Chapter 3

Three new co-ordination polymers of zinc (II) and cadmium (II) with dicarboxylate and bipyridine ligands: Synthesis, structure and luminescence study

Published in

J. Inorg. Organomet. Polym. 25 (2015)1151–1159

3.1. Introduction

In recent years, the design and construction of metal–organic coordination polymers (MOF) have been at the forefront in the research for new functional materials with applications such as gas adsorption, magnetism, luminescence and catalysis technologies beside their fascinating variety of architectures and topologies [144-146]. In the process of synthesis for such complexes, the key factor is the rational assembly of transition metal ions and organic ligands [147-148]. Many reports illustrate the use of aromatic dicarboxylic acids acting as organic spacers in the preparation of coordination polymers, [149-151] and the dianionic isophthalate is one of the most common among these ligands. [152-154] In fact dicarboxylate species can bridge metal cations while providing the structural integrity and the required charge balance for the formation of stable neutral crystalline frameworks. In this field 5-nitroisophthalic acid (H_2NIPH) represents a modified organic linker where the electron-withdrawing nitro group could act as possible hydrogen bond acceptor or provide a useful variation affecting the polymer topology, being rather rarely engaged in coordination towards metals as for example in lanthanide networks of 5-nitroisophthalic acid and 1,10-phenanthroline (phen) as ancillary ligand. [155] Nevertheless, in spite of these advantages, the usefulness offered by the 5-nitroisophthalic acid as a possible linker in the assembly of MOFs is still to be exploited in detail.[156-158] Di- or multidentate aromatic polycarboxylates have also been used to form robust frameworks since the carboxylate functional groups can exhibit a variety of coordination modes and several groups reported the synthesis and characterization of a large number of carboxylato-bridged multidimensional architectures in the presence of nitrogen donor co/bridging neutral ligands. [159-161] Diverse structural topologies are observed in these systems, depending on the coordination environment preferences at metal ions, the geometric orientation of the carboxylate groups on the aromatic ring, and the inclusion of any dipodal nitrogen-base tethering ligands [162] 1,4-Benzenediacrylic acid (H_2BDAC), as a member of multidentate aromatic dicarboxylic acids, can exhibit different coordination modes [163-164] and for its length can lead to cavities and interpenetrated structures. It is evident that the features of auxiliary ligands including symmetry, configurations, steric and species of substituted groups, have significant effects on the architecture dimension and properties of the MOFs produced [165-167].

Continuing our research focused to the auxiliary ligand-directed synthesis of the metal–carboxylate frameworks, in this chapter, we report a series of Zn(II) and Cd(II) coordination polymers, namely **{**$[Zn(bipy)(NIPH)].1.5H_2O\}_n$ (**3**), **{**$[Cd_2(bipy)_2(NIPH)_2].2H_2O$**}**$_n$ (**4**), and **{**$[Cd_2(bipy)_4(BDAC)(NO_3)](NO_3).6H_2O$**}**$_n$ (**5**),comprising the 2,2'-bipyridyl (bipy) ligand, which was selected as auxiliary ligand, being as an excellent chelate group. The compounds have been characterized by fluorescent spectroscopy, IR spectrumand elemental analysis, as well as by single-crystal X-ray diffraction analysis. Differences in their structures and physical behaviors result from the presence of coexistent non-coordinated groups in dicarboxylate ligands.

3.2. Experimental

3.2.1. Materials

Cadmium nitrate tetrahydrate and zinc nitratehexahydrate were purchased from Merck. 5-nitroisopthalic acid, 1,4-phenylenediacrylic acid and 2,2'-bipyridyl were purchased from SIGMA-ALDRICH Inc.

3.2.2. Physical Measurements

As mentioned in Section 2.2.2 in Chapter 2.

3.2.3. Synthesis of the complexes

3.2.3.1. Synthesis of {[Zn(bipy)(NIPH)].1.5H_2O}$_n$ (3)

$Zn(NO_3)_2.6H_2O$(0.1487g, 0.5 mmol), 5-nitroisophthalic acid (0.1056 g, 0.5mmol) and bipy (0.078g ,0.5mmol) in a molar ratio of 1:1:1 were dissolved in 10 mL of deionized water. The pH of the solution was adjusted to ca. 8 by drop wise addition of a 1 M solution of NaOH. The mixture was then transferred into a 25 mL Teflon-lined stainless steel vessel and heated at 160 °C for 72 h. The mixture was allowed to cool to room temperature to get needle shaped crystals. Single crystals were isolated by decanting the supernatant liquid and were washed with deionized water, ethanol and dried in air. Yield 56 %.Anal. Calc. for $C_{18}H_{14}N_3O_{7.50}Zn$(457.69): C, 47.24; H, 3.08; N, 9.18 %. Found: C, 47.18; H, 3.05; N, 9.16 %. FT- IR (cm^{-1}): 551 (m), 630 (w), 660 (w), 728 (s), 767 (s), 924 (s), 972 (w), 1031 (m), 1081 (m), 1100 (m), 1168 (m), 1247 (m), 1355 (s), 1403 (w), 1453 (m), 1541 (m), 1569 (w), 1639 (s), 1863 (m), 1952 (w), 2029 (w), 2275 (w), 2392 (w), 2471 (w), 2569 (w), 2872 (w), 3109 (m), 3439 (broad), 3844 (w).

3.2.3.2. Synthesis of {[Cd_2(bipy)$_2$(NIPH)$_2$].2H_2O}$_n$(4)

$Cd(NO_3)_2.4H_2O$ (0.154 g, 0.5 mmol), 5-nitroisopthalic acid (0.1056 g, 0.5mmol) and bipy (0.078 g, 0.5mmol) were dissolved in 10 mL deionized water. The pH of the solution was adjusted to ca. 5 by drop wise addition of 1 M NaOH solution. The mixture was then transferred into a 25 mL Teflon-lined stainless steel vessel and heated at 160 °C for 72 h. The mixture was allowed to cool to room temperature and the resulting needle shaped crystals were isolated by decanting the supernatant liquid. Crystals were washed with deionized water, ethanol and dried in air.Yield:60%. Anal. Calc. for $C_{36}H_{26}Cd_2N_6O_{14}$ (991.43): C,43.61;H,2.64;N,8.48. Found: C, 43.54; H, 2.62; N, 8.42. FT-IR (cm^{-1}): 523 (w), 650 (m), 737 (s), 767 (s), 796 (w), 924(s), 983 (w), 1022 (s), 1090 (s), 1159 (s), 1237 (m), 1364 (m), 1443 (m), 1512 (w), 1560 (w), 1589 (w), 1628 (m), 1697 (w), 1854 (m), 1913 (w), 1984 (w), 2011 (w), 2266 (w), 2549 (w), 2637 (w), 2804 (w), 2863 (w), 3098 (m), 3421 (broad).

3.2.3.3. Synthesis of $\{[Cd_2(bipy)_4(BDAC)(NO_3)](NO_3).6H_2O\}_n$ (5)

$Cd(NO_3)_2.4H_2O$ (0.154 g, 0.5 mmol), 1,4-benzenediacrylic acid (0.109 g, 0.5 mmol), and bipy (0.078g ,0.5mmol) were dissolved in 10 mL deionized water. The pH of the solution was adjusted to ca. 8 by drop wise addition of 1 M NaOH solution. The mixture was then transferred into a 25 mL Teflon-lined stainless steel vessel and heated at 160 °C for 72 h. The mixture was allowed to cool room temperature and the resulting needle shaped crystals were isolated by decanting the supernatant liquid and were washed with deionized water, ethanol and dried in air. Yield: 60%. Anal . Calc. for $C_{52}H_{52}Cd_2N_{10}O_{16}$ (1297.84): C, 48.12; H, 4.04; N, 10.79 %. Found: C, 48.08; H, 4.01; N, 10.72. IR (cm^{-1}): 555 (m), 630 (w), 728 (m), 767 (m), 826 (s), 885 (m), 983 (s), 1011 (w), 1109 (s), 1168 (m), 1188 (w), 1325 (w), 1384 (m), 1423 (w), 1551 (m), 1649 (s), 1863 (w), 1913 (w), 2382 (m), 3037 (w), 3430 (broad).

3.3. X-ray diffraction crystallography

Data collections of compounds **3-5** were carried at room temperature on a Bruker APEX-II diffractometer equipped with Mo-Kα graphite monocromatized radiation (λ = 0.71073 Å). Cell refinement, indexing and scaling of data sets was carried out using Bruker-Nonius program suite Saint Plus [135] and corrected for Lorentz polarization, background and absorption effects [135-136]. The structures were solved by using direct method and subsequent Fourier analyses [137] and refined by the full-matrix least-squares method based on F^2 with all observed reflections [137]. In compound **3** a lattice water molecule at half occupancy and in **5** water molecule O3w was found disorder over two positions (occupancies of 0.6/0.4). Hydrogen atoms were placed at calculated positions with exception of those of water molecules in **3**. All the calculations were performed using the Win GX System, Ver 1.80.05 [138]. Molecular graphics were performed using the ORTEP3 for Windows [139] and Diamond [140]. The crystallographic data and refinement parameters for the structures reported are given in Table 3.1. [CCDC number: 1041647-1041649].

Table 3.1. Crystallographic Data and Details of Refinements for Complexes **3-5**.

	3.1.5H_2O	**4**.2H_2O	**5**.6H_2O
Empirical formula	$C_{18}H_{14}N_3O_{7.50}Zn$	$C_{36}H_{26}Cd_2N_6O_{14}$	$C_{52}H_{52}Cd_2N_{10}O_{16}$
M	457.69	991.43	1297.84
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*C* 2/c	$P\bar{1}$	*C* 2/c
a /Å	31.118(3)	10.1632(3)	20.5678(12)
b /Å	9.2715(4)	13.1218(4)	17.6161(7)
c /Å	15.0086(13)	14.7388(4)	16.6561(7)
α /°	90.0	96.459(3)	90.0
β /°	123.828(12)	107.840(3)	111.951(6)
γ /°	90.0	98.789(3)	90.0
V /$Å^3$	3597.1(6)	1822.36(10)	5597.4(5)
Z	8	2	4
Dcalc /g cm^{-3}	1.690	1.807	1.540
μ /mm^{-1}	1.419	1.247	0.837
F(000)	1864	980	2632

θrange /°	2.58-25.99	2.92-26.00	2.64-26.99
Total data	7865	31040	26618
Unique data	3538	7134	6101
Rint	0.0374	0.0442	0.0828
Reflections$I>2\sigma(I)$	2958	6366	4362
Parameters	274	529	390
Goodness-of-fit	1.061	1.183	1.038
R_1	0.0360	0.0489	0.0639
wR_2 $(I>2\sigma(I))$ [a]	0.0751	0.1221	0.1541
Residuals /e Å^{-3}	0.432, –0.440	1.936, –0.800	1.034, –0.538

[a] $R1 = \Sigma\ \lvert Fo\rvert - \lvert Fc\rvert\rvert\ /\ \Sigma\lvert Fo\rvert$, $wR2 = [\Sigma w\ (Fo^2 - Fc^2)^2 / \Sigma w\ (Fo^2)^2]^{1/2}$.

3.4. Results and discussion

3.4.1. Description of crystal structures

3.4.1.1. Structural description of {[Zn(bipy)(NIPH)].1.5H_2O}$_n$ (3).

The crystal structure of compound **3** reveals a zig-zag coordination running along axis *c*, chain built by Zn(bipy) units connected by the 5-nitro-isophthalate anions (NIPH) through the carboxylic groups. The bond length and bond angles are listed in Table 3.2. The coordination geometry presents a highly distorted trigonalbipyramidal (trigonality index of 0.46), where O2' and N2 donors are located at axial positions (N(2)-Zn-O(2') bond angle = 154.05(8)°), shown in Fig. 3.1. Each Zn(II) ion is five coordinated by the nitrogen donors of the bipy ligand (Zn–N = 2.043(2), 2.049(2) Å) and by three oxygen atoms from one mono-dentate (Zn–O3 = 1.944(19) Å

) and one chelating carboxylate group (Zn–O = 2.029(18) and 2.409(19) Å) from two separate (symmetry related) NPIH ligands. It is worth of note the asymmetric chelating mode of the carboxylate group O1/O2, as indicated by the Zn-O bond values differing by ca. 0.4 Å. The metals are spaced in the chain at 9.929(1) Å with an intermetallic angle of 98.187(4)°.

It is worth of note the geometrical features detected in the crystal packing. In fact the N2 bipy rings of four different 1D zigzag chains are interdigitated to form a supramolecular 3D arrangement through π–π stacking (alternated centroid-to-centroid distance of 3.683(2) and 3.870(3)Å).This supramolecular architecture is further connected through hydrogen bonds involving the lattice water molecules. The structure is isomorphous and isostructural with the phenanthroline derivative**,** [Zn(phen)(NPH)], [168] where the intermetallic distance was found to be just a little longer, of 9.949 Å.

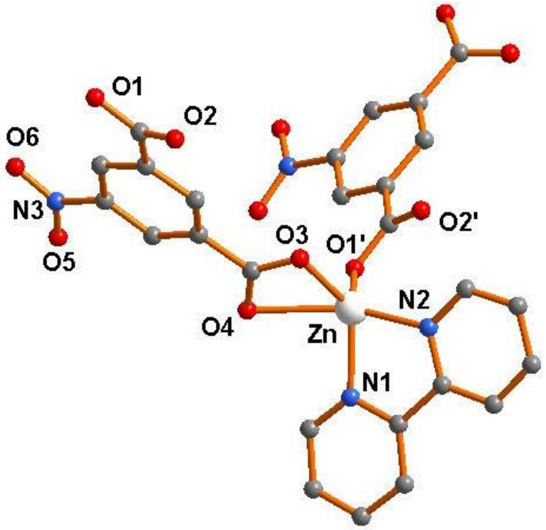


Fig.3.1 Coordination sphere of Zn ion in compound **3**

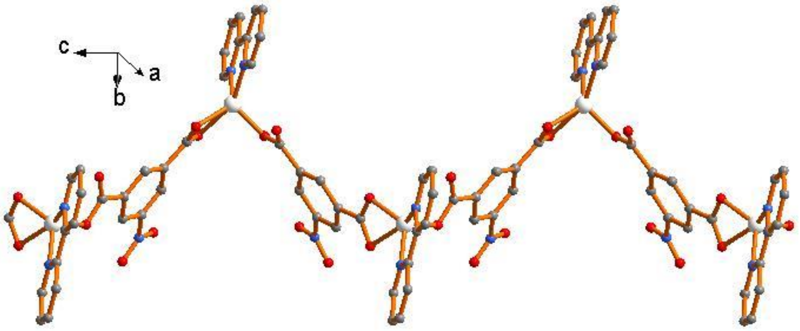


Fig.3.2 Zig-zag coordination polymer of **3**

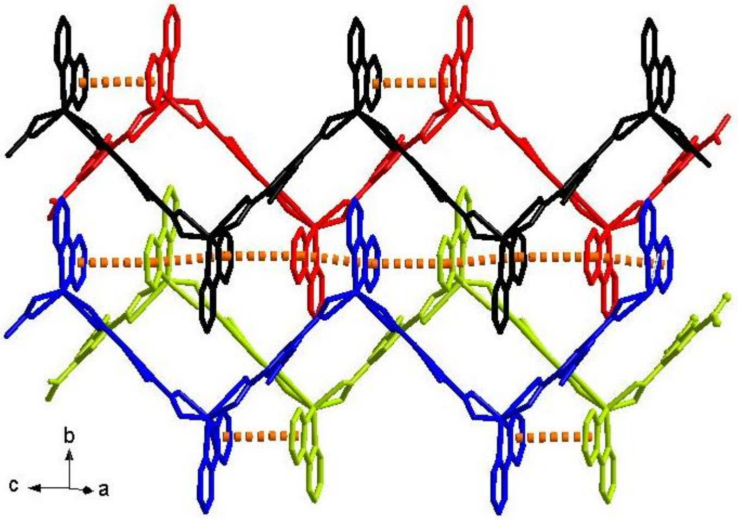


Fig. 3.3 The coordination polymers connected by π-π interactions occurring between bipy rings.

Table 3.2 Selected bond lengths (Å) and angles (°) for compound **3**.

Zn-O(1')	2.029(18)	Zn-N(1)	2.043(2)
Zn-O(2')	2.409(19)	Zn-N(2)	2.049(2)
Zn-O(3)	1.944(19)		

O(1')-Zn-O(2')	59.10(7)	O(3)-Zn-N(1)	112.86(8)
O(1')-Zn-N(1)	127.11(8)	O(3)-Zn-N(2)	118.63(9)
O(1')-Zn-N(2)	110.54(8)	N(1)-Zn-O(2')	87.88(7)
O(3)-Zn-O(1')	105.97(8)	N(1)-Zn-N(2)	80.76(8)
O(3)-Zn-O(2')	87.27(7)	N(2)-Zn-O(2')	154.05(8)

Primed atoms at x, 1−y, 0.5 +z

3.4.1.2. Structural description of {[Cd(bipy)(NIPH)]$_2$.2H$_2$O}$_n$ (4).

In compound **4** the metal: bipy: NIPH stoichiometry ratio (1:1:1) is similar to that of **3**, but due to a different coordination geometry of the cadmium atom, the1D coordination polymer is completely different from that described above. The X-ray diffraction analysis detects two crystallographic independent cadmium ions Cd1 and Cd2 have a hexa and hepta coordination number, respectively, of which the pertinent bond distances and angles are reported in Table 3.3 and the coordination sphere is sketched in Fig. 3.4. The Cd-N(bipy) distances fall in between 2.273(5) - 2.336(5) Å, while the Cd-O ones show a larger range (2.296(4) - 2.572(4) Å). In addition the Cd-O4’ distance of 2.77 Å, which is outside the range reported, does not exclude an interaction with the metal. Compound **4** displays a 1-D ladder-like chain where each distinct cadmium ion forms an array running parallel to crystallographic axis *a*. The Cd(bipy) moieties are bridged by NIPH anions through carboxylic groups acting as chelating groups. The double chain is generated by carboxylate groups O3/O4 and O7/O8 bridging the (Cd1)$_n$ and (Cd2)$_n$ arrays. In order to favor this arrangement (Fig. 3.5) these carboxylic groups O3/O4 and O7/O8 are slightly out of plane from the aromatic rings, forming a dihedral angle of 14.4 and 19.8° with it. The intermetallic Cd1-Cd1 and Cd2-Cd2 distances are 10.163(3) Å, corresponding to the repeating unit along axis *a*, while the separation between the metal rails is ca. 2.86 Å. The lattice water molecule O1w (in turn bound to another water, O2w) binds O2 and O10 through H-bonds (O…O distance of 2.893(8) and 2.854(7) Å, respectively) and strengthens the double chain. The crystal packing evidences the ribbons slightly interacting by π–π stacking of N4 bipy rings (centroid-to-centroid distance of 3.781(4) Å, slippage of 1.40Å). The structure is close comparable to the phenantroline derivative, $[Cd_2(phen)_4(NIPH)_2]$, that lacks of lattice water molecules [169] with metals separated by a sensibly longer distance, 10.206(3) Å.

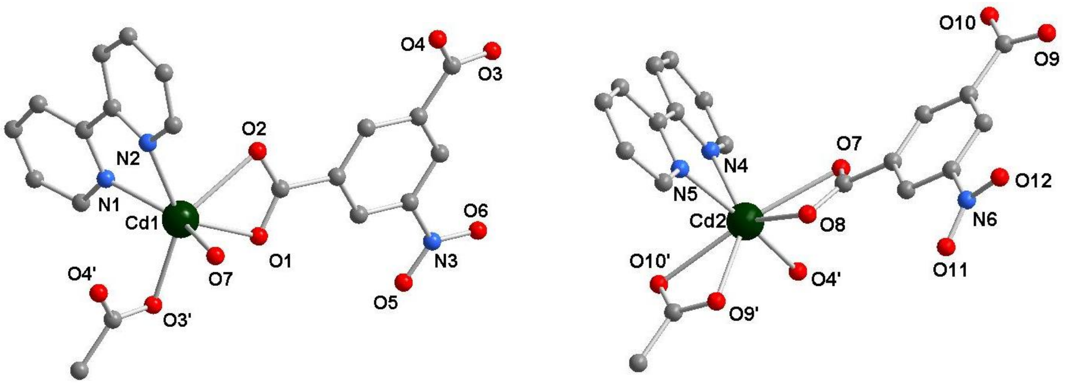


Fig. 3.4 Coordination sphere of the two independent cadmium atoms in **4**.

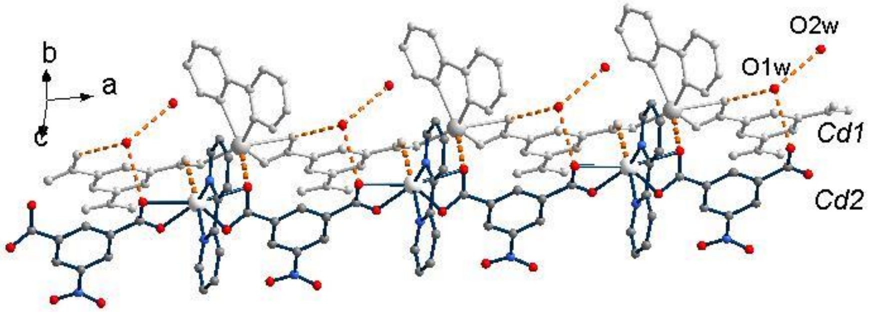


Fig. 3.5 The couple of coordination polymers formed by Cd1 and Cd2 ions in compound **4**. The H-bond connections of O1w with carboxylate oxygens of the chains are also shown.

Table 3.3 Selected bond lengths (Å) and angles (°) for compound **4**.

Cd(1)-O(1)	2.308(4)	Cd(2)-O(4)^{i}	2.341(4)
Cd(1)-O(2)	2.477(4)	Cd(2)-O(7)	2.572(4)
Cd(1)-O(3)^{i}	2.296(4)	Cd(2)-O(8)	2.335(4)
Cd(1)-O(7)	2.314(4)	Cd(2)-O(9)^{i}	2.250(4)
Cd(1)-N(1)	2.312(5)	Cd(2)-O(10)^{i}	2.607(4)
Cd(1)-N(2)	2.325(5)	Cd(2)-N(4)	2.273(5)
		Cd(2)-N(5)	2.336(5)

O(1)-Cd(1)-O(2)	54.72(15)	O(9)^{i}-Cd(2)-O(10)^{i}	53.80(14)
O(1)-Cd(1)-N(1)	114.46(17)	O(9)^{i}-Cd(2)-O(7)	131.69(15)
O(1)-Cd(1)-N(2)	134.90(17)	O(9)^{i}-Cd(2)-O(8)	84.02(15)
O(1)-Cd(1)-O(7)	97.55(15)	O(9)^{i}-Cd(2)-N(4)	140.08(17)
O(3)^{i}-Cd(1)-O(2)	136.23(15)	O(9)^{i}-Cd(2)-N(5)	89.92(18)
O(3)^{i}-Cd(1)-O(1)	82.09(15)	O(7)-Cd(2)-O(10)^{i}	163.88(14)
O(3)^{i}-Cd(1)-N(1)	88.06(18)	O(8)-Cd(2)-O(4)^{i}	103.77(16)
O(3)^{i}-Cd(1)-N(2)	142.34(17)	O(8)-Cd(2)-O(10)^{i}	137.26(14)
O(3)^{i}-Cd(1)-O(7)	95.10(17)	O(8)-Cd(2)-O(7)	53.62(14)
N(1)-Cd(1)-O(2)	102.53(16)	O(8)-Cd(2)-N(5)	87.61(18)
N(1)-Cd(1)-N(2)	71.39(19)	N(4)-Cd(2)-O(4)^{i}	99.24(16)
N(1)-Cd(1)-O(7)	147.95(17)	N(4)-Cd(2)-O(10)^{i}	88.94(16)
N(2)-Cd(1)-O(2)	80.18(16)	N(4)-Cd(2)-O(7)	88.13(16)
O(7)-Cd(1)-O(2)	97.09(15)	N(4)-Cd(2)-O(8)	128.50(17)

O(7)-Cd(1)-N(2)	87.52(17)	N(4)-Cd(2)-N(5)	71.72(19)
O(4)^{i}-Cd(2)-O(10)^{i}	86.75(14)	N(5)-Cd(2)-O(4)^{i}	168.49(17)
O(4)^{i}-Cd(2)-O(7)	78.08(14)	N(5)-Cd(2)-O(10)^{i}	85.98(17)
O(9)^{i}-Cd(2)-O(4)^{i}	92.98(16)	N(5)-Cd(2)-O(7)	108.08(17)

Primedatomsat−1+x,y,z

3.4.1.3. Structural description of $\{[Cd_2(bipy)_4(BDAC)(NO_3)](NO_3).6H_2O\}_n$(5).

The crystal structure of compound **5** reveals a 1D zig-zag coordination chain built by Cd(bipy)$_2$ units alternatively connected by a bridging nitrate and a benzenediacrylate anion. The Cd ion is thus chelated by two bipy ligands and one carboxylic group, and completes the coordination sphere with nitrate oxygen (Fig. 3.6). The bond length and angles are listed in Table 3.4. The Cd-N bond distances in between 2.327(5) - 2.431(4) Å are slightly longer than those measured in **4**, while the Cd-O (carboxylate) bond values of 2.425(5) and 2.488(6) Å are slightly longer compared to that of the nitrate, of 2.390(5) Å. These connections give rise to a polymeric species as depicted in Fig. 3.7, where the metals are alternatively separated by 16.065(1)Å (through benzenediacrylate) and 6.660(1)Å (though nitrate). The intermetallic angle is of 85.79(1) °. In the crystal the bridging nitrate is located on a crystallographic two-fold axis comprising the N3-O4 bond, while the aromatic ring of the organic anion is sitting on an inversion center, so that the benzenediacrylate adopts a trans conformation with symmetric chelating behavior of carboxylate groups. The dihedral angle formed by the CH=CH-COO^{-}groups with the phenyl ring is of 9.3°, indicating the presence of a π-π electronic conjugation in the BDAC moiety.

When viewed down axis *c* the crystal packing of compound **5** shows 1-D channels occupied by uncoordinated nitrate anions and lattice water molecules (one of which disordered,

Fig.3.8) that connect the coordination chains through H-bonds to give rise to a 3D supramolecular network. The program Platon calculated a volume of 616.6Å^3 (11.0 % of the unit cell) accessible to solvent molecules.

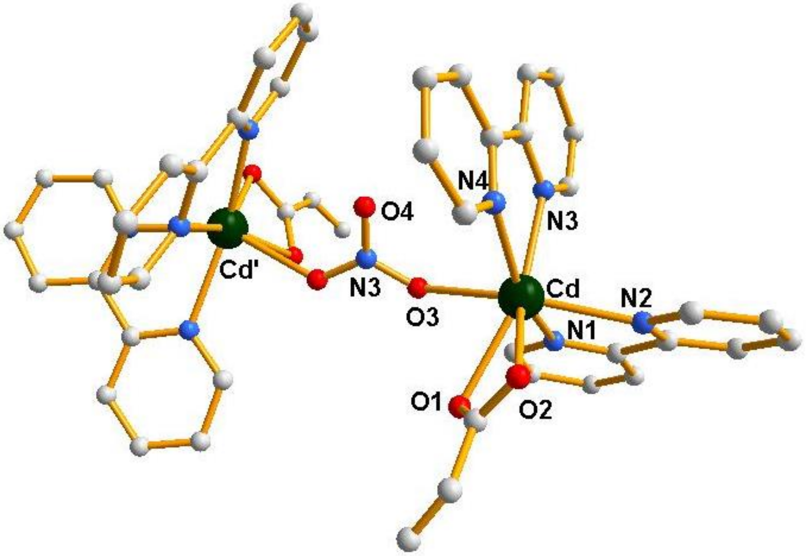


Fig. 3.6 Coordination sphere of cadmium atom in **5**. The bridgingnitrate is located on a crystallograhic two-fold axis.

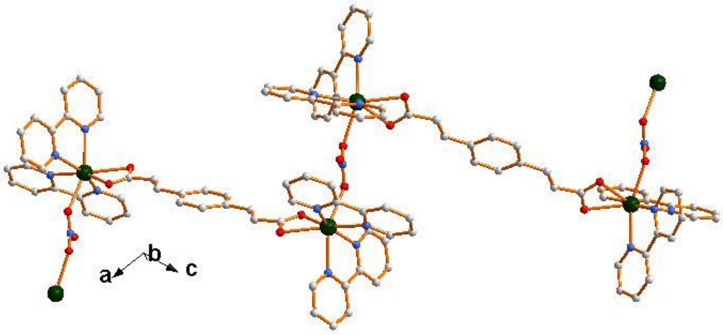


Fig. 3.7 Coordination polymer of compound **5**.

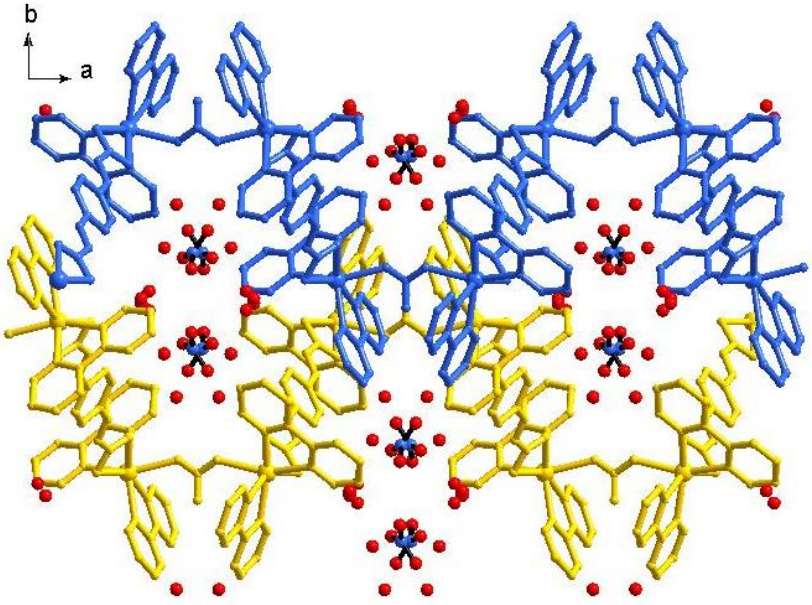


Fig. 3.8 Crystal packing viewed down axis *c* of compound **5** showing two coordination polymers and the channels filled by lattice water molecules and uncoordinated nitrate anions.

Table 3.4. Selected bond lengths (Å) and angles (°) for compound **5**.

Cd(1)-O(1)	2.425(5)	Cd(1)-N(1)	2.342(5)
Cd(1)-O(2)	2.488(6)	Cd(1)-N(2)	2.355(5)
Cd(1)-O(3)	2.390(5)	Cd(1)-N(3)	2.431(4)
		Cd(1)-N(4)	2.327(5)

O(1)-Cd(1)-O(2)	52.40(2)	N(2)-Cd(1)-O(1)	85.63(18)
O(1)-Cd(1)-N(3)	156.63(18)	N(2)-Cd(1)-O(2)	120.72(18)
O(3)-Cd(1)-O(1)	72.57(19)	N(2)-Cd(1)-O(3)	83.20(19)
O(3)-Cd(1)-O(2)	113.90(2)	N(2)-Cd(1)-N(3)	86.10(16)
O(3)-Cd(1)-N(3)	84.76(17)	N(3)-Cd(1)-O(2)	147.77(19)
N(1)-Cd(1)-O(1)	107.08(18)	N(4)-Cd(1)-O(1)	116.40(17)
N(1)-Cd(1)-O(2)	83.60(2)	N(4)-Cd(1)-O(2)	83.08(19)

N(1)-Cd(1)-O(3)	152.90(2)	N(4)-Cd(1)-O(3)	92.86(17)
N(1)-Cd(1)-N(2)	69.90(2)	N(4)-Cd(1)-N(1)	110.30(2)
N(1)-Cd(1)-N(3)	90.45(16)	N(4)-Cd(1)-N(2)	155.43(17)
		N(4)-Cd(1)-N(3)	69.37(17)

3.4.2. Luminescence study

The luminescence study of the ligands and related complexes were performed in solid state at room temperature. Free H_2NIP ligand exhibits an intense emission maximum at 430 nm and a shoulder peak at 461 nm upon excitation with a wavelength of 280 nm (Fig. 3.9). When complex **3** is excited at 295 nm, a strong emission band is observed at 465 nm (Fig. 3.10), which is red shifted in comparison to its related ligand H_2NIP. On the other hand, during the study of compound **4** with a λ_{Ex} of 280 nm an emission band at 420 nm is observed (Fig. 3.11). Here the band is blue shifted with respect to the free ligand. The second ligand H_2BDAC shows peaks at 406 and 427 nm, when excited with a wavelength of 280 nm (Fig. 3.12). The related Cd (II) complex **5** under same excitation wavelength show red shifted emission band at 452 nm when excited at 243 nm (Fig. 4.13). Since both Zn(II) and Cd(II) are d^{10} systems, it is really difficult for these to undergo oxidation or reduction process. The spectral behavior of these complexes is neither due to metal-to-ligand nor ligand-to-metal charge transfer transition. Hence, metal perturbed intraligand π–π* charge transfer transition is responsible for the emission behavior of the reported complexes. [170]

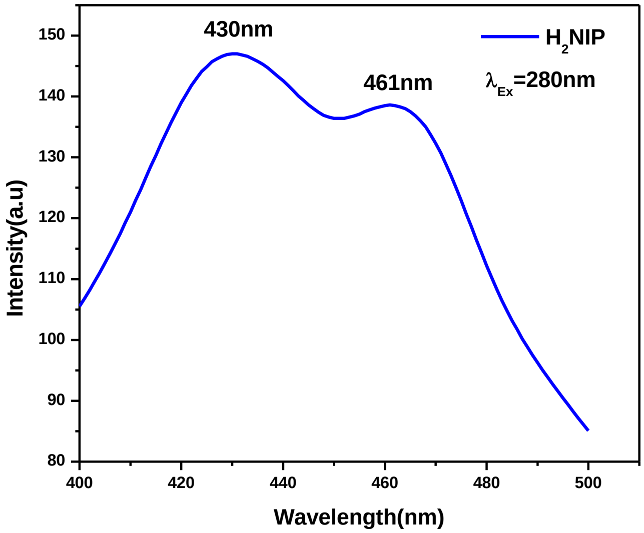


Fig. 3.9 Emission spectrum of 5-nitro-isophthalic acid, H_2NIP (λ_{Ex} = 280 nm).

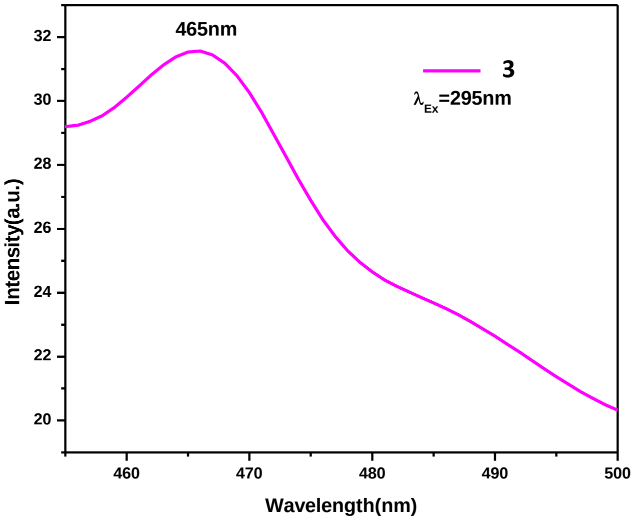


Fig. 3.10 Emission spectrum of **3**(λ_{Ex} = 295 nm).

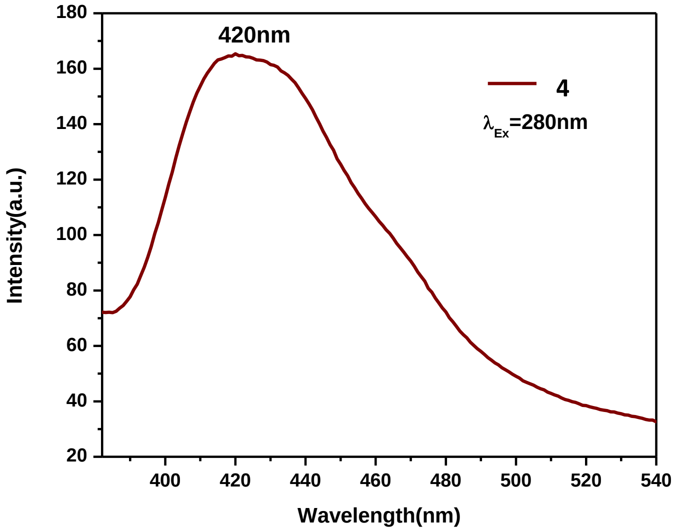


Fig. 3.11 Emission spectrum of **4**(λ_{Ex} = 280 nm).

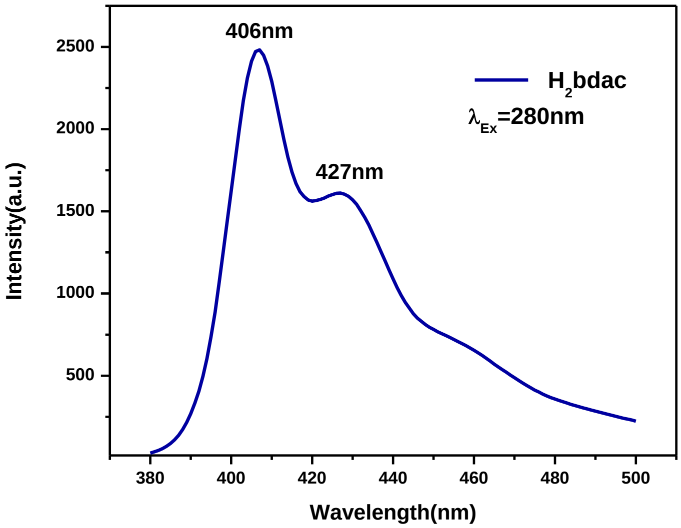


Fig. 3.12 Emission spectrum of 1,4-benzenediacrylic acid, H_2BDAC (λ_{Ex} = 280 nm).

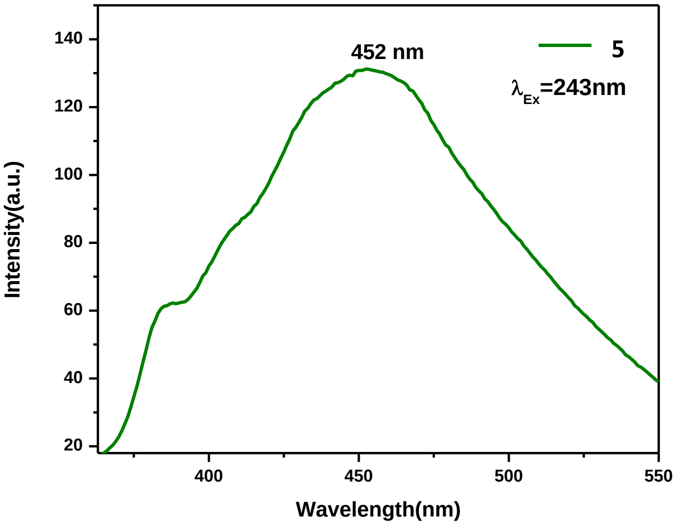
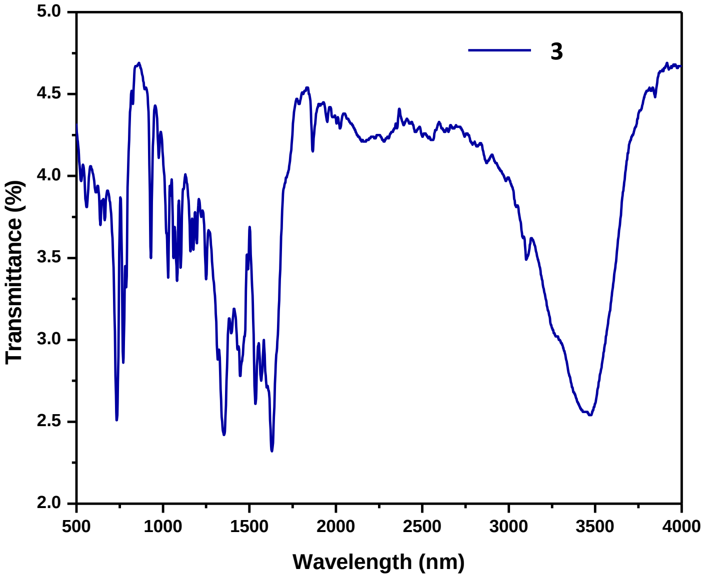
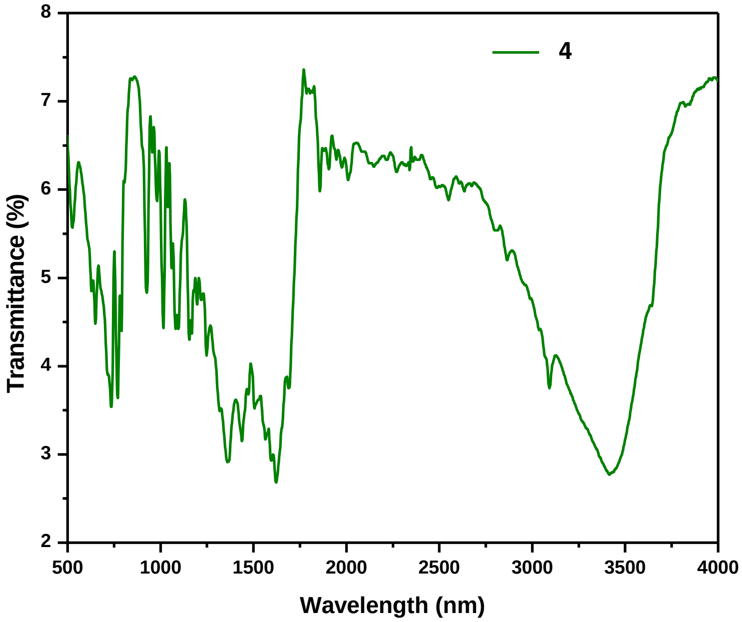


Fig. 3.13 Emission spectrum of **5** (λ_{Ex} = 243 nm)

3.4.3. IR study

The IR spectral analysis of complexes **3-5** shows a broad band in the region 3200-3500 cm^{-1} [ν(O-H)], suggesting the presence of H_2O molecules [44]. ν_{as}(OCO), ν_s(OCO) bands (in cm^{-1}) appear at 1639, 1453; 1697, 1443 and 1647,1423 for **3**, **4** and **5**, respectively, indicating the involvement of carboxylate in the coordination.





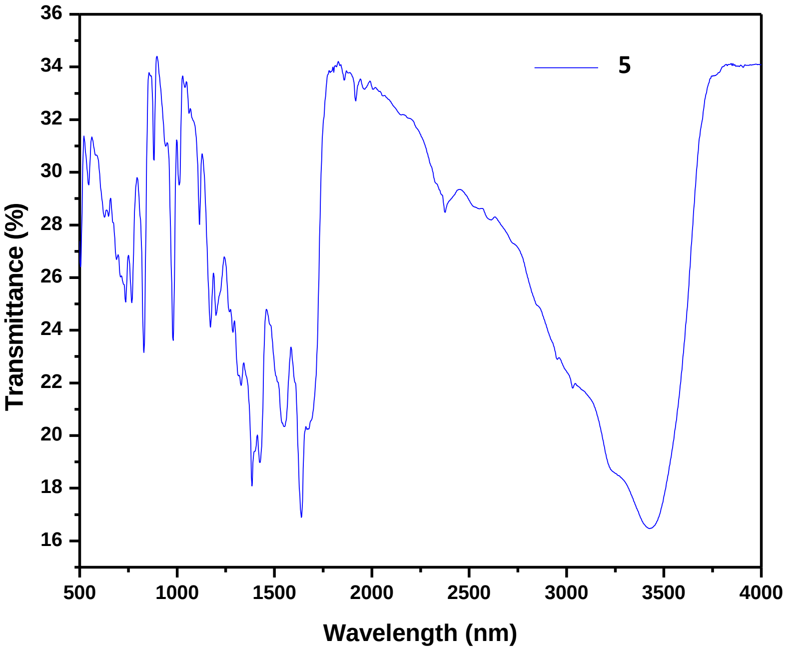


Fig. 3.14 IR spectrum of complex **3, 4** and **5.**