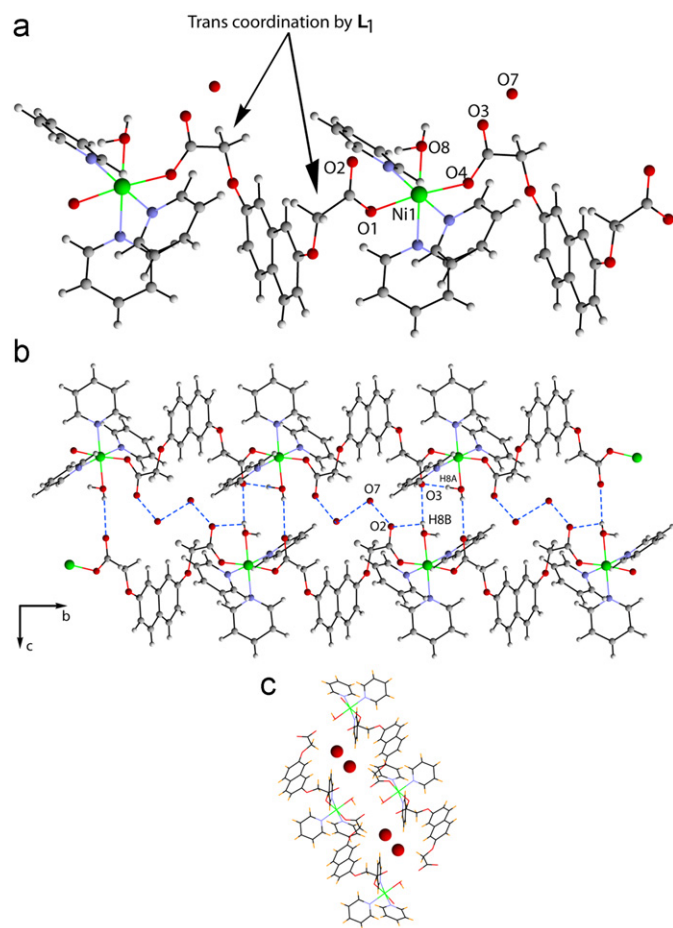


Fig. 3. (a) Crystal structure of coordination polymer **2** showing the $\text{trans } \mu^2-\eta^1:\eta^1$ binding mode of L_1 (the hydrogen atom in oxygen O7 could not be located), (b) self-assembly of complex **2** through weak interactions and (c) water channels encapsulated by the 1D chains of **2**.

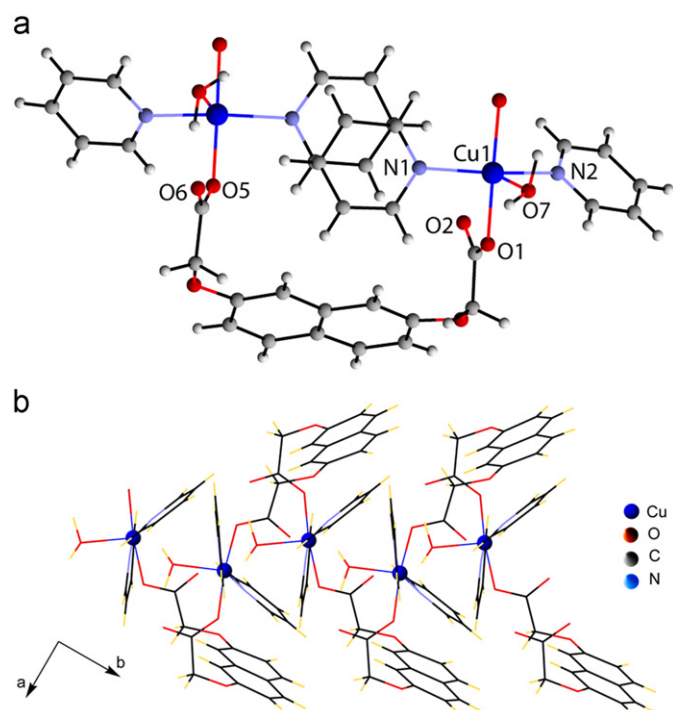


Fig. 4. (a) $\text{cis } \mu^2-\eta^1:\eta^1$ binding mode of L_1 in coordination polymer **3** and (b) formation of one dimensional coordination polymer in complex **3**.

coordinated with three of the coordination sites occupied by the carboxylate ligand and other two by aquo ligands. These coordination lead to a slightly distorted ($\tau=0.18$) trigonal bipyramidal geometry around the zinc(II) centers. Equatorial positions in the trigonal bipyramid are occupied by the three carboxylate oxygens with bond distances of Zn1–O5, 1.96 Å; Zn1–O7, 1.97 Å and Zn1–O1, 2.00 Å while the axial sites are occupied by two aquo ligands with bond distances Zn1–O6, 2.08 Å and Zn1–O8, 2.14 Å. The bridging binding mode leads to binuclear zinc(II) units that are connected to each other through the monodentate binding mode of the spacer ligand L_1 at the rear end. This bridging extends the molecule along the b crystallographic axis resulting in the 1D coordination polymer. In the crystal lattice the polymeric chains are held together via inter-molecular hydrogen bonding through water molecules and formed a layer structure. The aquo groups between the layers are inter-molecularly hydrogen-bonded with oxygen atoms of carboxylates via O6–H6 \cdots O4, O6–H6b \cdots O1, O6–H6b \cdots O2, and O8–H8 \cdots O4 interactions. The hydrogen bond parameters are included in supplementary table 1s. Besides these, the polymeric chains are also interconnected by weak C2–H2a \cdots O3, 2.73 Å and C13–H13 $\cdots\pi$, 2.85 Å interactions. We had earlier shown that the zinc complexes derived from analogous isomeric ligand of naphthalene on coordination generate template to coordinate sodium ions [42], but such observations are not observed with the L_1 . The paddle wheel structures of carboxylate coordination polymer are generally formed at room temperature reactions of terephthalate type of ligands [46] (Fig. 5).

The ligand L_1 reacts with cadmium chloride monohydrate to result in the formation of one dimensional coordination polymer **5** $[(\text{Cd}L_1(\text{H}_2\text{O})_3)\cdot\text{H}_2\text{O}]_n$. The FT-IR spectra show the stretching frequencies for the carboxylate ligands appearing at 1614 and 1391 cm^{-1} due to the asymmetric and symmetric stretching mode. The stretching due to aquo ligands as well as the water of crystallization appears at 3463 cm^{-1} . All the cadmium(II) centers are hepta coordinated by four oxygen atoms of carboxylates and three aquo molecules. All the Cd–O bond distances are in the range 2.23–2.46 Å. There is one water molecule of crystallization that remains hydrogen bonded in the crystal lattice. However the hydrogen atoms attached to this oxygen atom O10 could not be located due to the poor reflection data. The carboxylate ligand is coordinated to the metal centers with $\mu^2-\eta^2:\eta^2$ binding mode as both the carboxylate groups are in chelating mode. This bridging extends the coordination polymer along the c crystallographic axis. The aquo ligands in the molecule are involved in hydrogen bonding through O9–H9a \cdots O7, O9–H9b \cdots O4, O8–H8a \cdots O2, O8–H8b \cdots O9, O7–H7a \cdots O10 interactions which lead to a complicated three dimensional hydrogen bonded network. For simplicity, only some of these interactions in the coordination polymer are shown in Fig. 6.

It is interesting to note here that the use of the isomeric ligand (5-carboxymethoxy-naphthalen-1-yloxy)-acetic acid (L_2H_2) in place of the L_1H_2 in a similar reaction with metal(II) chloride results in the formation of salts comprising of hexa-aquometal(II) ion and (5-carboxymethoxy-naphthalen-1-yloxy)-acetate ions (L_2) crystallizing with a water molecule (Scheme 2). This type of products are obtained in the case of the reaction of (5-carboxymethoxy-naphthalen-1-yloxy)-acetic acid with both manganese chloride tetrahydrate and cadmium chloride hydrate in water in the presence of sodium hydroxide. Both complexes are characterized by conventional spectroscopic methods as well as by single crystal and X-ray powder diffraction techniques. However the diffraction data obtained for the salt of hexa-aquomanganese(II) ion and (5-carboxymethoxy-naphthalen-1-yloxy)-acetate ion co-crystallized with a water molecule is of poor quality to be reported, nevertheless it is good enough to make sure about the

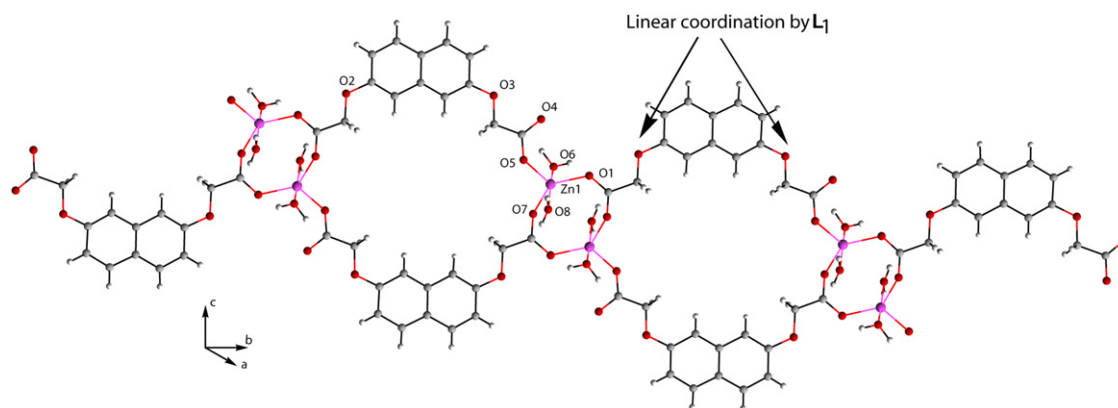


Fig. 5. Formation of one dimensional coordination polymer **4** through $\mu^2-\eta^2:\eta^1$ coordination mode of **L**₁.

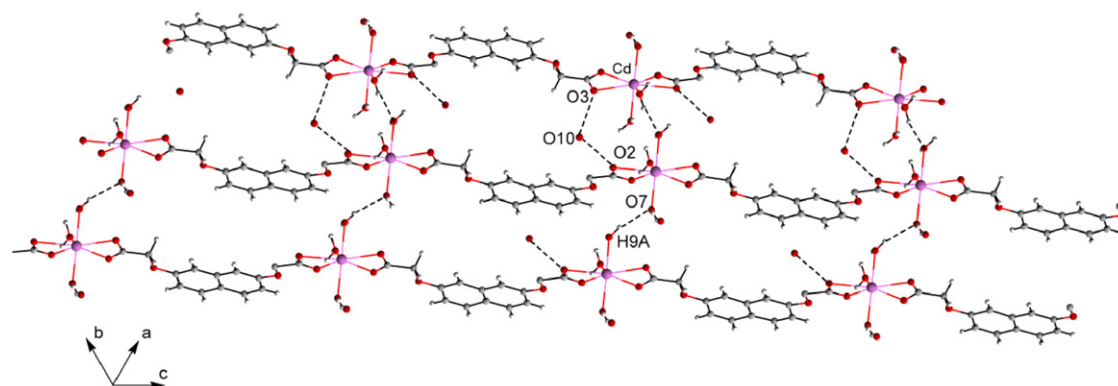
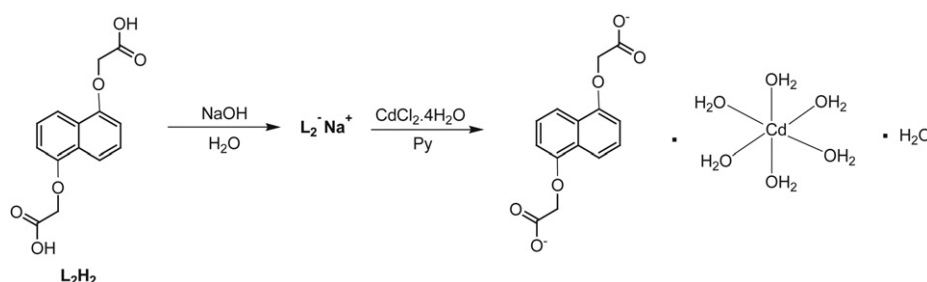


Fig. 6. Hydrogen bonding in the one dimensional chains of coordination polymer **5**.



Scheme 2. Synthesis of cadmium complex of **L**₂.

structural pattern. The crystal structure of the hexa-aquocadmium(II) ion and (5-carboxymethoxy-naphthalen-1-yloxy)-acetate ion is shown in Fig. 7a. There is one uncoordinated water molecule in the lattice. The complex cation, the dicarboxylate anions and the water molecules are connected by a number of hydrogen bond interactions such as O4–H4b...O1, O5–H5a...O7, O7–H7a...O1, O7–H7b...O2, etc. as shown in Fig. 7b. The hydrogen bond parameters are tabulated in supplementary table 1s.

In order to confirm the phase purity of the bulk materials, powder X-ray diffraction (PXRD) of all the compounds were determined. The PXRD experimental and simulated patterns of all of them are shown in the supplementary materials. As shown in Fig. 8, all major peaks of experimental powder X-ray patterns (PXRD) of compound **1** matches well that of simulated PXRD, indicating their reasonable crystalline phase purity. PXRD analysis of the bulk samples of the other coordination polymers **2–5** and the molecular complex **6** are carried out and found to match

well with the simulated patterns (please refer to the supplementary materials).

The thermal stability of all these complexes was studied by thermogravimetry. The curves for weight loss vs. temperature at heating rate 5 °C/min up to 550 °C from room temperature have shown that each complex except compound **6** loses the solvent molecules acting either as solvent of crystallization or ligands, at relatively low temperature (cf. < 250 °C). The theoretical and experimental weight losses are calculated on the basis of the formula obtained from single crystal X-ray. The calculated and experimental values tallies well with such loss of weight. The complex **6** loses weight continuously from 250 to 550 °C to form cadmium carbonate. In the case of zinc complex the final weight of the residue is close to zinc acetate; whereas in the case of manganese, nickel and copper complexes corresponding stable oxides are observed as residues. Metal carboxylate complexes on heating generally leads to metal oxides [50–51]. In some of our

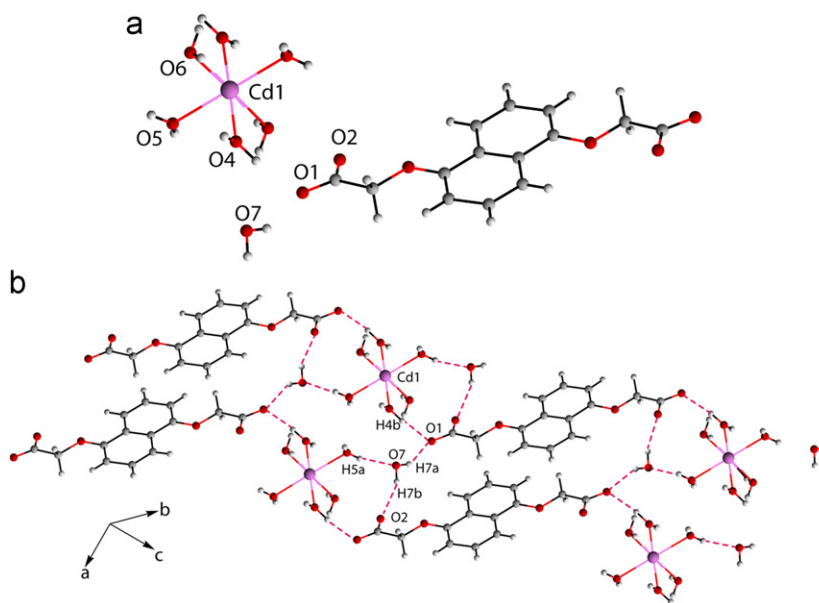


Fig. 7. (a) Crystal structure of molecular complex **6** and (b) hydrogen bonded self-assembly of complex **6** through weak interactions.

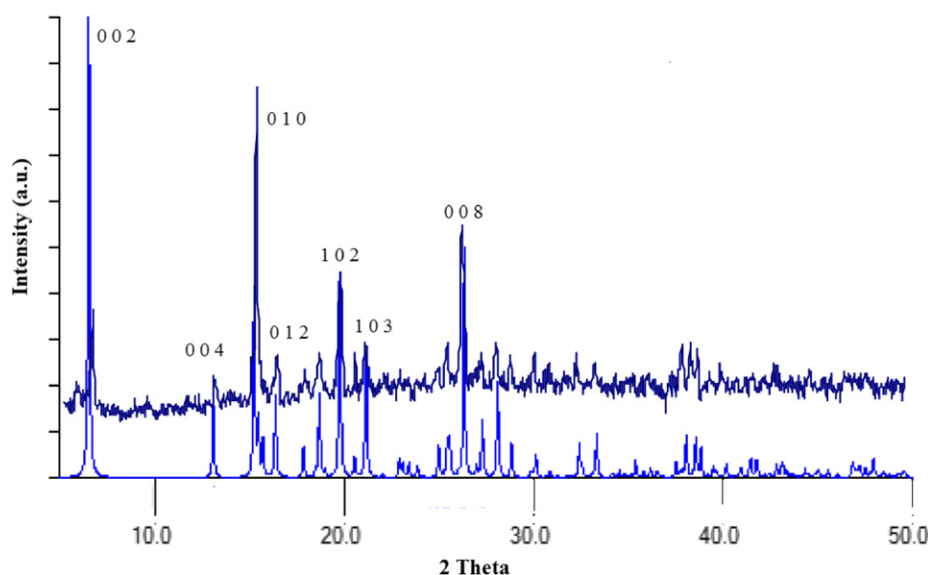


Fig. 8. Experimental and simulated PXRD pattern for the coordination polymer **1** (top: experimental; bottom: simulated).

cases such as cadmium we have obtained carbonate derivatives residues, such observations are not exceptional to carboxylate complexes of f-block metal but are less frequent [52].

5. Photoluminescence study

Photoluminescence properties of the acid (7-carboxymethoxynaphthalen-2-ylidene)-acetic acid as well as the coordination polymers **4** and **5** are studied in the solution state. The UV absorption spectra show that the methanolic solution of the acid has three absorption bands at 273, 309 and 323 nm. Among them the band at 273 nm arises due to π – π^* transition of the ligand. Emission spectra were recorded for the samples by exciting them at 260 nm. Upon excitation, **L₁H₂** emits at 333 nm. We have tried to follow a fluorometric titration of the acid with incremental addition of metal(II) acetate viz. Zn(OAc)₂ and Cd(OAc)₂. However, the addition of a metal salt to the solution of **L₁H₂**

results in precipitation. As this precipitate can be dissolved in pyridine we have tried to carry out the fluorometric titration in pyridine as solvent. Interestingly, in pyridine (7-carboxymethoxynaphthalen-2-ylidene)-acetic acid is not fluorescence active, in fact, addition of pyridine solution (10^{–2} M, methanol) to a 10^{–4} M solution of **L₁H₂** results in quenching of fluorescence (please refer to supplementary material). Compounds **4** and **5** are soluble in dimethylsulfoxide (DMSO); we have recorded the fluorescence spectrum of these compounds in DMSO. Comparison of the emission spectra of the free acid with the coordination polymers shows that the free acid, **4** and **5** emit at the same wavelength 333 nm. As the MLCT or LMCT transitions can be ignored in case of a *d*¹⁰—electronic configuration the emission observed in compounds **4** and **5** are only because of the π – π^* transition of the ligand. The emission spectra for the compounds as well as for the ligand are shown in Fig. 9. We have not observed any significant change by adding pyridine to the DMSO solutions of compounds **4** and **5**. However, there is reduction of intensity of

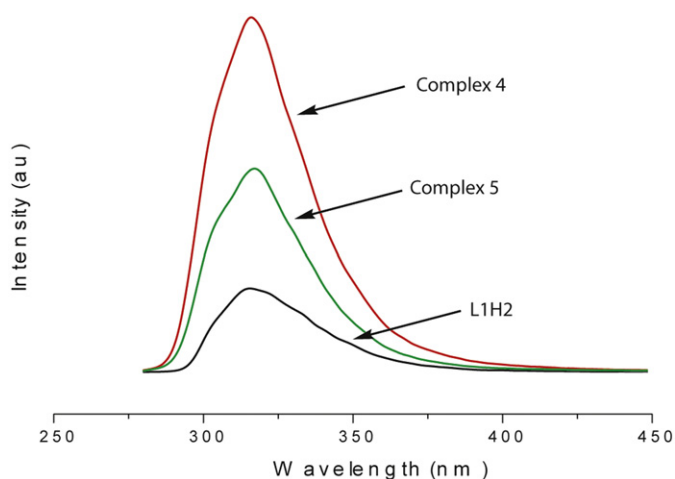


Fig. 9. Fluorescence emission spectra for compounds **4**, **5** and **L1H₂**.

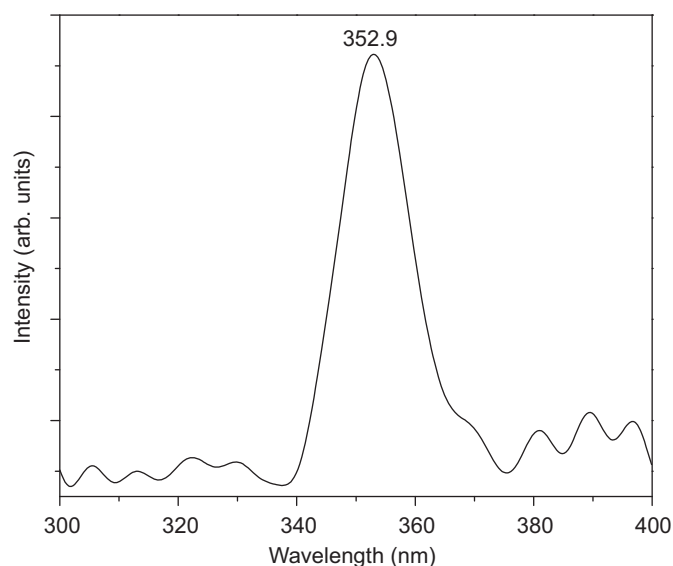


Fig. 10. Multiphoton induced emission in UV range, confirming frequency up conversion in compound **3**.

fluorescence similar but less prominent than the one dissolved in pyridine. Thus, it suggests that complexes **4** and **5** dissociates in DMSO solution and fluorescence emission of the ligand as well as undissociated forms are observed, which shows quenching of fluorescence of the complexes in comparison to the metal complexes. Naphthalene derivatives are known to form intramolecular exciplex [53] and nitrogen heteroaromatic molecules such as pyridine, picoline, etc. are known to be quencher for such exciplex fluorescence [54]. In our case also fluorescence quenching is presumably through exciplex quenching upon addition of pyridine.

6. SHG properties

Since coordination polymer **3** crystallizes in a non-centrosymmetric space group it is expected to show nonlinear optical properties [55,56]. To explore the nonlinearity in the compound, a film was prepared by the deposition of drop of a solution of the sample in pyridine–water mixed solvent (1:2 ratio) over glass plates followed by room temperature drying. This resulted in the thin film on cover slit. The 632.8 nm He:Ne laser was focused on to the thin film sample to a power density of 10^6 W/m². The laser was launched at an angle

incidence of 45°. The emitted signal was collected by a lens on to the monochromator. Monochromator was scanned in the ultraviolet range from 300 to 400 nm. The broadband ultra-violet fluorescence was observed centered at 352.9 nm as shown in Fig. 10. The proposed mechanism for the observed fluorescence is three-photon absorption induced fluorescence. This multiphoton absorption confirms that the coordination polymer **3** may have scope for nonlinear optical application in particular for frequency up conversion.

7. Conclusion

In conclusion, we have synthesized five coordination polymers of dicarboxylate of (7-carboxymethoxy-naphthalen-2-yloxy)-acetic acid with transition metal ions viz. Mn(II), Ni(II), Cu(II), Zn(II) and Cd(II), respectively, with or without ancillary ligand at ambient conditions. Three different orientations of the ligand are identified and observed that the ligand **L₁** can coordinate to metal with: in plane-linear coordination mode, out of plane *cis* coordination mode and out of plane *trans* coordination mode. Coordination polymer **1** has a two dimensional architecture whereas all other polymers under consideration are one dimensional coordination polymers. The aquoligands in coordination polymers **2**, **4** and **5** are involved in hydrogen bonding among each other; there by leads to three dimensional supramolecular architecture. It is observed that in case of the coordination polymers **1**, **4** and **5** where water is the only ancillary ligand, the ligand **L₁** adopts the in-plane linear coordination mode. However, in coordination polymers **2**, **L₁** adopts the out of plane *trans* coordination mode and in **3** it adopts the out of plane *cis* coordination mode and in both the cases pyridine remains coordinated to the metal center. Therefore, it can be concluded that the *cis* and *trans* out-of-plane coordination modes are found to exist only if the ancillary ligand pyridine also remains coordinated to the metal center along with aquoligands and origin of the different orientation of the ligand lies at the steric congestion around the metal center. If the aquoligands happen to be the only ancillary ligand the in-plane linear coordination mode of **L₁** predominates. Literatures are there accounting for such dependence of architecture of coordination polymers on the coordination environment [18]. The isomeric (5-carboxymethoxy-naphthalen-1-yloxy)-acetic acid does not lead to coordination polymer, rather remain as anion for hexa-aquometal (II) cation. The thermal as well as luminescence properties of the acid **L₁H₂** and the complexes are studied. (7-Carboxymethoxy-naphthalen-2-yloxy)-acetic acid is highly fluorescence active and quenching of fluorescence can be obtained by addition of pyridine to a solution containing **L₁H₂**; however, the zinc (II) and cadmium (II) complexes are fluorescence active. The coordination polymer **3** may have scope for nonlinear optical application as confirmed by the multiphoton absorption process.

Supplementary materials

The hydrogen bond parameters, fluorescence emission of complexes, powder diffractions of the polymers, CIF files for the coordination polymers **1–6** are given as supplementary materials. The crystallographic data files of the compounds are submitted to Cambridge Crystallographic Database and have the CCDC numbers 774467, 774468 and 779596–779599.

Acknowledgments

The authors thank Department of Science and Technology, New Delhi, India for financial support. The author R.S. thanks CSIR, New Delhi, India for fellowship.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2011.05.004](https://doi.org/10.1016/j.jssc.2011.05.004).

References

- [1] S. Kitagawa, R. Kitaura, S.I. Noro, *Angew. Chem. Int. Ed.* 43 (2004) 2334–2375.
- [2] H. Li, M. Eddaoudi, M.O. Keefe, O.M. Yaghi, *Nature* 402 (1999) 276–279.
- [3] D. Maspoeh, D. Ruiz-Molina, J. Veciana, *J. Mater. Chem.* 14 (2004) 2713–2723.
- [4] J.Y. Lu, *Coord. Chem. Rev.* 246 (2003) 327–347.
- [5] C. Ruiz-Perez, P. Lorenzo-Luis, H.M. Molina, M.M. Laz, F.S. Delgado, P. Gili, M. Julve, *Eur. J. Inorg. Chem.* (2004) 3873–3879.
- [6] K.M. Fromm, *Coord. Chem. Rev.* 252 (2008) 856–885.
- [7] A.Y. Robin, K.M. Fromm, *Coord. Chem. Rev.* 250 (2006) 2127–2157.
- [8] S.R. Batten, K.S. Murray, *Coord. Chem. Rev.* 246 (2003) 103–130.
- [9] D. Bradshaw, J.B. Claridge, E.J. Cussen, T.J. Prior, M.J. Rosseinsky, *Acc. Chem. Res.* 38 (2005) 273–282.
- [10] J.L.C. Rowsell, O.M. Yaghi, *Microporous Mesoporous Mater.* 73 (2004) 3–14.
- [11] D.N. Dybtsev, H. Chun, S.H. Yoon, D. Kim, K. Kim, *J. Am. Chem. Soc.* 126 (2004) 32–33.
- [12] M.P. Suh, Y.E. Cheon, E.Y. Lee, *Coord. Chem. Rev.* 252 (2008) 1007–1026.
- [13] B. Zhao, X.Y. Chen, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang, *J. Am. Chem. Soc.* 126 (2004) 15394–15395.
- [14] D. Venkataraman, G.F. Gardner, S. Lee, J.S. Moore, *J. Am. Chem. Soc.* 117 (1995) 11600–11601.
- [15] W. Fujita, K. Awaga, *J. Am. Chem. Soc.* 123 (2001) 3601–3602.
- [16] K. Ramesha, L. Sebastian, B. Eichhorn, J. Gopalakrishnan, *Chem. Mater.* 15 (2003) 668–674.
- [17] F.S. Delgado, M. Hernandez-Molina, J. Sanchiz, C. Ruiz-Perez, Y. Rodriguez-Martin, T. Lopez, F. Lloret, M. Julve, *CrystEngComm* 6 (2004) 106–111.
- [18] M. Fujita, J.Y. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* 116 (1994) 1151–1152.
- [19] R. Kitaura, G. Onoyama, H. Sakamoto, R. Matsuda, S.I. Noro, S. Kitagawa, *Angew. Chem. Int. Ed. Eng.* 43 (2004) 2684–2687.
- [20] X.R. Meng, Y.L. Song, H.W. Hou, Y.T. Fan, G. Li, Y. Zhu, *Inorg. Chem.* 42 (2003) 1306–1315.
- [21] C. Mellot-Draznieks, G. Férey, *Prog. Solid State Chem.* 33 (2005) 187–197.
- [22] O.M. Yaghi, M. Keefe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, *Nature* 423 (2003) 705–714.
- [23] X. Zhao, B. Xiao, A.J. Fletcher, K.M. Thomas, D. Bradshaw, M.J. Rosseinsky, *Science* 306 (2004) 1012–1015.
- [24] B. Moulton, M.J. Zaworotko, *Chem. Rev.* 101 (2001) 1629–1658.
- [25] S. Noro, S. Kitagawa, M. Kondo, K. Seki, *Angew. Chem. Int. Ed. Eng.* 39 (2000) 2081–2084.
- [26] P.J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem. Int. Ed. Eng.* 38 (1999) 2638–2684.
- [27] J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim, *Nature* 404 (2000) 982–986.
- [28] S.M. Humphrey, J.-S. Chang, S.H. Jhung, J.W. Yoon, P.T. Wood, *Angew. Chem. Int. Ed. Eng.* 46 (2007) 272–2715.
- [29] O. Fabelo, L. Canadillas-Delgado, F.S. Delgado, P. Lorenzo-Luis, M.M. Laz, M. Julve, C. Ruiz-Perez, *Cryst. Growth Des.* 5 (2005) 1163–1167.
- [30] J.J. Vittal, *Coord. Chem. Rev.* 251 (2007) 1781–1795.
- [31] F.A. Cotton, C. Lin, C.A. Murillo, *Acc. Chem. Res.* 34 (2001) 759–771.
- [32] M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. Keefe, O.M. Yaghi, *Acc. Chem. Res.* 34 (2001) 319–330.
- [33] S.L. James, *Chem. Soc. Rev.* 32 (2003) 276–288.
- [34] R. Murugavel, M.G. Walawalkar, M. Dan, H.W. Roesky, C.N.R. Rao, *Acc. Chem. Res.* 37 (2004) 763–774.
- [35] Y. Rodriguez-Martin, M. Hernandez-Molina, F.S. Delgado, J. Pasan, C. Ruiz-Perez, J. Sanchiz, F. Lloret, M. Julve, *CrystEngComm* 4 (2002) 522–535.
- [36] A. Erxleben, *Coord. Chem. Rev.* 246 (2003) 203–228.
- [37] A.J. Fletcher, K.M. Thomas, M.J. Rosseinsky, *J. Solid State Chem.* 178 (2005) 2491–2510.
- [38] K. Uemura, R. Matsudab, S. Kitagawa, *J. Solid State Chem.* 178 (2005) 2420–2429.
- [39] F.S. Delgado, C. Ruiz-Perez, J. Sanchiz, F. Lloret, M. Julve, *CrystEngComm* 8 (2006) 530–554.
- [40] J. Pasan, J. Sanchiz, C. Ruiz-Perez, F. Lloret, M. Julve, *Inorg. Chem.* 44 (2005) 7794–7801.
- [41] P. Lightfoot, A. Snedden, *J. Chem. Soc. Dalton Trans.* (1999) 3549–3551.
- [42] A. Karmakar, J.B. Baruah, R.B. Shankar, *CrystEngComm* 11 (2009) 832–840.
- [43] X.-M. Zhang, *Coord. Chem. Rev.* 249 (2005) 1201–1219.
- [44] P. Mondal, A. Karmakar, W.M. Singh, J.B. Baruah, *CrystEngComm* 10 (2008) 1159–1550.
- [45] G.M. Sheldrick, *Acta Crystallogr. A* 64 (2008) 112–122.
- [46] J. Yang, G.-D. Li, J.-J. Cao, Q. Yue, G.-H. Li, J.-S. Chen, *Chem. Eur. J.* 13 (2007) 3248–3261.
- [47] E. Ferentinos, D. Maganas, C.P. Raptopoulou, A. Terzis, V. Psycharis, N. Robertson, P. Kyritsis, *Dalton Trans.* 40 (2011) 169–180.
- [48] O. Rotthaus, F. Thomas, O. Jarjays, C. Philouze, E. Saint-Aman, J.L. Pierre, *Chem. Eur. J.* 12 (2006) 6953–6962.
- [49] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, *J. Chem. Soc. Dalton Trans.* (1984) 1349–1356.
- [50] T.S. Stamatatos, E. Katsoulakou, V. Nastopoulos, C.P. Raptopoulou, E. Manessi-Zoupa, S.P. Perlepes, *Z. Naturforsch.* 58B (2003) 1045–1054.
- [51] L. Tian, N. Ren, J.-J. Zhang, S.-J. Sun, H.-M. Ye, J.-H. Bai, R.-F. Wang, *J. Chem. Eng. Data* 54 (2009) 69–74.
- [52] C. Brouca-Cabarrecq, J. Dexpert-Ghys, A. Fernandes, J. Jaud, J.C. Trombe, *Inorg. Chim. Acta* 361 (2008) 2909–2917.
- [53] C. Pac, H. Sakurai, *Chem. Lett.* (1976) 1067–1068.
- [54] M. Itoh, N. Takita, *Chem. Phys. Lett.* 62 (1978) 279–282.
- [55] J.A. McCleverty, T.J. Meyer, *Nonlinear optical properties of metal complexes*, in: B.J. Coe (Ed.), *Comprehensive Coordination Chemistry*, vol. 2, Elsevier, Pergamon, 2004.
- [56] H.S. Nalwa, S. Miyata (Eds.), *Nonlinear Optics of Organic Molecules and Polymers*, CRC Press, Boca Raton, FL, 1997.