Chapter 2

Two three-dimensional coordination polymers of lead (II) with iminodiacetate and naphthalene-dicarboxylate anions: Synthesis, characterization and luminescence behavior

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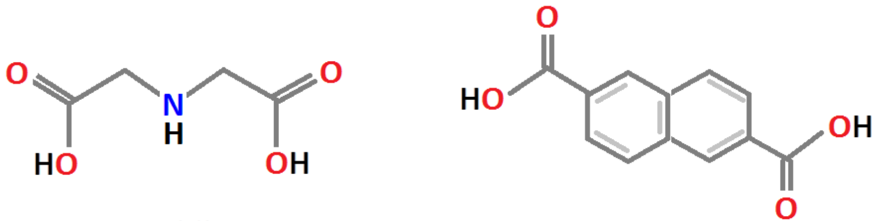
2.1. Introduction

Metal–organic frameworks (MOFs)/coordination polymers (CPs) with variety of metal ions having fascinating structures and interesting material properties, like ions exchange, catalysis, opto-electronic, electrical, magnetic devices and many more, have attracted intense attention in recent time. [109-110,25]. It is an established fact that large variety of coordination networks having Interesting topologies and preferred properties can be synthesized by planned combination of ligand molecules and metal ions. Literature study reveals that till date most of the efforts have been devoted to the study of transition metal coordination polymers [111-113]. On the contrary, relatively less attention has been paid to coordination polymers of main group metal ions; however, they have great applications in the area of electroluminescent devices [114] or organic light-emitting diode (OLED) technology. [115]

Lead(II) coordination polymers are famous for their unlike structural networks in comparison to the coordination polymers formed by transition metal ions and became a topic of interest for the researchers due to two major points: (i) large ionic radius of lead(II) induces a wide range of coordination numbers (2 to 10), which in turn opens-up the possibility for the construction of a variety of Pb(II) functional materials [116] and (ii) the presence of the $6s^2$ outerelectrons make lead(II) frameworks unique. Such intrinsic feature of Pb(II) finds great application in coordination chemistry, photophysics and photochemistry [117]. The toxicity of lead in the environment is due to its frequent industrial applications. The understanding of the coordination properties of lead (II) ion is vital to realize the toxicological properties of this metal and the development of efficient chelating agents for the remediation of polluted water and soil. [118, 119]

In continuation to our work on coordination polymers with Pb(II) metal ion [120-123], in this chapter we describe the use of iminodiacetic and naphthalene-2,6-dicarboxylic acid as ligand (Scheme 2.1) for the construction of two novel coordination polymers of lead(II). Literature study revealed that the use of iminodiacetic acid as organic ligand with a variety of metal ions or combination of different metal ions led to a number of compounds having different interesting structural, chemical and physical properties.



H_2idiac

H_2ndc

Scheme2.1 The ligand

In fact from a structural point of view a novel family of lanthanide hybrid frameworks was Synthesized with iminodiacetic acid showing intricate networks. [124] In addition Ln-Cu coordination polymers with idiac give rise to nanoporous material, [125] while Zhou *et. al.* reported of an anomalous dielectric behavior and thermal motion of guest water molecules confined in the channels of porous crystals. [126] Iminodiacetate was used also in a polymeric Mn(II) complex showing excellent catalytic activity and selectivity for oxidation of various alcohols and sulfides to the corresponding aldehydes/ketone and sulfoxides [127] and in a 2D acentric Mn(II)-coordination polymer having a strong second-order nonlinear optical effect. [128] Such a versatile range of properties in coordination polymers built by idiac anions denotes the importance of this acid as ligand in the synthesis of coordination networks, nevertheless examples of lead compounds built with iminodiacetic acid are rather rare [129-130].

Napthalene-2,6-dicarboxylate has not been used so much in the synthesis of coordination networks and papers reported describe Zn-coordination polymers showing exceptional surface area, [131] a 3D Cd(II)-coordination polymer [132], a tin based coordination compound [133] among others. At our knowledge only one naphthalene-2, 6-dicarboxylate framework of lead has been reported with 3-fold interpenetrated structure. [134]

In this paper we report two new Pb(II) coordination polymers of composition [Pb3(idiac)$_3$(phen)$_2$(H_2O)].2(H2O) (**1**) and [Pb(ndc)]$_n$ (**2**); where H_2idiac = iminodiacetic acid, phen= 1,10-phenanthroline and H2ndc = naphthalene-2,6-dicarboxylic acid. X-ray structure analysis revealed that both the complexes display three dimensional polymeric structures. Significant weak interactions are identified in the structural network of **1** and **2**. Luminescence study revealed that for both the complexes emission is ligand centered and the blue-shifting of emission bands in complexes (with respect to free ligand) are due to the introduction of rigidity in the ligand system via coordination to metal center.

2.2. Experimental

2.2.1. Materials

Lead acetate trihydrate and o-phenanthroline were purchased from Merck.Iminodiacetic acid and naphthalene-2,6-dicarboxylic acid were purchased from SIGMA-ALDRICHInc. All the chemicals were used without any further purification.

2.2.2. Physical Measurements

Spectroscopic data were collected as follows: IR spectra for **1** and **2**were recorded in a Perkin Elmer Spectrum Two spectrometer in the range 4,000–400 cm^{-1}. Elemental analyses (C, H, N) were carried out on a 240C Elemental analyzer. The fluorescence spectra of the ligands and complexes were measured in the solid state at room temperature using a HITACHI F-7000 spectrofluorimeter.

2.2.3. Synthesis

2.2.3.1. Synthesis of $[Pb_3(idiac)_3(phen)_2(H_2O)].2(H_2O)$ (1)

10 ml methanolic solution of 1,10-phenanthroline (0.5 mmol, 0.099 g) was added drop wise to an aqueous solution (20 mL) of $Pb(OAC)_2\cdot3H_2O$ (1 mmol, 0.379 g) with constant stirring. After half an hour an aqueous solution of iminodiacetic acid (1 mmol, 0.133 g) was added to the mixture and the mixture was homogenized. The transparent solution was poured into a 100 ml beaker and refluxed for 4h. The resulting solution was cooled to room temperature and filtered. The transparent solution was kept in room temperature. Colourless block shaped single crystals were obtained from the solution after 3 days. The crystals were isolated by decanting the supernatant liquid and washed with deionized water, ethanol and dried in air. Yield: 70%. Anal. Calc. for $C_{36}H_{37}N_7O_{15}Pb_3$: C, 30.25; H, 2.6; N, 6.8. Found: C, 30.22; H,2.58; N, 6.82, %. IR (KBr,cm^{-1}): 475 (w), 559 (w), 592 (w), 626 (w), 716 (w), 919 (m), 972 (w), 1032 (m), 1113 (m), 1288 (m), 1402 (s), 1557 (s), 2976 (s), 3430 (broad).

2.2.3.2. Synthesis of $[Pb(ndc)]_n$ (2)

$Pb(CH_3COO)_2.3H_2O$ (0.5 mmol, 0.1896 g) and naphthalene-2,6-dicarboxylic acid (0.5 mmol, 0.065 g) were dissolved in10 mL water. To this solution aqueous NaOH solution (1 mmol, 0.04 g) was added drop wise with constant stirring until a homogeneous mixture was obtained. The mixture was transferred into a Teflon-lined autoclave (23 mL) and heated at 160 °C for 4 day. After cooling the solution to room temperature colourless needle shaped crystals were isolated by filtering the supernatant liquid and washed with deionized water and dried in air. Yield: 65%. Elemental analysis, calcd.for C12H6O4Pb: C, 34.2; H, 1.4. Found: C, 34.22; H, 1.43. IR (KBr, cm^{-1}): 435 (w), 475 (m), 537 (w), 650 (w), 722 (w), 795 (m), 950 (m), 1000 (m), 1083 (m), 1195 (s), 1248 (w),1288 (m), 1423 (s), 1557 (s), 1650 (w), 2935 (w), 3418 (broad).

2.3. X-ray Crystallography

Data collections of **1** and **2** 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-Noniusprogramsuite 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]. Hydrogen atoms were placed at calculated positions with exception of those of water molecules in **1**. All the calculations were performed using the WinGX 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 **1** and **2** are given in Table 2.1.

[CCDC number 991343 and 991344]

Table2.1. Crystal data and details of refinements for **1** and **2**

	1	**2**
Empirical formula	$C_{36}H_{37}N_7O_{15}Pb_3$	$C_{12}H_6O_4Pb$
Formula weight	1429.30	421.36
Crystal system	Monoclinic	Monoclinic
Space group	*C* 2/c	C2/c
a, Å	18.4854(7)	22.995(4)
b, Å	8.8120(3)	5.5880(8)
c, Å	25.1098(8)	7.6869(12)
β, deg	106.355(2)	91.833(5)

Volume, Å^3	3924.7(2)	987.2(3)
Z	4	4
dcalc, Mg/m^3	2.419	2.835
μ, mm^{-1}	12.919	17.087
F(000)	2672	768
Reflections collected	25056	6796
Reflections unique	6252	1806
R(int)	0.0728	0.0920
parameters	298	90
Goodness-of-fit on F^2	1.135	1.141
Final R indices [I>2σ(I)] *R*1, *w*R2	0.0455 = 0.0926	0.0360, 0.0880
R indices (alldata) *R*1, *w*R2	0.0583,0.0968	0.0395, 0.0899
Residuals, e.Å^{-3}	3.912, –3.133	2.865, –3.798

2.4. Results and Discussion

2.4.1. Crystal structure of1

Compound **1** is a trinuclear discrete molecular complex that is best described to comprise a central [Pb(idiac)(H_2O)] unit connected to two side located [Pb(idiac)(phen)] fragments as shown in (Fig. 2.1). However the central lead ion is positioned at a distance of 0.645 Å from a twofold axis and this imposed crystallographic symmetry leads to a positional disorder for this atom and for the coordinated water molecule. The metal coordination sphere of the two independent metals is different (Fig. 2.2). Pb1 ion is chelated by the phen and by the tridentate idiac ligand, of which the carboxylate oxygen O(1b), behaving as a bridging donor, bounds the central lead Pb(2).On the other hand Pb2 is chelated by the tridentate idiac anion through the central N and the oxygen donors from the carboxylic groups, and in addition by an aqua ligand and the oxygen (O(1b) at x, y-1, z) from the carboxylate of the indiac chelating Pb1. Both the metal centers are five coordinated with close comparable Pb-N and Pb-O bond distances involving the iminodiacetato ligand. On the other hand the Pb-N(phen) bond lengths are of 2.605(6) and 2.611(6) Å that lead to a narrow chelating N(1a)-Pb(1)-N(2a) of 63.27(18)°. The Pb(2)-O(1w) distance involving the water (of 2.400(10)Å) is the shorter observed.

Due to the $6s^2$ electron pair in the electron configuration of Pb^{2+}, both the metals exhibit a hemidirected disposition of donor atoms in the coordination sphere, i.e. the bonds to ligand atoms are directed throughout only part of the sphere. [141] This feature leads the lead (II)atoms to exhibit a highly distorted square bipyramid geometry (ψ-octahedron) atom with the lone pair occupying one of the bipyramid axial vertices. The three nuclear building block depicted in Fig. 2.1 gives rise to a 2D coordination network developing in the ab-plane. Fig. 2.3 shows this 2D polymer of (4, 4) rhomboidal topology, being the disordered Pb(2) ions the nodes and the Pb(1)(idiac) the sides. The layers have the phenrings (not shown for clarity in Fig. 2.3) pendant at both sides and are packed to form a 3D architecture where interdigitated phenantroline ligands give rise to strong $\pi - \pi$ interactions (Fig. 2.4).The centroid-to-centroid distances between the rings of the chelating aromatic ligands are of 3.565(5) and 3.571(4) Å.

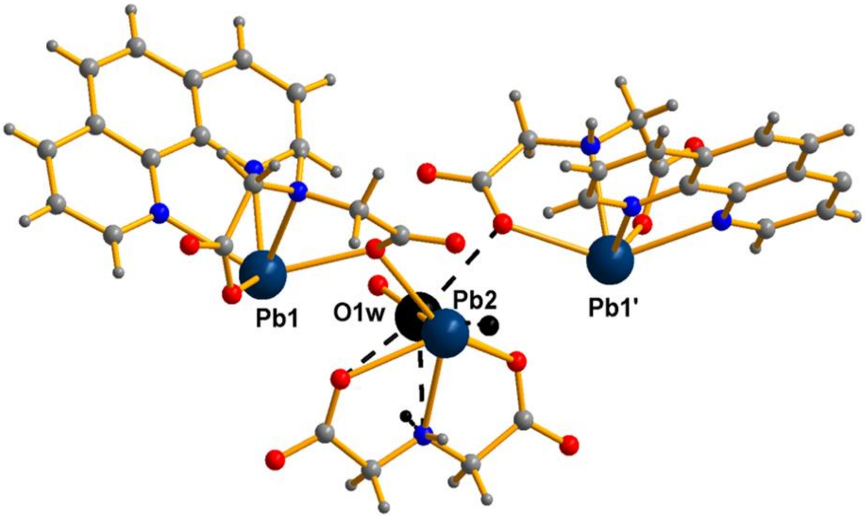


Fig. 2.1 The trinuclear synthon in complex **1** that gives origin to 2D corrugated layer.

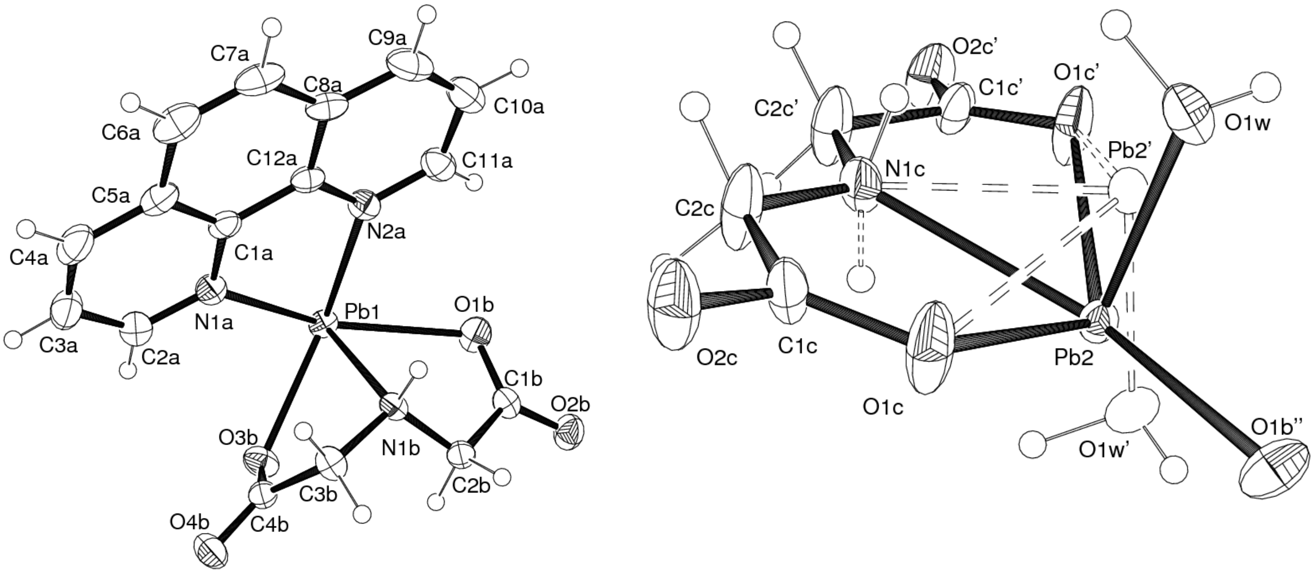


Fig. 2.2 Coordination sphere of Pb1 and Pb2 in **1**. Of the latter the crystallographic disorder is shown.

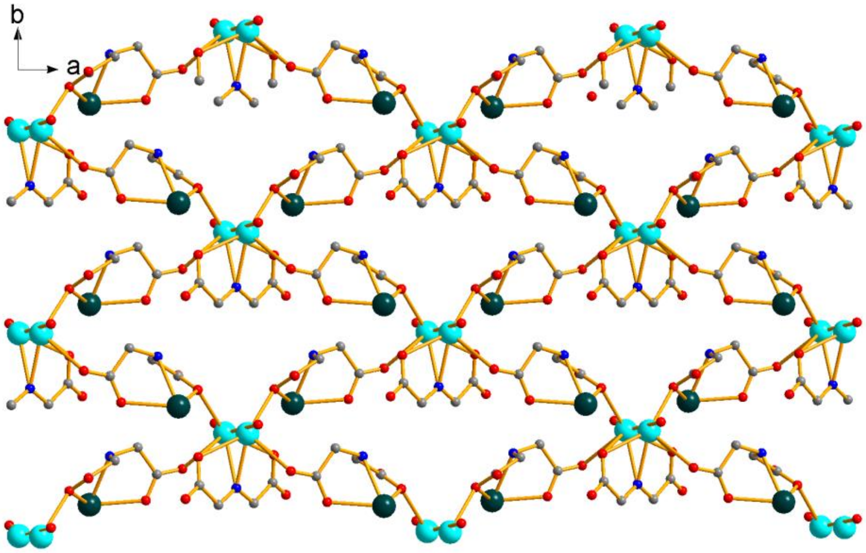


Fig. 2.3 The 2D network in the *ab*-plane (for clarity phen ligands not shown) for **1**. The light blue spheres indicated the disordered Pb(2) ions.

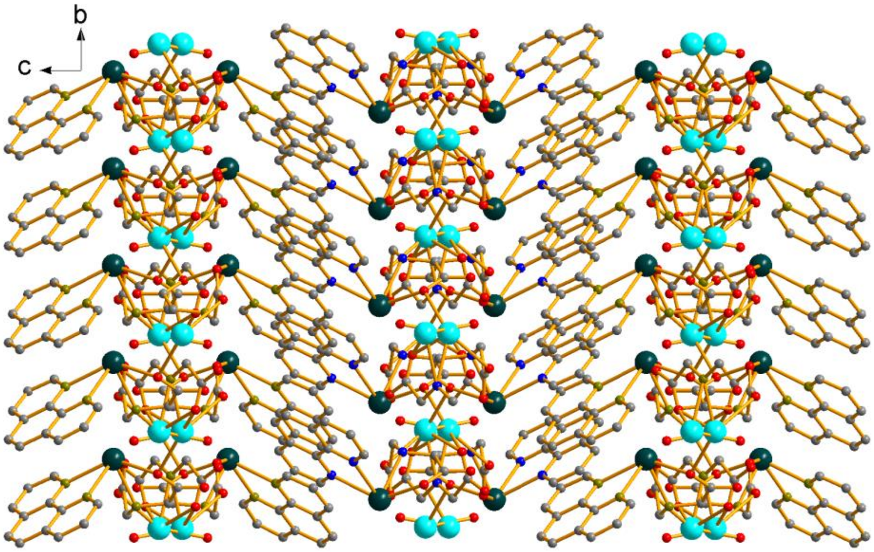


Fig. 2.4 Perspective view of the interdigitated 2D layers with o-phen molecules interacting through π – π interactions in **1**.

2.4.2. Crystal structure of 2

The crystallographic independent unit of the compound comprise a lead (II) ion located on a two-fold axis and half naphthalene-2,6-dicarboxylato anion, which in turn is positioned on a center of symmetry. Each Pb ion is coordinated by four carboxylic oxygen atoms from different symmetry related ligands with Pb(1)-O(1) and Pb(1)-O(2)' bond lengths of 2.521(4) and 2.312(4)Å, respectively. An ORTEP view of the metal coordination sphere is shown in Fig. 2.5 and the crystallographic independent coordination bond distances and angles are reported in Table 2.3.The carboxylate group results almost coplanar with the naphthalene moiety assuring an electron delocalization over the whole ligand. Again here the metal atom exhibits a hemidirected disposition of O-donors [142] and has a disphenoidal coordination geometry (ψ-trigonalbipyramidal with the lone pair of electrons in the equatorial plane). [143] This feature affects the topology of the 3D architecture as described below.

In the three dimensional network [Pb(carboxylate)2]n polymeric chains can be evidenced (as shown in Fig.2.6), where the metals are separated by 5.2248(6) Å with an intermetallic angle of 94.719(1)°. The eight-membered rings are referred by the crystallographic glide plane in the direction of axis-c. These chains through the naphthalene-dicarboxylato give rise to a 3D architecture (displayed in Fig. 2.7) where the NDC ligand adopts a bis(bidentate-bridging) coordination mode where every NDC ligand bridges four Pb(II) cations. The crystal packing does not evidenced any significant $\pi - \pi$ interaction, being the shorter distance between the naphthalene rings of 4.5 Å, but rather C-H...π-ring interactions, where the H…ring distance is of 2.89(8) / 2.92(6) Å and C-H..ring centroid angle of 142(5)and 119(6)° are measured.

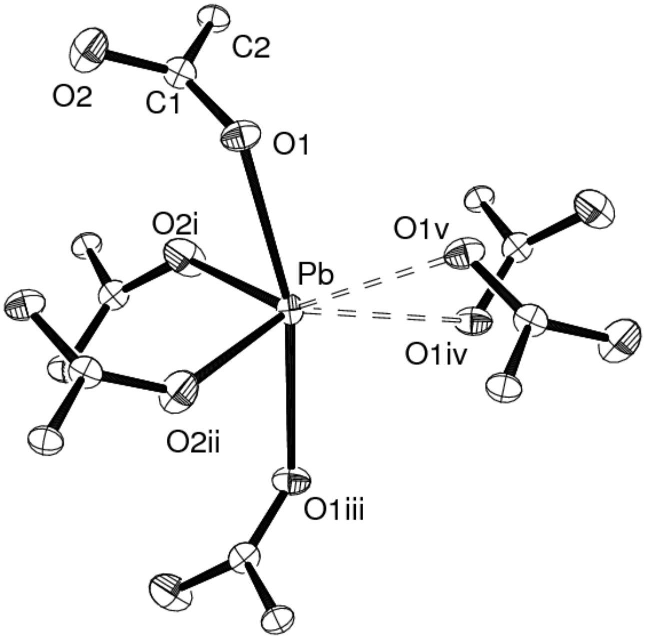


Fig. 2.5 ORTEP drawing (ellipsoids at 40% probability) of the coordination sphere of the lead(II) ion in complex **2**. The Pb-O(1)^{iv} and Pb-O(1)^{v} are long distances of 2.931(5) Å.

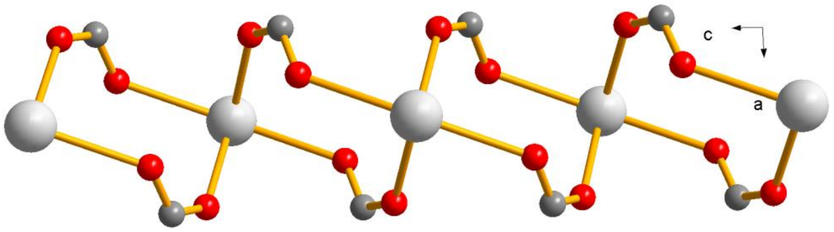


Fig. 2.6 The one-dimensional Pb chains connected by the bridging carboxylates groups in **2**.

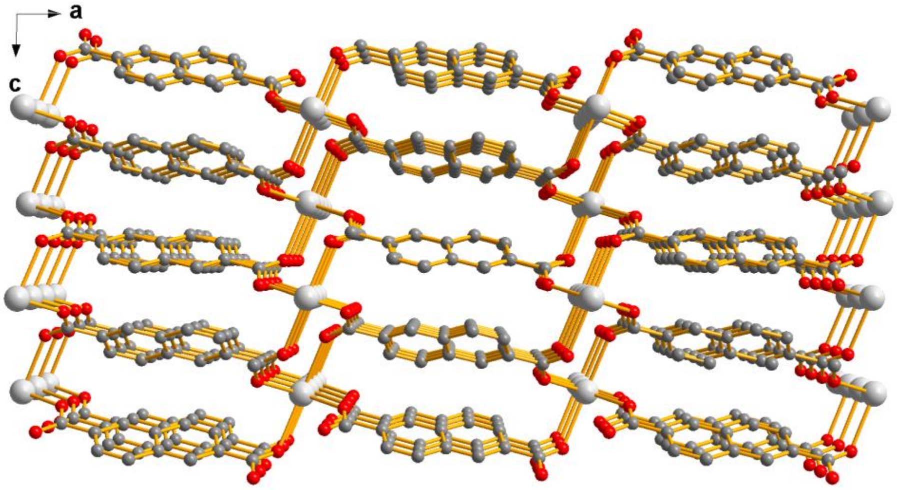


Fig. 2.7 The inorganic-organic hybrid structure 3D structure of **2**.

Table 2.2. Coordination bond lengths (Å) and angles (°) for**1**.

Pb(1)-N(1a)	2.605(6)	Pb(2)-N(1c)	2.478(8)
Pb(1)-N(2a)	2.611(6)	Pb(2)-O(1c)	2.521(6)
Pb(1)-N(1b)	2.479(5)	Pb(2)-O(1c)'	2.647(5)
Pb(1)-O(1b)	2.518(5)	Pb(2)-O(1w)	2.400(10)
Pb(1)-O(3b)	2.487(5)	Pb(2)-O(1b)"	2.690(5)
N(1a)-Pb(1)-N(2a)	63.27(18)	N(1c)-Pb(2)-O(1c)	65.27(12)
N(1a)-Pb(1)-N(1b)	83.39(18)	N(1c)-Pb(2)-O(1c)'	63.38(12)
N(1a)-Pb(1)-O(1b)	137.87(19)	N(1c)-Pb(2)-O(1w)	85.4(3)
N(1a)-Pb(1)-O(3b)	77.95(17)	N(1c)-Pb(2)-O(1b)"	133.66(11)
O(1b)-Pb(1)-N(2a)	82.02(18)	O(1w)-Pb(2)-O(1c)	73.8(3)

O(3b)-Pb(1)-N(2a)	128.86(17)	O(1w)-Pb(2)-O(1c)'	86.0(3)
N(1b)-Pb(1)-N(2a)	77.31(17)	O(1w)-Pb(2)-O(1b)"	73.3(3)
N(1b)-Pb(1)-O(3b)	65.77(16)	O(1c)-Pb(2)-O(1c)'	125.8(2)
N(1b)-Pb(1)-O(1b)	65.39(16)	O(1c)-Pb(2)-O(1b)"	69.37(17)
O(3b)-Pb(1)-O(1b)	110.75(17)	O(1c)'-Pb(2)-O(1b)"	150.01(18)

Table2.3. Coordination bond distances (Å) and angles(°) for **2**.

Pb(1)-O(1)x2	2.521(4)	Pb(1)-O(2)'x2	2.312(4)
O(2)"-Pb(1)-O(1) x2	81.88(17)	O(2)'-Pb(1)-O(1) x2	89.44(17)
O(2)'-Pb(1)-O(2)"	103.5(2)	O(1)-Pb(1)-O(1)"'	166.0(3)

Symmetry codes: (') –x,–y,–z+1; (") x,–y,z+1/2

2.4.3. Luminescence study

The room temperature solid state emission spectra of 1, 10-phen and complex **1** are given in Fig. 2.8. The ligand 1, 10-phen shows a broad emission band in the region of 414 - 442 nm (λ_{Ex} 365 nm). The intra ligand π*–π and π*–n charge transfer transitions are responsible for the emission behaviour. Complex **1** shows a broad band with emission maxima at 380 nm (λ_{Ex} 295 nm). In comparison to the free ligand the blue shifted emission in **1** may be assigned as π*–π and π*–n charge transfer transition of the o-phen ligand. The 1, 10-phen coordination to the metal centres in **1** introduced conformational rigidity in the system which is responsible for this blue shifted fluorescence emission in **1**. [123]

The room temperature solid state luminescent spectra of free 2,6-ndcH$_2$ and complex **2** are shown in Fig.2.9. The ligand 2, 6-ndcH$_2$ shows emission band with maxima at 415 nm (λ_{Ex} 275 nm) in the higher energy region (due to the π*-π and/or π*-n transitions). However, complex **2** exhibits an intense emission maximum at 354 nm and a shoulder peak at 368 nm (λ_{Ex} 248 nm). Here the emission bands of **2** are blue shifted by 61 and 47 nm respectively (in comparison to the free 2, 6-ndcH$_2$). Such emission behaviour of **2** may originate from the intraligand transition of naphthalenedicarboxylate[143]. The significant blue shift of the emission bands for 2 may be assigned to the incorporation effect of metal perturbed intra ligand transition and deprotonation of the ligand. [134]

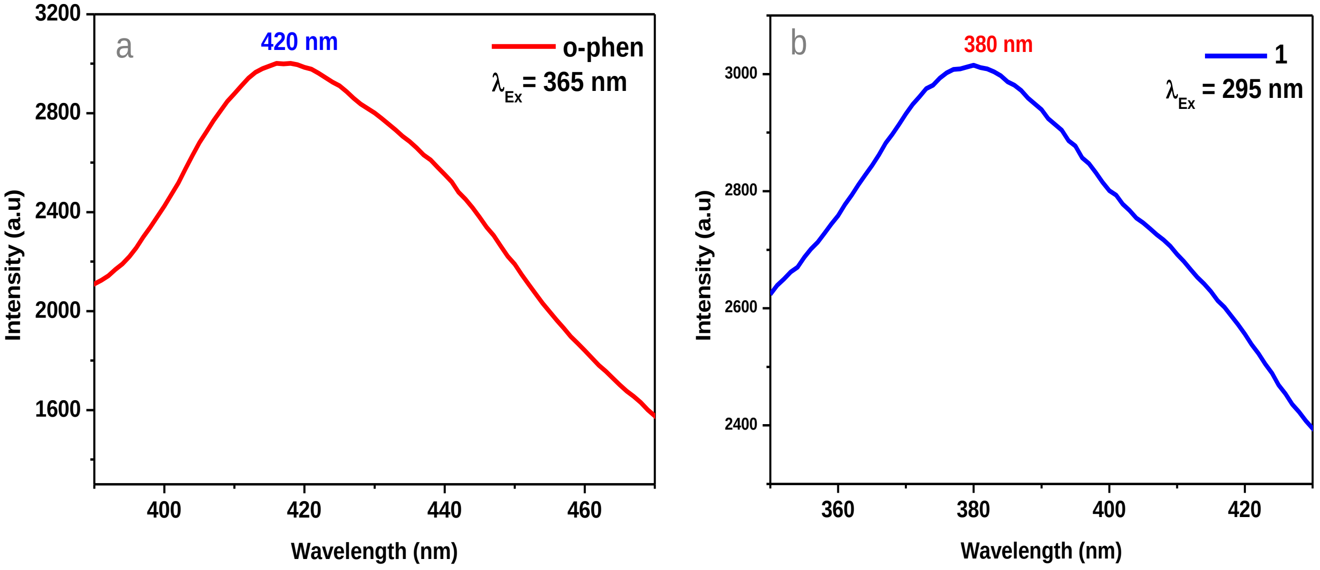


Fig. **2.8** Emission spectra of (a) O-phen, (b) complex **1**

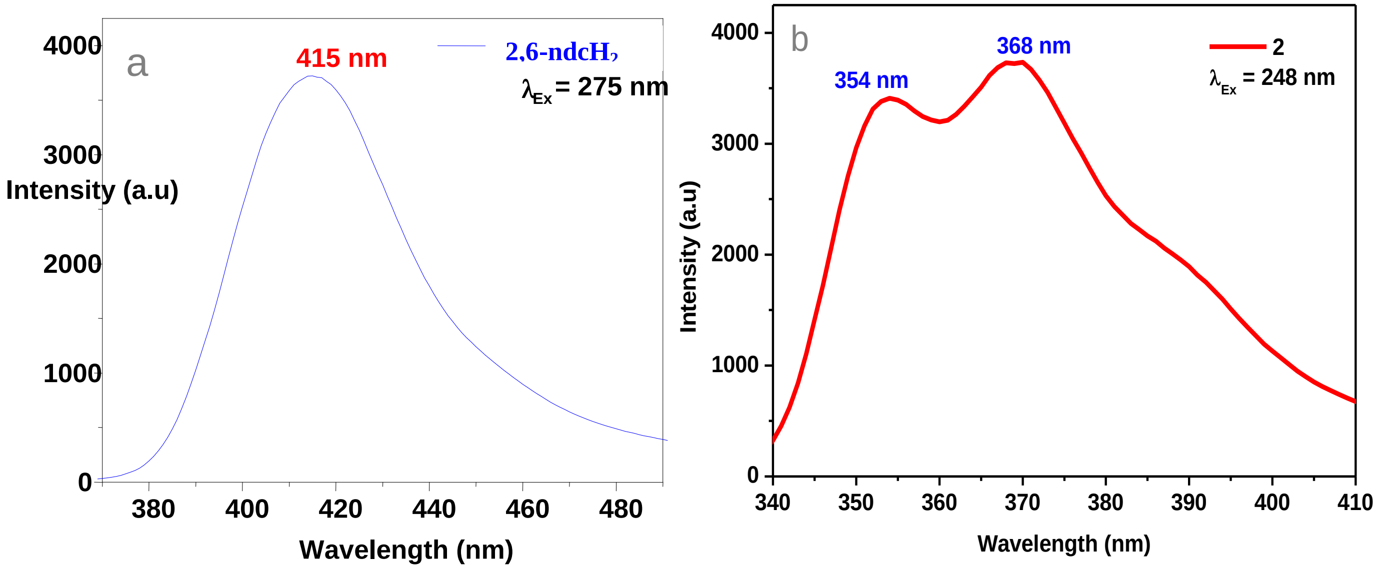


Fig. **2.9** Emission spectra of (a) ndc, (b) complex **2**.

2.4.4. IR study.

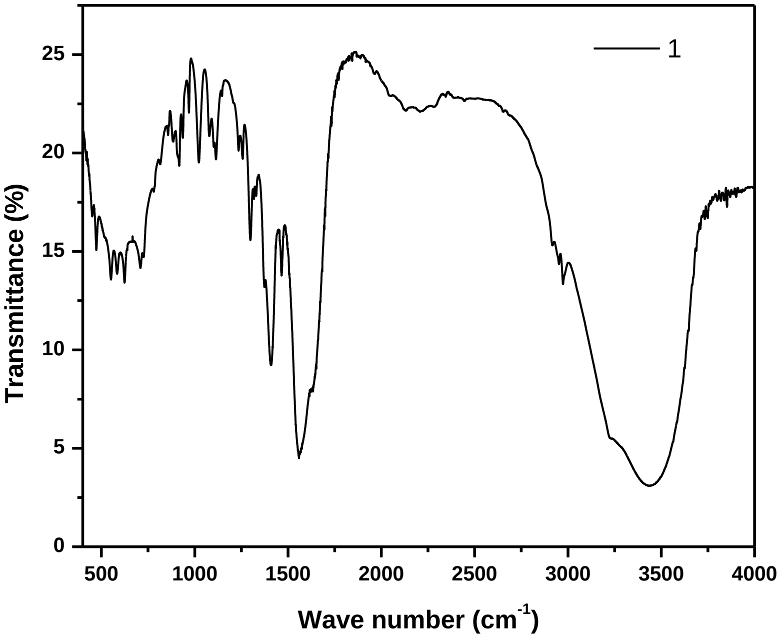


Fig. **2.10** IR spectrum of complex **1**

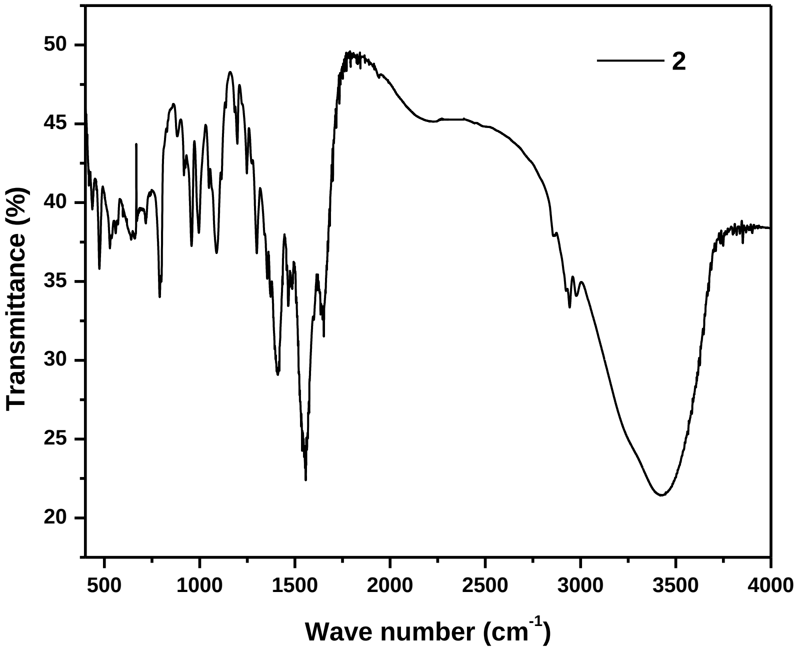


Fig. **2.11** IR spectrum of complex **2**