Chapter 4

Three new manganese(II) coordination polymers with mixed donor ligands: synthesis, x-ray structures and luminescence properties

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4.1. Introduction

Coordination polymers (CPs) of different dimensionality are among the most flourishing studied classes with in organic–inorganic hybrid functional materials [171]. Crystal engineering of CPs has attracted great interest in recent years due to their enormous potential as possible application in catalysis, chirality, conductivity, luminescence, magnetism, spin-transition (spin-crossover), non-linear optics (NLO) and porosity or zeolitic behavior upon which potential applications could be based. [172] The chemistry of the coordination polymers has in recent years advanced expansively, affording a variety of architectures, which are constructed from a variety of molecular building blocks with different interactions between them. [109] Design and prediction of the final material having the desired crystalline framework represent a big challenge, because many factors such as metal ion type, connectivity of organic ligands, solvent, pH, and temperature of the reaction system could play a great influence on the self-assembly process and thus on the properties of final products [173]. Literature survey shows that the most commonly used strategies for the synthesis of MOFs are the use of (a) anionic bridging ligands, which, in addition, can partially or fully counterbalance the charge of the metal centers, (b) suitable anionic as well as neutral spacers to increase the possibility of enhancing the dimension of the coordination polymers, and (c) only neutral spacers, where charges of the metal centers are counterbalanced by non-coordinating anions.

For the synthesis of benzene multi-carboxylate CPs essentially two strategies have been adopted. The first one was the systematic use of benzene multi-carboxylate ligands with various substituent groups on the benzene ring, [174-184] while the second is characterized by a new family of flexible benzene derivatives with long-spanning carboxyl groups.[185] There are several CPs with fascinating topologies formed by semi-rigid benzene dicarboxylate ligands combining rigid –COOH and flexible $–CH_2COOH$ carboxyl groups, and 1,4-phenylenediaceticacid (H_2pda) and 3-(4-carboxyphenyl)propionic acid are distinctive examples of such flexible ligands. This kind of flexible phenyl dicarboxylate ligands can adopt various conformations according to geometric requirements when they react with different metal salts and may afford unpredictable and intriguing frameworks, furnishing further understanding of the assembly process of supramolecular networks. In addition with the aim to obtain coordination metal complexes with various topologies, multi-carboxylates are often selected not only for their versatile coordination modes as bridging ligands but also for their strong ability to act as hydrogen bonding acceptors and donors [186-188, 57,189]. Therefore the combination of both dicarboxylate species and N-containing auxiliary ligands (such as bridging 4,4'-bipyridine or chelating 1,10-phenanthroline) provides a suitable choice and is of great potential for the construction of novel topological CPs.[190] The nitro group with electron withdrawing effect has been introduced into phthalic acid to get 4-nitrophthalic acid, a coordinating anion used in this study having different electronic effect and bulk.

In this chapter, we have successfully synthesized three new Mn(II) coordination polymers based on ligands with different hetero donors of composition $[Mn_3(phen)_2(phdac)_3].2H_2O$ (**6**), $[Mn(4,4'\text{-bipy})(H_2O)_4](cbprop)$ (**7**) and $[Mn(2,2'\text{-bipy})(4\text{-nph})(H_2O)_2]_2$ (**8**) (phen = 1,10-phenanthroline, 4,4´-bipy = 4,4´-bipyridine, 2,2´-bipy = 2,2´-bipyridine, H_2phdac = 1,4-phenylenediacetic acid, H_2cbprop = 4-carboxybenzenepropanoic acid and H_2nph = 4-nitrophtalic acid). The three compounds have been characterized by IR spectroscopy, elemental analysis and fluorescent spectroscopy. The X-ray single-crystal diffraction analysis has been also performed in order to elucidate the detailed crystal structures of these species.

4.2. Experimental

4.2.1. Materials

Manganese acetate tetrahydrate was purchased from Merck. 1,10-phenanthroline, 4,4'-bipyridine, 2,2'-bipyridine,1,4-phenylenediacetic acid, 4-carboxybenzenepropanoic acid and 4-nitrophtalic acid were purchased from Sigma-Aldrich Inc.

4.2.2. Physical Measurements

As mentioned in Section 2.2.2 in Chapter 2.

4.2.3. Synthesis of the complexes

4.2.3.1. Synthesis of $[Mn_3(phen)_2(phdac)_3].2H_2O$ (6)

$Mn(OAc)_2{}^{\cdot}4H_2O$ (0.5 mmol, 0.1225 g), 1,4-phenylene diacetic acid (1mmol, 0.1941 g), 1,10-phenanthroline (1 mmol, 0.1980 g) were stirred in deionized water (10mL) at room temperature until a homogeneous mixture was obtained. The mixture was transferred into a Teflon-lined autoclave (25mL) and heated at 180°C for 2 days and then cooled to room temperature under ambient conditions. Colorless block single crystals were isolated by decanting the supernatant liquid and washed with deionized water, ethanol and dried in air. Yield: 56% Anal. Calc. (%) for $C_{54}H_{44}Mn_3N_4O_{14}$ (1137.75): C, 57; H, 3.89; N, 4.92. Found (%): C, 56.98;H, 3.91; N, 4.93. IR (cm^{-1}): 580 (W), 683 (s), 731 (s), 784 (m), 812 (w), 856 (s), 936 (m), 999 (w), 1034 (w), 1097 (w), 1149 (w), 1195 (w), 1230 (w), 1310(w), 1417 (broad), 1605 (broad), 3483 (broad).

4.2.3.2. Synthesis of [Mn(4,4'-bipy)(H_2O)$_4$](cbprop)(7)

$Mn(OAc)_2{\cdot}4H_2O$ (1mmol, 0.2450 g), 3-(4-carboxyphenyl)propionic acid (1mmol, 0.1941 g) and 4,4'-bipyridine (0.1561 mmol, 1 g) were dissolved in10 mL of deionized water in 1:1:1 ratio. The pH of the resulting solution was adjusted to 5 by the 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 at room temperature and the resulting needle shaped crystals were isolated by decanting the supernatant liquid, then washed with deionized water, ethanol and dried in air. Yield: 58% Anal. Calc. (%) for $C_{20}H_{26}MnN_2O_9$ (493.37): C, 48.68; H, 5.31; N, 5.67. Found (%): C, 48.70;H, 5.30; N, 5.70. IR (cm^{-1}): 535 (w), 616 (m), 624 (s), 722 (w), 784 (w), 812 (w), 946 (w), 1008 (s), 1044 (s), 1070 (s), 1132 (w), 1185 (m), 1221 (w), 1247 (w), 1373 (w), 1417 (s), 1569 (m), 1650 (broad), 1961 (w), 3466 (broad).

4.2.3.3. Synthesis of [Mn(2,2'-bipy)(4-nph)(H_2O)$_2$]$_2$ (8)

$Mn(OAc)_2{\cdot}4H_2O$ (0.5 mmol, 0.1225 g), 4-nitrophthalic acid (1mmol, 0.2111 g) and 2,2'-bipyridine (1 mmol, 0.1561 g) were taken in a 50 ml round bottom flask in a molar ratio of 1:2:2. 10 ml of deionized water were added and the whole mixture was refluxed for 3 h. Then the solution was allowed to cool to room temperature and filtered. The filtrate was kept in desiccator in dark for crystallization. Diffraction quality single crystals were obtained from the transparent solution after 3 days. Single crystals were isolated by decanting the supernatant liquid and were washed with deionized water, ethanol and dried in air. Yield 54 %.Anal. Calc. (%) for $C_{18}H_{15}MnN_3O_8$ (456.27): C, 47.55; H, 3.31; N, 9.20; Found: C, 47.58; H;3.33; N,9.22 . FT- IR (cm^{-1}): 652 (m), 741 (s), 767 (s), 803 (w), 838 (m), 901 (s), 972 (w), 1061 (m), 1070 (m), 1160 (s), 1240 (m), 1355 (w), 1390 (w), 1426 (w), 1443 (w), 1479 (m), 1515 (w), 1596 (broad), 1792 (w), 3483 (broad).

4.3. X-ray diffraction crystallography

Data collections of compounds **6** and **8** were carried at 120(2) K on a Xcalibur Sapphire3 diffractometer, while intensities data of **7** were collected at 100(2) K on a Bruker APEX-II CCD diffractometer, all equipped with Mo-Kα graphite monochromatized radiation ($\lambda = 0.71073$ Å). Cell refinement, indexing and scaling of the data sets were carried out using the CrysAlisPro,[191] Bruker APEX2 and Bruker SAINT packages [192]. All the structures were solved by using direct methods and subsequent Fourier analyses, [137, 192] and refined by the full-matrix least-squares method based on F^2 with all observed reflections [137]. One methylene group of the 1,4-phenylenediacetate anion was found disordered over two close positions with 0.6/0.4 occupancies based on the electron density map heights. Hydrogen atoms were placed at calculated positions with exception of those of water molecules detected on the difference Fourier map. In compound **7** some O-H distances were restrained at 0.83(1) or 0.85(1) Å, while in compound **8** water H atoms were treated with instruction AFIX 7 of Olex2 program [192]. Molecular graphics were done using the Diamond program. [140] Crystal data and details of refinements are given in Table 4.1.

Table 4.1. Crystallographic data and details of refinements for complexes **6-8**.

	6	**7**	**8**
Empirical formula	$C_{54}H_{44}Mn_3N_4O_{14}$	$C_{20}H_{26}MnN_2O_9$	$C_{18}H_{15}MnN_3O_8$
M	1137.75	493.37	456.27
Crystal system	Triclinic	Triclinic	Triclinic

Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a /Å	10.8218(2)	7.7180(6)	7.0819(4)
b /Å	11.1145(2)	12.0620(9)	10.3438(6)
c /Å	12.5413(3)	13.1994(9)	12.7279(7)
α /°	107.0477(18)	110.800(2)	90.275(5)
β /°	100.3527(18)	91.295(2)	102.952(5)
γ /°	116.759(2)	106.262(2)	100.302(5)
V /Å^3	1198.81(5)	1092.50(14)	893.01(9)
Z	1	2	2
Dcalc /g cm^{-3}	1.576	1.500	1.697
μ /mm^{-1}	0.854	0.662	0.796
F(000)	583	514	466
Total data	109682	26690	7825
Unique data	10562	7476	4091
Rint	0.0524	0.0326	0.0317
Reflections$I>2\sigma(I)$	8897	6857	3370
Parameters	352	311	274
Goodness-of-fit	1.056	1.157	1.050
R_1	0.0310	0.061	0.0406
wR_2 ($I>2\sigma(I)$) [a]	0.0766	0.1500	0.0802
Residuals /e Å^{-3}	0.611, –0.316	1.848, –1.815	0.387, –0.342

[a] $R1 = \Sigma\, |Fo|–|Fc||\, /\, \Sigma|Fo|$, $wR2 = [\Sigma w\, (Fo^2– Fc^2)^2/\, \Sigma w\, (Fo^2)^2]^{½}$

4.4. Results and discussion

4.4.1. Description of crystal structures

4.4.1.1. Structural description of $[Mn_3(phen)_2(phdac)_3].2H_2O$ (6).

The X-ray structural analysis of compound **6**, of formulation $[Mn_3(phen)_2(phdac)_3].2H_2O$, revealed that it forms a 2D coordination polymer parallel to the (111) crystallographic planes. The crystal packing shows trinuclear manganese (II) entities featuring two Mn(phen) moieties that sandwich another manganese ion by means of six bridging carboxylate groups in a centrosymmetric fashion (Fig. 4.1). In fact Mn1 and Mn2, at a distance of 3.6036(1) Å, are bridged by carboxylate groups O1/O2, O3/O4 and in addition by single carboxylate oxygen (O5). Both the independent Mn1 and Mn2 ions present an octahedral geometry with a N_2O_4 and O_6 octahedral coordination geometry, respectively, and in case of Mn1 the coordination geometry considerably deviates from the ideal values. A selection of coordination bond distances and angles for the two metal ions is shown in Table 4.2. The Mn-O bond lengths vary in a wide range from 2.0813(8) to 2.3692(8)Å, showing a variable interaction of oxygen donors towards the metals, while the Mn1-N bond distances are of 2.2374(9) and 2.2724(9)Å, with a chelating N1-Mn1-N2 bond angle of 74.06(3)°.

The crystal packing is a 2D coordination polymer of (4,4) topology where the trinuclear units represent the nodes and the edges are formed by a pair of phdac (through O1/O2/O3/O4 oxygen atoms) and by a single phdac anion (O5/O6), the latter positioned on a center of symmetry (Fig. 4.2). The layers are interdigitated so that facing phen pyridine rings interact through π-π interactions (centroid-to-centroid distance of 3.7438(1) Å). In addition lattice water molecules bridge carboxylate oxygen O3 and O6 of different layers by means of weak H-bonds (O1w…O6 = 2.9772(1)Å; O1w…O3 = 3.0144(1)Å), thus forming a 3D architecture, as depicted in Fig. 4.3. The compound is iso-structural to the bipy derivative reported a few years ago [193], while a dinuclear complex with a phdac anion connecting two [Mn(phen)(H_2O)$_3$] units has been also reported [194]. The bond distances and angles of these compounds compare well with those here reported.

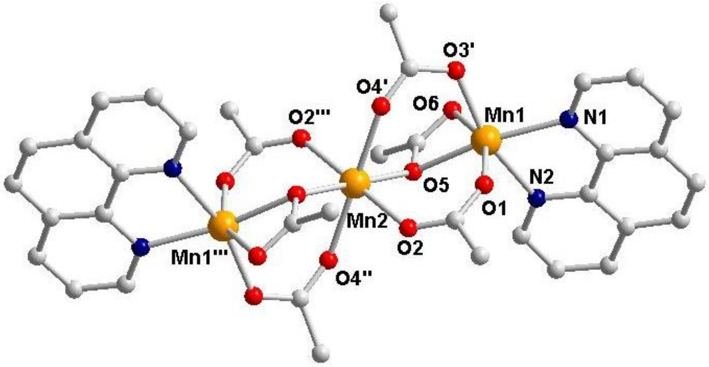


Fig. 4.1 The centrosymmetric trinuclear unit in compound **6**.

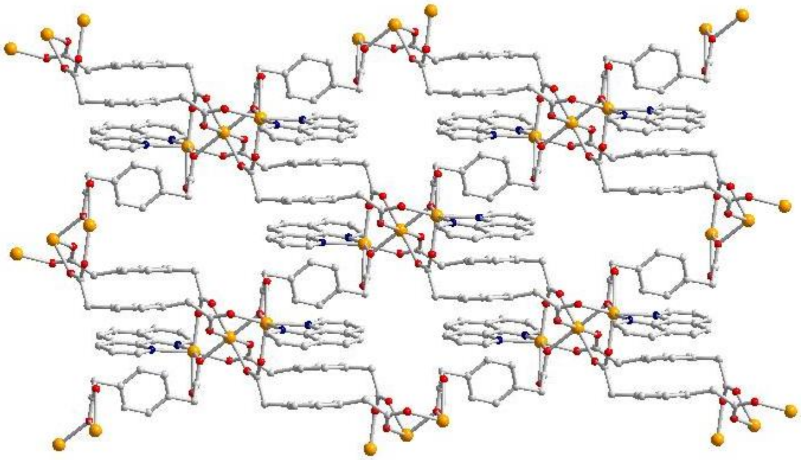


Fig.4.2 The 2D architecture of compound **6**.

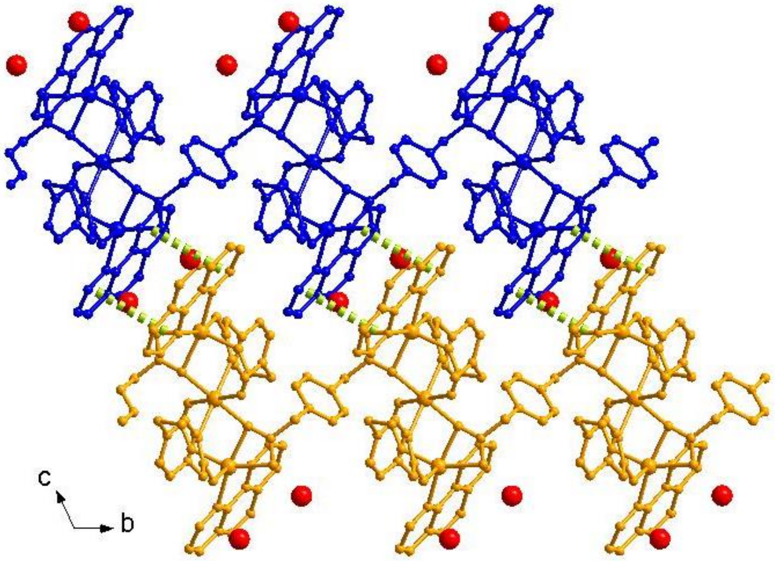


Fig. 4.3 2D layers viewed down axis *a* with indications of π-π interaction (in green). Lattice water molecules indicated as big red sphere also connect the polymeric layers through H-bonds.

Table 4.2. Bond distances (Å) and angles (°) for complex **6**$^{(a)}$

Mn(1)-O(1)	2.0813(8)	Mn(2)-O(2)	2.1491(7)
Mn(1)-O(3')	2.0980(7)	Mn(2)-O(4')	2.2362(7)
Mn(1)-O(5)	2.2222(7)	Mn(2)-O(5)	2.1955(7)
Mn(1)-O(6)	2.3692(8)		
Mn(1)-N(1)	2.2374(9)	O(5)-Mn(1)-O(6)	57.25(3)
Mn(1)-N(2)	2.2724(9)	O(5)-Mn(1)-N(1)	166.19(3)
		O(5)-Mn(1)-N(2)	92.72(3)
O(3')-Mn(1)-O(5)	98.24(3)	N(1)-Mn(1)-O(6)	117.33(3)
O(3')-Mn(1)-O(6)	84.96(3)	N(1)-Mn(1)-N(2)	74.06(3)
O(3')-Mn(1)-N(1)	93.66(3)	N(2)-Mn(1)-O(6)	89.06(3)
O(3')-Mn(1)-N(2)	162.00(3)	O(2)-Mn(2)-O(4')	94.03(3)
O(1)-Mn(1)-O(3')	98.25(3)	O(2)-Mn(2)-O(4")	85.97(3)

O(1)-Mn(1)-O(5)	96.85(3)	O(2)-Mn(2)-O(5''')	87.76(3)
O(1)-Mn(1)-O(6)	154.03(3)	O(2)-Mn(2)-O(5)	92.24(3)
O(1)-Mn(1)-N(1)	88.30(3)	O(5)-Mn(2)-O(4')	86.84(3)
O(1)-Mn(1)-N(2)	94.56(3)	O(5)-Mn(2)-O(4")	93.16(3)

(a) Mn2 located on a crystallographic inversion center. Symmetry codes: (') 1+x, y, z; (") -x, 1-y, 1-z; ("') 1-x,1-y,1-z.

4.4.1.2. Structural description of [Mn(4,4'-bipy)(H_2O)$_4$](cbprop)(7).

The asymmetric unit of compound **7** is shown in Fig. 4.4 and comprises the metal unit Mn(4,4´-bipy)(H_2O)$_4$ beside the 4-carboxyphenylpropionate dianion and a lattice water molecule. The structural determination of the this complex reveals Mn(H_2O)$_4$units bridged by 4,4´-bipyridine ligands with the occurrence of 1D coordination polymeric chains. In the chain the metal exhibits a slightly distorted octahedral geometry with a MnN_2O_4 chromophore, where the metal coordination sphere is completed by four water molecules. The four water molecules form the equatorial plane around each metal with Mn-O distances in between 2.151(2)-2.222(2) Å; the 4,4´-bipy nitrogen atoms N(1) and N(2) occupy the *trans* axial positions at slightly longer distances (Mn-N(1) 2.255(2), Mn-N(2) 2.293(2)Å) (Table 3). The 4,4´-bipy bridging ligands are located on crystallographic inversion centers and thus have coplanar atoms, but the mean planes of the two independent ligands are tilted by ca. 60.09°, as evident from Fig. 4.5. The carboxylate groups of the dicarboxylate anion are tilted by 7.5 and 71.0° with respect the mean plane through the aromatic ring; a conformation likely dictated in order to form H-bonds as described below.

The crystal packing evidences the 4-carboxyphenylpropionate dianions encapsulated among the polymeric chains to give rise to a 3D structure through an ordered H-bonded scheme assisted also by lattice water molecules. The H-bond parameters are reported in Table 4.5. A 3D architecture is thus created by the described H-bond scheme and in addition by weak π-π

interactions between the 4-carboxyphenylpropionate ring and pyridine ring N1 (centroid-to-centroid distance of 4.0058(3) Å). The bridging 4,4´-bipy ligand spans the metals at 11.610 and 11.704 Å, while the shorter inter chain Mn-Mn separation in the 3D architecture is 6.805 Å. A number of analogous [Mn(4,4´-bipy)(H_2O)$_4$]$_n$ structural motives have been reported having aromatic dianions (i.e. terephthalate [195] and croconate [196]) encapsulated among the coordination chains.

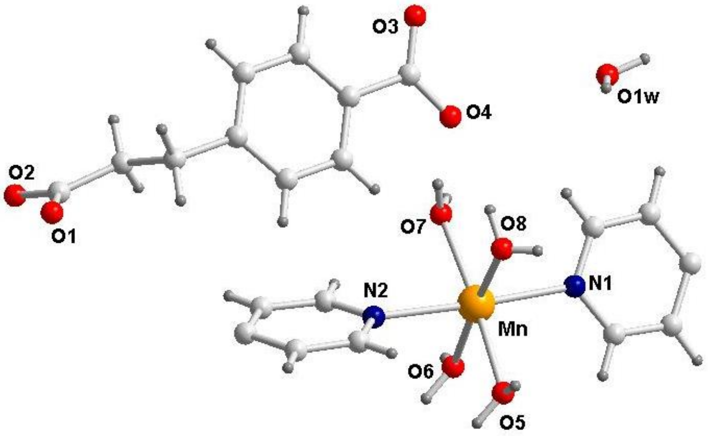


Fig. 4.4 A symmetric unit of compound **7** with label scheme of N and O atoms.

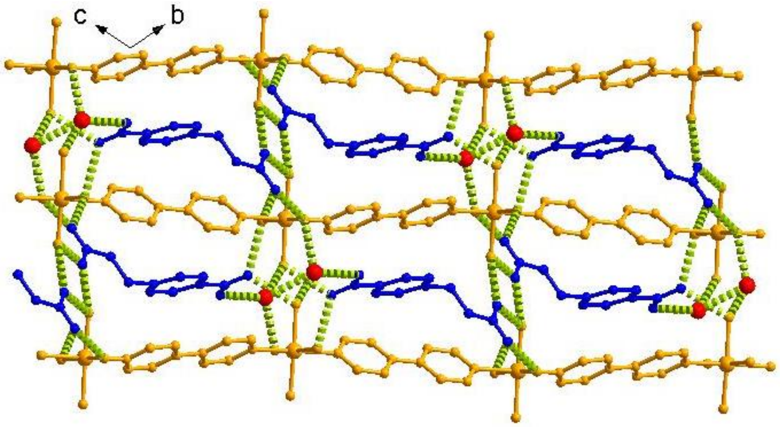


Fig. 4.5 Crystal packing of compound **7** with indication of H-bonds among the [Mn(H_2O)$_4$(bipy)]$_n$ polymers, the dicarboxylate anions and the lattice water molecule.

Table 4.3 Bond distances (Å) and angles (°) for complex **7**

Mn-O(5)	2.174(2)	Mn-O(8)	2.222(2)
Mn-O(6)	2.151(2)	Mn-N(1)	2.255(2)
Mn-O(7)	2.163(2)	Mn-N(2)	2.293(2)
O(6)-Mn-O(7)	100.28(9)	O(7)-Mn-N(1)	91.75(8)
O(6)-Mn-O(5)	83.06(9)	O(5)-Mn-N(1)	94.27(8)
O(7)-Mn-O(5)	173.08(8)	O(8)-Mn-N(1)	90.25(8)
O(6)-Mn-O(8)	173.71(9)	O(6)-Mn-N(2)	88.53(10)
O(7)-Mn-O(8)	85.87(8)	O(7)-Mn-N(2)	84.62(9)
O(5)-Mn-O(8)	90.69(8)	O(5)-Mn-N(2)	89.43(9)
O(6)-Mn-N(1)	90.84(8)	O(8)-Mn-N(2)	90.79(9)
		N(1)-Mn-N(2)	176.14(9)

Table 4.5 H-bond parameters (Å/deg) for complex **7** and **8**.

Complex 7						
D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A	Symmetry code A
O(5)-H(5a)	0.83	1.91	172	2.7323(2)	O(9)	-x,1-y,1-z
O(5)-H(5b)	0.83	1.86	170	2.6835(2)	O(2)	-x,1-y,-z
O(6)-H(6a)	0.89	1.82	174	2.7015(2)	O(1)	-x,1-y,-z

O(6)-H(6b)	0.83	1.87	160	2.6653(2)	O(1)	x,-1+y,z
O(7)-H(7a)	0.85	1.78	171	2.6296(2)	O(2)	1-x,1-y,-z
O(7)-H(7b)	0.81	1.95	167	2.7471(2)	O(4)	-
O(8)-H(8a)	0.77	1.90	172	2.6670(2)	O(4)	1-x,1-y,1-z
O(8)-H(8b)	0.86	2.22	168	3.0623(2)	O(4)	-
O(9)-H(9a)	0.86	1.94	161	2.7629(2)	O(8)	-
O(9)-H(9b)	0.87	1.77	161	2.6123(2)	O(3)	-1+x ,y, z

Complex 8						
O1w-H1a	0.87	2.42	134	3.0818(2)	O4	1+x,1+y,z
O1w-H1a	0.87	2.24	138	2.9401(2)	O6	-x,2-y,-z
O1w-H1b	0.87	1.95	165	2.7981(2)	O2	1+x,1+y,z
O2w-H2a	0.87	2.20	129	2.8307(2)	O2	1+x,1+y,z
O2w-H2b	0.87	1.86	171	2.7192(2)	O5	-

4.4.1.3. Structural description of [Mn(2,2’-bipy)(4-nph)(H_2O)$_2$]$_2$ (8).

Compound **8**, [Mn_2(2,2'-bipy)(4-nph)(H_2O)$_2$]$_2$, is a centro-symmetric binuclear species where the Mn(II) atom has a distorted octahedral geometry being coordinated by a chelating 2,2'-bipy ligand, two mono-dentate carboxylate anions from two symmetry related 4-nitro-phthalates and two water molecules. The 4-nitro-phthalate anions, both in a bis-monodentate mode, bridge the metal ions to form the binuclear unit with inter metallic Mn-Mn distance of 5.1301(3) Å (Fig. 4.6). A selection of bond distances and angles is listed in Table 4.4. The Mn-O bond distances fall in a range 2.1291(16)-2.2170(15) Å and Mn-N1 and Mn-N2 distances are of 2.2728(17) and 2.2516(19)Å, respectively. These values are close comparable to those detected in the structure of the analogous centrosymmetric phen derivative [197] and in the range of those measured in other complexes here reported. Although the corresponding Mn complex with phen has close comparable geometry, it crystallizes in different space group (*P*bca), a feature likely due to a different π-π interaction arrangement among the complexes that addresses the final packing. In compound **8** intra-molecular O-H···O hydrogen bonds (Table 4.5) between the aqua ligands and uncoordinated carboxylate O atoms reinforce the whole structure (Fig. 4.6). In addition the water molecules link the dinuclear complexes to form supra-molecular chains propagating parallel to [100] direction (Fig. 4.7).

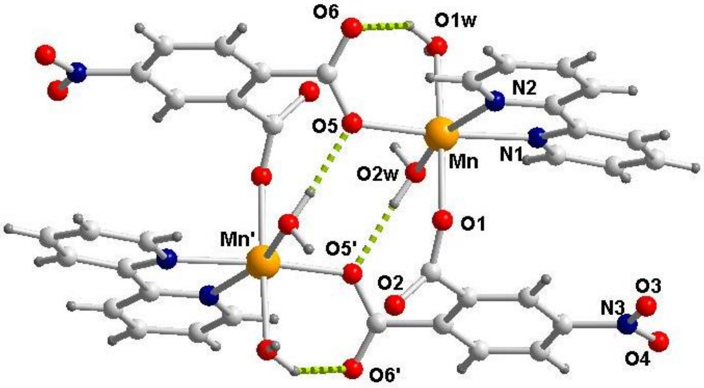


Fig. 4.6 The centrosymmetricdinuclear entity in compound **8** with indication of intramolecular H-bonds.

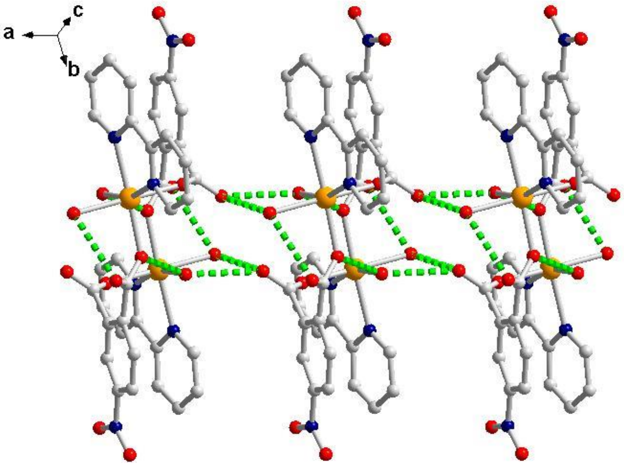


Fig. 4.7 H-bonds connecting dinuclear complexes to form a polymeric chain along axis *a*.

Table 4.4. Bond distances (Å) and angles (°) for complex **8**.

Mn-O(1)	2.1291(16)	Mn-O(2w)	2.2007(15)
Mn-O(5)	2.1373(14)	Mn-N(1)	2.2728(17)
Mn-O(1w)	2.2170(15)	Mn-N(2)	2.2516(19)
O(1)-Mn-O(5)	90.36(6)	O(5)-Mn-O(1w)	88.78(6)
O(1)-Mn-N(2)	89.73(6)	O(5)-Mn-O(2w)	93.35(6)
O(1)-Mn-N(1)	93.70(6)	N(2)-Mn-N(1)	72.57(6)
O(1)-Mn-O(1w)	176.80(6)	O(1w)-Mn-N(2)	93.47(6)
O(1)-Mn-O(2w)	89.32(6)	O(1w)-Mn-N(1)	87.33(6)
O(5)-Mn-N(2)	104.23(6)	O(2w)-Mn-N(2)	162.40(6)
O(5)-Mn-N(1)	174.80(6)	O(2w)-Mn-N(1)	89.95(6)
		O(2w)-Mn-O(1w)	87.65(6)

4.4.2. Luminescence study

The luminescence study of the complexes and related ligands were performed in solid state at room temperature. Free H_2phdac ligand exhibits an intense emission maximum at 287 nm upon excitation with a wavelength of 275 nm (Fig. 4.8) and phenanthroline shows emission maxima at 352 nm with a shoulder peak at 368 nm upon excitation with a wavelength of 243 nm (Fig. 4.9). When complex **6** is excited at 280 nm, a strong emission band is observed at 416 nm and a shoulder peak at 438 nm (Fig. 4.10), which is red shifted in comparison to the free ligands H_2phdac and phen. The emission behavior of the ligand may be explained as intra ligand π^*–π charge transfer transition.

The free H_2nph molecule shows emission bands at 430 nm upon excitation with a wavelength of 270 nm (Fig. 4.11), that can be ascribed as intraligand π^*–π or π^*-n charge transfer transitions [198-200]. However for complex **8** bands are observed at 414 and 467 nm, when excited at 300 nm (Fig. 4.12). The higher energy emission maximum of **8** is 16nm blue shifted while the low energy emission is red shifted by 37 nm in comparison to the free H_2nphligand. Since the Mn(II) ion is a d^5 system with stable half-filled electronic configuration, it is difficult for Mn(II) to get either oxidized or reduced.

The spectral behavior of these complexes is neither due to metal-to-ligand nor ligand-to-metal charge transfer transition. Hence the emission behavior of **6** and **8** are due to the metal perturbed intra ligand π^*–π charge transfer transition for **1** and π^*–πandπ^***-n** charge transfer transitions for **8**. [201]

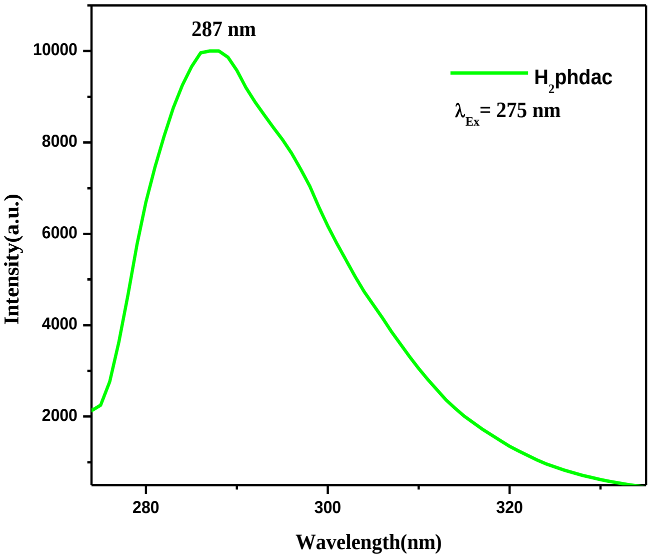


Fig.4.8 Emission spectrum of 1,4-phenylenediacetic, H_2phdac acid (λ_{Ex} = 275 nm).

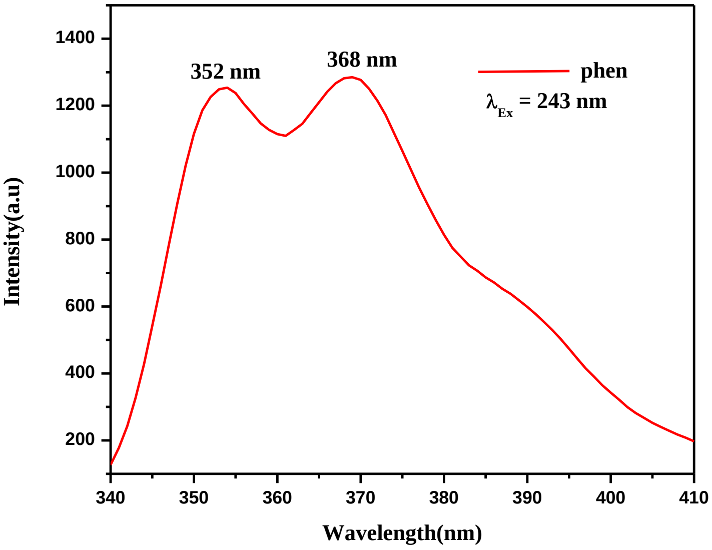
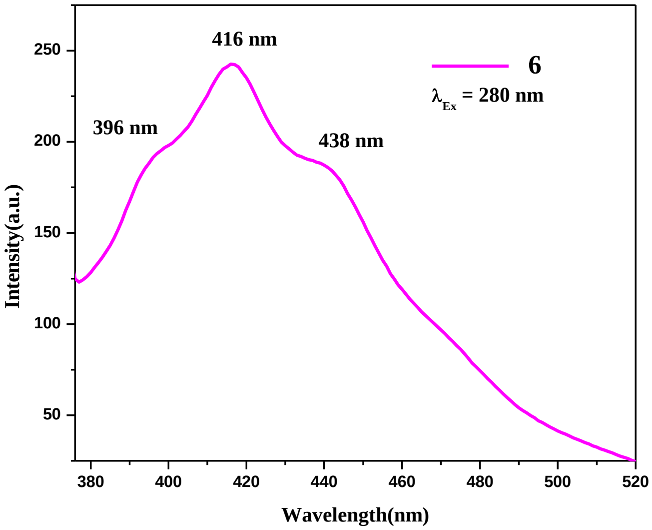


Fig.4.9 Emission spectrum of 1,10-phenethroline, phen (λ_{Ex} = 243 nm).



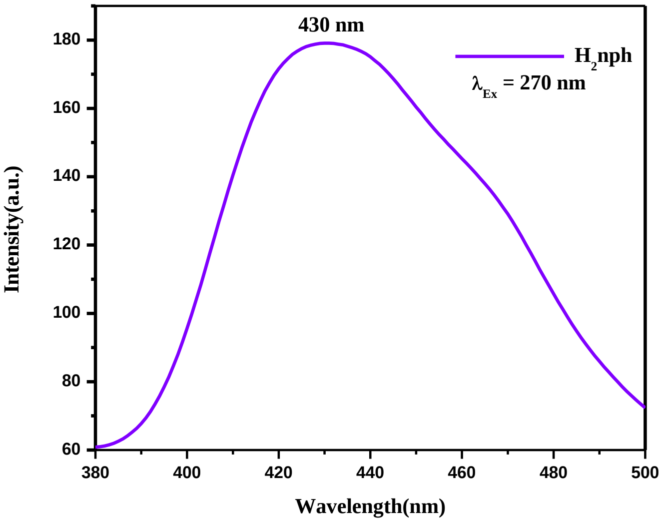


Fig.4.10 Emission spectrum of **6**(λ_{Ex} = 280 nm).

Fig.4.11 Emission spectrum of 4-nitrophtalic acid, H_2nph (λ_{Ex} = 270 nm).

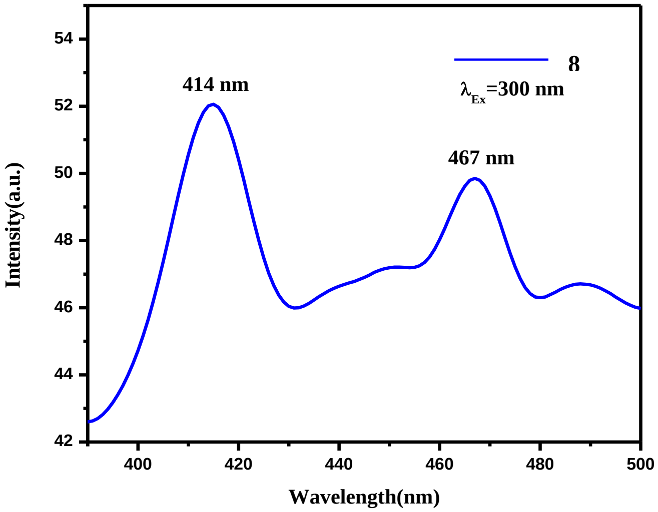


Fig. 4.12 Emission spectrum of **8** (λ_{Ex} = 300 nm).

4.4.3. IR spectra

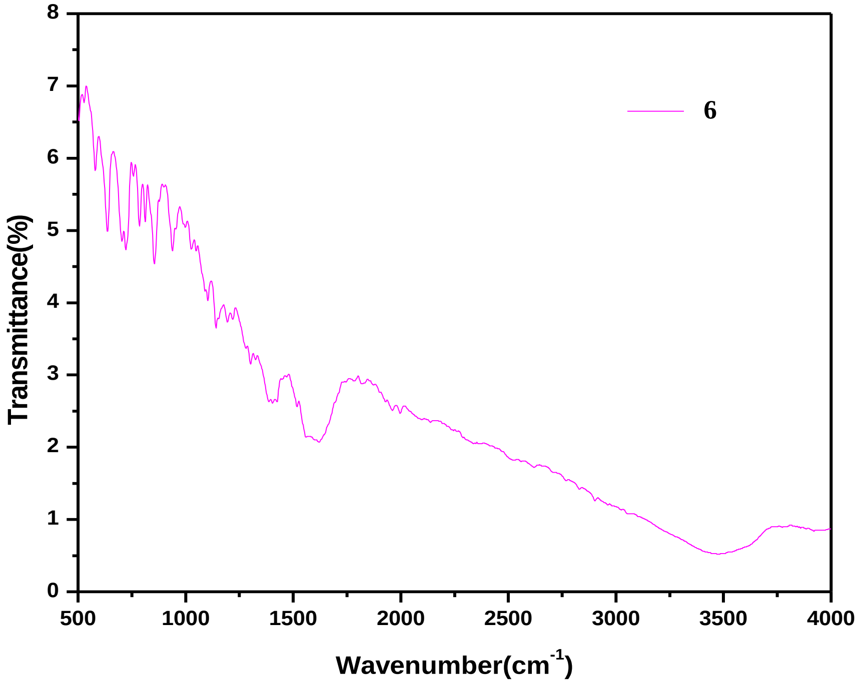


Figure 4.13 FT-IR Spectrum of **6**

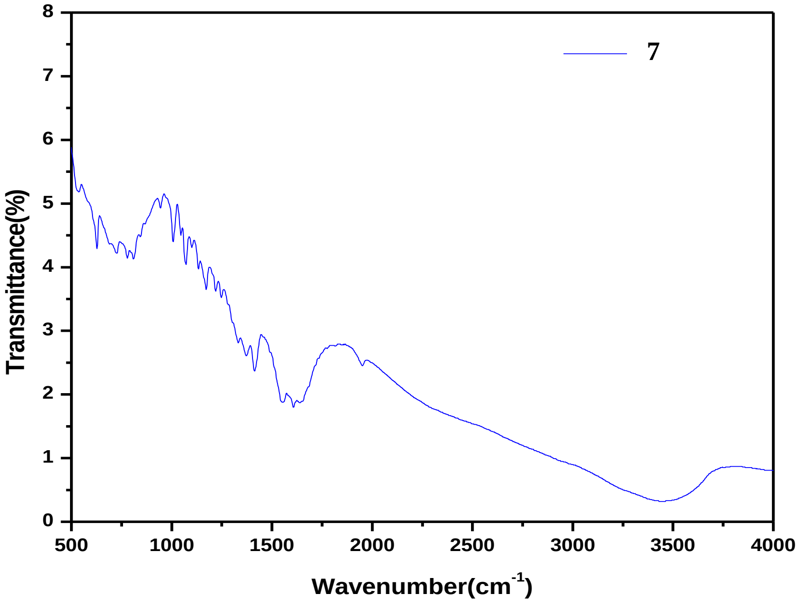


Figure 4.14 FT-IR Spectrum of **7**