

**SYNTHESIS AND CHARACTERIZATION OF METAL BASED  
PHENYLENEDIACRYLATES INCORPORATED WITH N-DONOR LIGANDS**



**DISSERTATION**

Submitted in partial fulfilment of

The degree of MSc. (Inorganic Chemistry)

By

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To

School of Chemical Sciences

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April 2020

## STATEMENT

I hereby declare that the matter presented in this dissertation entitled, **“Synthesis And Characterization Of Metal Based Phenylenediacylates Incorporated with N-Donor Ligands”** is based on the result of investigations carried out by me in the School Of Chemical Sciences, under the supervision of **Dr. S. N. Dhuri** and the same has not been submitted elsewhere for the award of a degree or diploma.

Ms. Riddhi Goltekar

CH-18-032, MSc-II,

Inorganic Chemistry

Date:

## **CERTIFICATE**

This is to certify that dissertation entitled **“Synthesis And Characterization of Metal Based Phenylenediacrylates Incorporated with N-Donor Ligands”** is bonafide work carried out by **Ms. Riddhi Goltekar** under my supervision in partial fulfilment of the requirement for the award of the degree of Master of Science in School Of Chemical Sciences, Goa University.

Dr. S.N. Dhuri  
Guiding Teacher,  
School Of Chemical Sciences  
Goa University  
Date:

## CERTIFICATE FROM DEAN

This is to certify that the dissertation entitle “**Synthesis And Characterization Of Metal Based Phenylenediacylates Incorporated with N-Donor Ligands**” is bonafide work carried out by Ms. Riddhi Goltekar under the supervision of Dr. **S. N. Dhuri** for the award of the degree of Master of science in chemistry at the School Of Chemical Sciences, Goa University.

Dean,  
School of Chemical Sciences  
Goa University

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Last but not the least I thank my parents for their great support, help, and encouragement throughout the work. I thank god for his abundant blessings on my dissertation work.

# CHAPTER 1

## INTRODUCTION

Coordination polymers (CPs) / Metal-Organic Frameworks (MOFs) is a metal organic unit that is linked together in at least one dimension through extended covalent or coordinate interactions forming an infinite array. J. C. Bailar in 1964 defined the term coordination polymer, on comparing organic polymers with inorganic compounds and said that they can be thought as polymeric species. Crystal engineering mainly focuses on understanding the growth of crystalline solids in terms of the supramolecular interactions. This field deals with the weak noncovalent interactions, while those with metal coordination bonds were given the name inorganic crystal engineering. The majority of the studies deals with engineering of CPs or MOFs. One of the most important class of porous materials is the crystalline metal-organic frameworks (MOFs) that find their use in adsorption, catalysis, magnetism, conductivity, sensing, gas storage, gas separation and drug delivery. A huge numbers of non-porous MOFs are also found having important application that is magnetism, luminescence and sensor depending on the metal and ligand used.

MOFs /CPs has a presence of metal centers called as “nodes” and show bonding with specific number of ligands. The number of ligands to which central metal atom is attached is called as coordination number which further determines the dimensionality of the structure. Transition metals (e.g. Cu, Zn), alkaline earth metals (e.g. Sr, Ba), p-block elements (e.g. In, Ga), actinides (e.g. U, Th), even mix metals are used for synthesis of MOFs. Metal atoms such as Cu(II), Co(II), Ni(II) adopts various geometry such as tetrahedral, square planar, octahedral, square pyramidal and can also form multi-dimensional network.

MOF structure depends on the selectivity of ligands and metals, various organic ligands of different shape and size. Examples of ligands which are used are Carboxylates which is O- donors and Amines which are N-donors. Di-carboxylates ligands used can function as ligand which links metal cation into higher dimensionality and can also act as a charge balancing anion.

MOFs is used for adsorption and separation of gases such as CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> due to their porous nature. Coordination compound is any compound that contains a coordination entity. A coordination entity is an ion or neutral molecule that is composed of a central atom, usually that of a metal, to which is attached a surrounding array of atoms or groups of atoms each of which is called a ligand. MOFs are constructed by connecting secondary building units (SBUs) with organic spacers to create divers network which can be altered to controls the pore environment of MOFs. The Synthesis of MOFs involves various methods which includes the slow evaporation method, solvothermal synthesis, microwave assisted synthesis, electrochemical synthesis, mechanochemical synthesis and sonochemical synthesis.

## **1. SLOW EVAPORATION METHOD**

Is conventional method for MOFs synthesis. This method do not require any external energy and is room temperature process. This method require more time as compared to other methods. In this process starting material is concentrated at fixed temperature (mostly at room temperature) by slowly evaporating the solvent. Solubility of the reagent can be increased by mixing the solvents thus making the process faster by evaporating the low boiling solvent.

## 2. SOLVOTHERMAL SYNTHESIS

These reactions are carried in closed vessels under at autogenic pressure and temperature above the boiling point of solvent. High boiling organic solvents have been used for solvothermal reactions. The most commonly used organic solvents are DMF, diethyl formaide,acetonitrile, acetone, methanol. Solvothermal reactions are carried out in different temperature ranges depending on the requirement of the reaction. Glass vials are used for lower temperature reactions, while reactions performed at temperatures higher than 400 K require Teflon-lined autoclave



Fig. Teflone lined stainless steel autoclave and oven

## 3. MICROWAVE-ASSISTED SYNTHESIS

Is very rapid method for synthesis of MOFs. This has been used for synthesis of nanosize metal oxides. The solution is heated with microwave for an hour to produce nanosized crystal. Microwave-assisted solvothermal synthesis is a technique used for synthesis of MOFs. MOFs synthesis is much quicker by this method as compared to solvothermal process but the quality of crystals obtained are same.



#### **4. ELECTROCHEMICAL SYNTHESIS**

In this method there is continuous production of MOF crystal without the use of metal salt due to which it has main advantage in an industrial process. In this process metal ion is provided by anodic dissolution into the mixture which contains organic linkers and electrolytes.

#### **5. MECHANOCHEMICAL SYNTHESIS**

In this method MOFs are synthesized in absence of solvents. For this synthesis the chemical reaction is carried out by applying mechanical force. Mechanochemical synthesis is also being employed for synthesis of MOFs using liquid assisted grinding (LAG) where in a small amount of solvent is added to the reaction mixture. By varying the solvents in LAG one, two and three dimensional coordination polymer for the same reaction can be obtained.

#### **6. SONOCHEMICAL SYNTHESIS**

It is a phenomenon by which molecule undergo chemical change due to the application of intensive ultrasonic radiation (20kHz-10 MHz). This method can generate homogeneous nucleation centre and reduce the crystallization time compared to hydrothermal method.

## **APPLICATIONS**

### **1. GAS ABSORPTION AND STORAGE**

MOFs can be used in the absorption and storage of gas due to its higher surface area, porous nature, functionalized polar groups, light weight, open metal centre and specific weak interaction. Gases such as H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, can be absorbed or stored using MOFs. MOFs are ideal material for H<sub>2</sub> storage at lower temperature. The most useful MOF for hydrogen storage is one which has hydrogen storage densities greater than 10 wt% and 58 gL<sup>-1</sup>(77K). MOF-177 is well known material used for H<sub>2</sub> storage which is constructed from [Zn<sub>4</sub>O] clusters and 4,4',4''- benzene-1,3,5- triyltribenzoate (BTB) as it has high surface area and large pore volume and shows gravimetric H<sub>2</sub> uptake of 7.5 wt% at 70 bar and 77K. MOF-210 is a MOF used for the absorption and storage of CO<sub>2</sub> which is constructed from 4,4',4''-[benzene-1,3,5-triyl-tris (ethyne-2,1-diyl)]tribenzoate (H<sub>3</sub>BTE), biphenyl-4,4'-dicarboxylate (H<sub>2</sub>BPDC) and zinc (II) nitrate hexahydrate as it has ultrahigh surface area

### **2. DRUG DELIVERY**

MOFs are efficient drug delivery material as their properties can be modified by adjusting the functional groups of the framework and finely tuning the pore size. MOFs having very large pore size allow large complex molecules such as any pharmaceutically active compounds to be inserted into them and these MOFs are used as a drug delivery agent.

### 3. CATALYSIS

MOFs are used as heterogeneous catalysts because of its high surface area, flexibility, tunable porosity, diversity in metal and functional groups. These catalysts possess size, shape and enantioselectivity. Due to their low chemical and thermal stability they are not applicable for reactions that requires severe conditions. MOFs were used as a catalyst or as a catalyst support for many organic transformation reactions such as Friedel-Crafts reactions, Knoevenagel condensation, aldol condensation, oxidation, coupling reactions, carbon dioxide fixation. Cu-MOF-74 was as used as a catalyst for Friedel-Crafts reaction because of its high catalytic activity, high stability and reusability. MOF-5 which was synthesized from zinc nitrate hexahydrate and 1,4-benzene dicarboxylic acid in N,N-diethyl formamide was used as a catalyst for Friedel-Crafts benzylation of toluene.

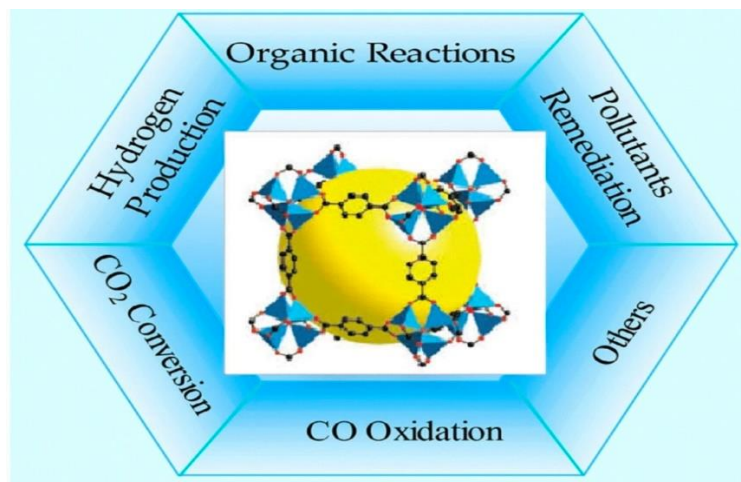


Fig. Application of MOFs in catalysis.

#### **4. CONDUCTIVITY**

MOFs can also exhibit good charge mobility and conductivity. The first conductive MOF reported was Cu[Cu(pdt)<sub>2</sub>] (pdt-2,3 pyrazinedithiolate) which has electrical conductivity of  $6 \times 10^{-4} \text{ S cm}^{-1}$  at 300K.

#### **5. MAGNETIC MATERIAL**

Magnetic property in solid is of importance due to its applications in electromagnetism, devices and sensing. Magnetism have been introduced into the MOFs through the use of paramagnetic 3d transition metal nodes and organic linkers and termed as MMOF (magnetic metal organic framework). Due to porous nature and magnetic property of MOFs it finds wide application in separation of air.

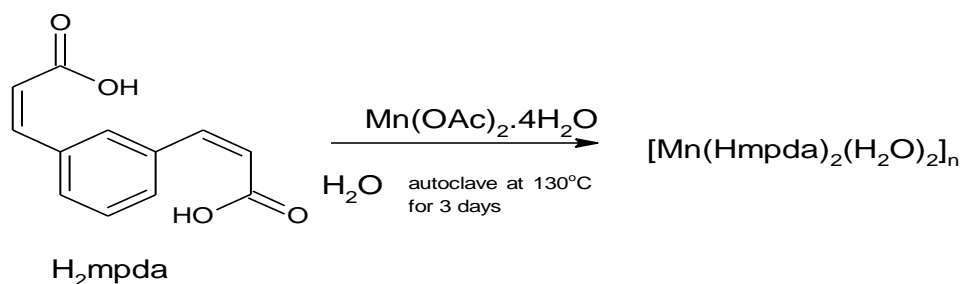
#### **6. SENSORS**

MOFs are used as luminescent material due to their potential application in small molecule sensors, pH sensors, light concentrators for photovoltaic devices, antennae in photosensitive bioinorganic compounds. MOF materials are of importance due to their hybrid nature, which includes inorganic metal ions and organic linkers. Lanthanide metal ions are mostly used for synthesis of luminescent MOFs because of their electronic transition from d to f shell, with photo emission. The lanthanide metal ions are coordinated by strongly absorbing ligands, which enhances its luminescent properties.

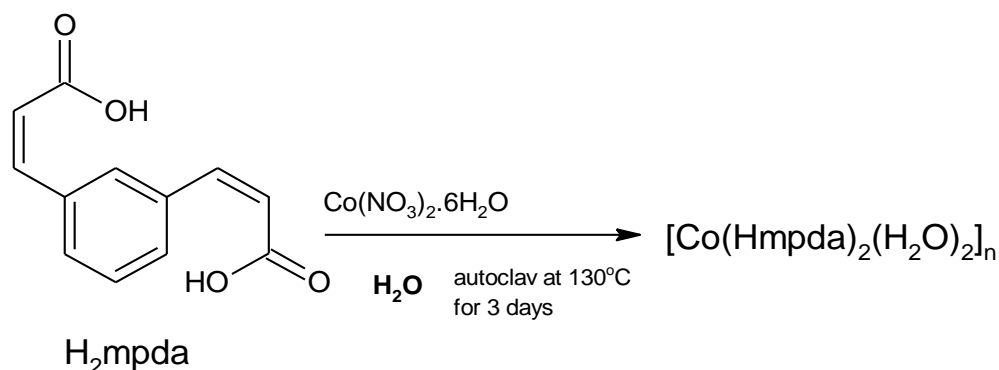
## LITERATURE SURVEY

- In the year 2017, three coordination polymers based on m-phenylenediacrylic acid ( $\text{H}_2\text{mpda}$ )
- were prepared by **Qian Sun et al** having the formulae  $[\text{Mn}(\text{Hmpda})_2(\text{H}_2\text{O})_2]_n$ ,  $[\text{Co}(\text{Hmpda})_2(\text{H}_2\text{O})_2]_n$ , and  $[\text{Co}(\text{mpda})(\text{H}_2\text{O})_2]_n$ . m-phenylenediacrylate ligand having a V-shaped geometry have been employed due to its planarity and its constitutional stiffness. These compounds were synthesized by the hydrothermal method at  $130^\circ\text{C}$  for 3 days.

1)



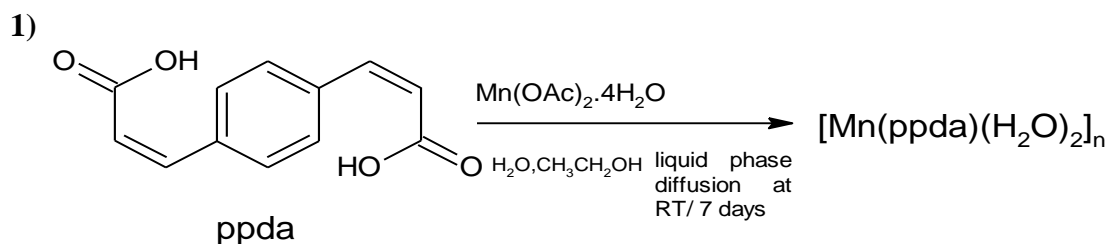
2)



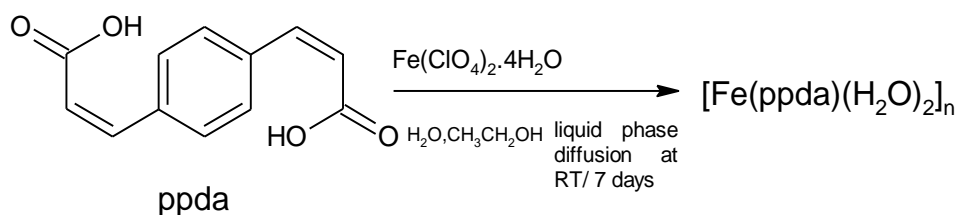
The compound were characterized by IR and showed carboxylate bands at  $1630\text{ cm}^{-1}$  for asymmetric vibration and  $1400\text{ cm}^{-1}$  for symmetric vibration complex 1 and 2 showed protonated

carboxylate group in region of 1710- 1730  $\text{cm}^{-1}$ . X-Ray analysis revealed that complex 1 and 2 are isomorphous having 2D structure showing trans octahedral geometry. Compound 3 has monoclinic space group  $P2_1/c$  having 1D structure and has distorted octahedral geometry. Magnetic properties of the complexes were studied, 1 and 2 showed intralayer antiferromagnetic property and 3 showed weak antiferromagnetic property.

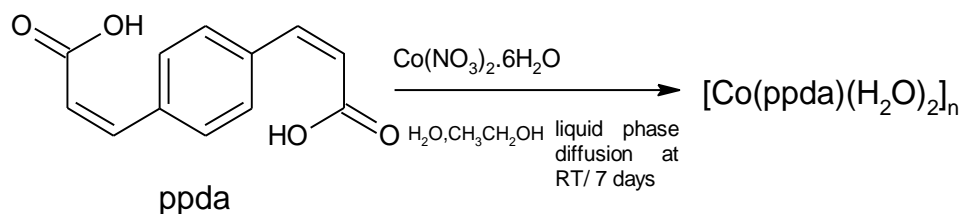
- In the year 2011, three coordination polymers were synthesized using p-phenylenediacrylic acid by Qian Sun et al having a formula  $[\text{M}(\text{ppda})(\text{H}_2\text{O})_2]_n$  where metal used was Mn(II), Fe(II), Co(II). The compound was synthesized by liquid phase diffusion method at room temperature for 7 days.



2)

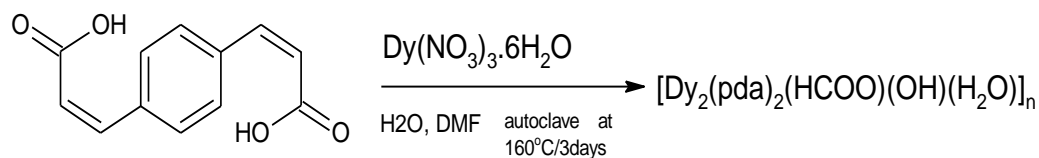


3)



IR analysis showed strong absorption in range of 1640-1645  $\text{cm}^{-1}$  and showed no absorption at 1700  $\text{cm}^{-1}$ . The X-Ray studies carried out revealed that all the compounds synthesized are isomorphous having 3D structure forming trans octahedral geometry. The photoluminescent properties were studied and displayed intense blue emission in solid state at room temperature. Magnetic studies showed that Co(II) do not show 3D magnetic ordering Mn(II) behaves as weak ferromagnet and Fe(II) behaves as metamagnet.

- In the year 2012, three three-dimensional lanthanide coordination polymers  $[\text{Ln}_2(\text{pda})_2(\text{HCOO})(\text{OH})(\text{H}_2\text{O})]_n$  was synthesized Xin-Hui Zhou et al solvothermally at 160°C for 3 days. The lanthanide used were (Ln = Dy, 1; Tb, 2; Ho, 3;) and the acid used was H2pda = p- phenylenediacrylic acid.

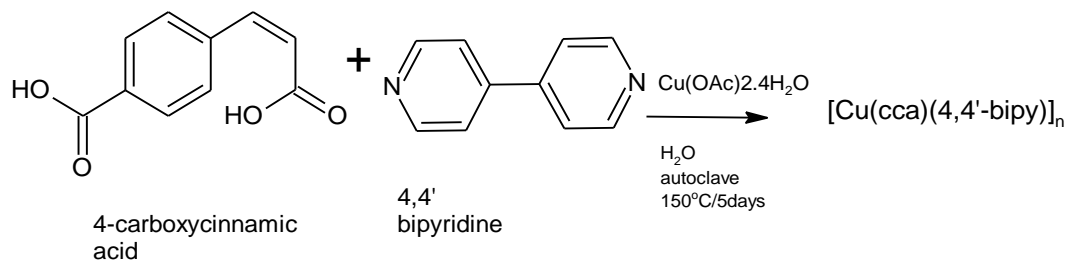


Compounds were characterized by IR and showed strong absorption peak at around 1639-1398  $\text{cm}^{-1}$  for carboxylate group. X-Ray analysis revealed that compound is isostructural having 3D structure. 1 crystallizes in the monoclinic space group  $\text{P2}_1/\text{n}$ . 2 and 3 cannot be analysed due to its poor crystal quality. Photoluminescent studies showed intense blue emission in the solid state at room temperature.

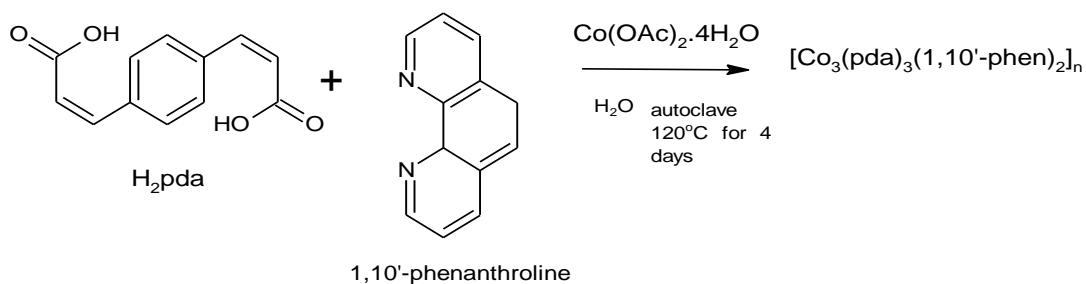
- In the year 2014, three 3-D coordination polymers, has been synthesized by Xiao-Guang Sang et al from 4-carboxycinnamic acid (cca), 1,4'-phenylenediacrylic acid (pda), 4,4'-

bipyridine (4,4'-bipy), 1,10'-phenanthroline (1,10'-phen) using transition metal such as copper and cobalt under having formula  $[\text{Cu}(\text{cca})(4,4'\text{-bipy})]_n$  (1),  $[\text{Co}_3(\text{pda})_3(1,10'\text{-phen})_2]_n$  (2), and  $[\text{Co}(\text{pda})(1,10'\text{-phen})]_n$  (3). The compound were synthesized hydrothermally under different condition.

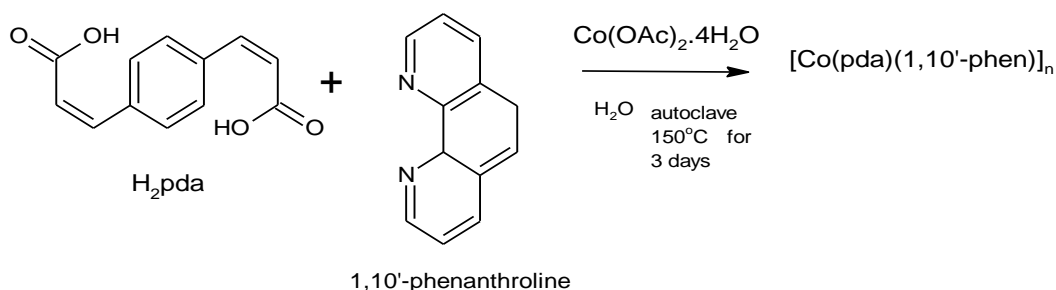
1)



2)



3)

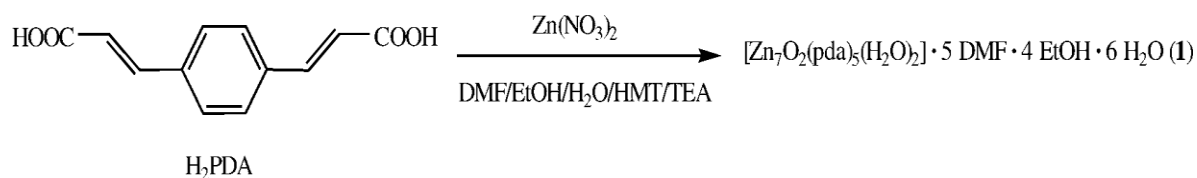


Single crystal X-ray diffraction analysis was carried out and it revealed that 1 and 3 has monoclinic crystal system having  $\text{C2/c}$  space group. 1 shows square pyramidal geometry and 3 has slightly distorted octahedron geometry. 2 has triclinic crystal system having P-1



space group. One Co forms octahedral geometry and other Co forms highly distorted trigonal bipyramidal geometry. Photocatalytic activity was carried out by degradation of RhB under UV light. Complex 2 showed better degradation as compared to complex 1 and 3.

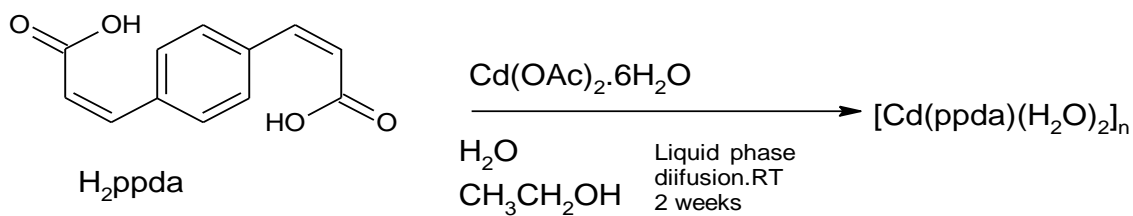
- In the year 2006, three-dimensional, non-interpenetrating microporous metal–organic framework (MOF),  $[\text{Zn}_7\text{O}_2(\text{pda})_5(\text{H}_2\text{O})_2] \cdot 5\text{DMF} \cdot 4\text{EtOH} \cdot 6\text{H}_2\text{O}$  (1) ( $\text{H}_2\text{PDA} = p$ -phenylenediacrylic acid,  $\text{DMF} = \text{N,N}$ -dimethylformamide,  $\text{EtOH} = \text{ethanol}$ ), was synthesized by constructing heptanuclear zinc carboxylate secondary building units (SBUs) and by using rigid and linear aromatic carboxylate ligands, PDA.



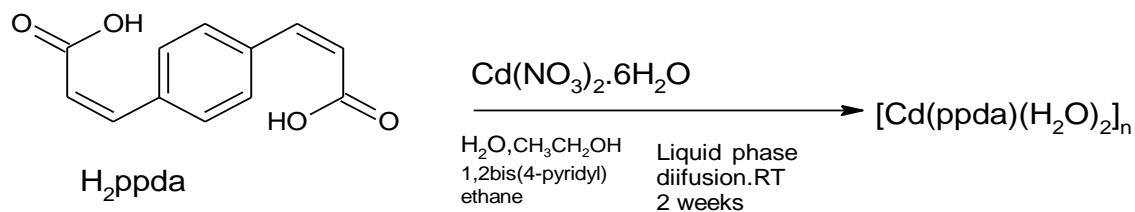
The X-ray crystallography analysis were carried out and it reveal that complex crystallizes in the tetragonal group having 14cm space group. There occurs seven zinc centers having three octahedral and four tetrahedral geometries and are held together with carboxylate group of pda ligand.

- Four isomeric coordination polymers of formula  $[\text{Cd}(\text{L})(\text{H}_2\text{O})_2]_n$  ( $\text{L} = \text{ppda}$  and  $\text{mpda}$ ) were synthesized from two isomeric dicarboxylic ligands,  $p$ -phenylenediacrylic acid ( $\text{H}_2\text{ppda}$ ) and  $m$ -phenylenediacrylic acid ( $\text{H}_2\text{mpda}$ ) by Qian sun et al in the year 2015. 1p 2p and 2m were synthesized by three layer diffusion method carried at room temperature and 1m were synthesized by hydrothermal method at  $110^\circ\text{C}$  for 5 days.

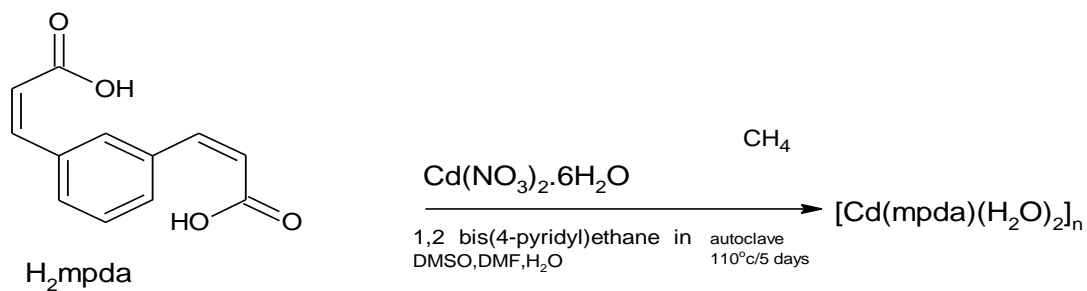
1p)



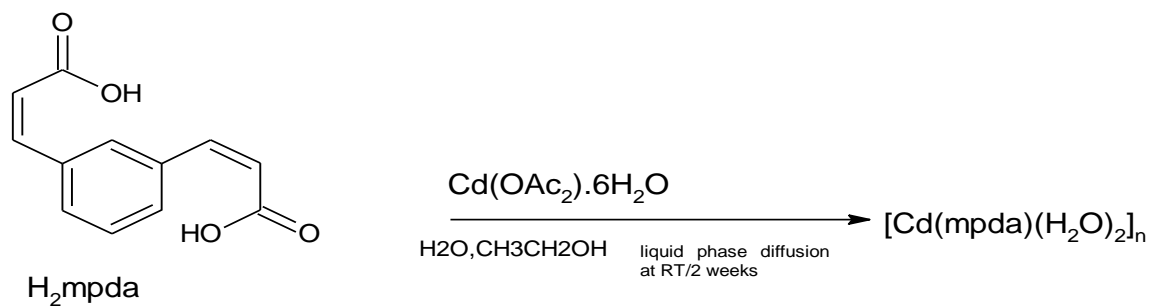
2p)



1m)



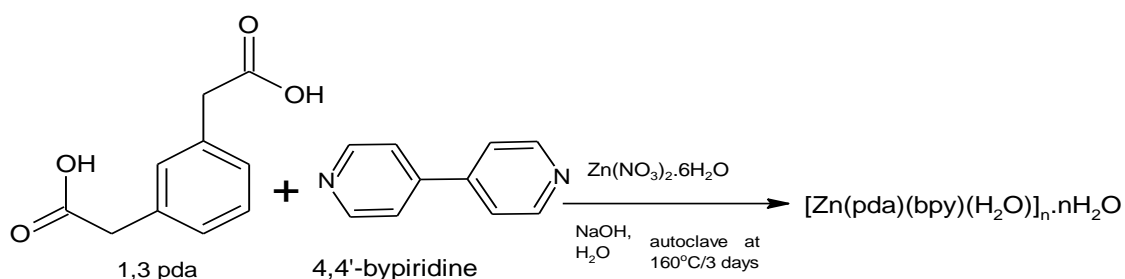
2m)



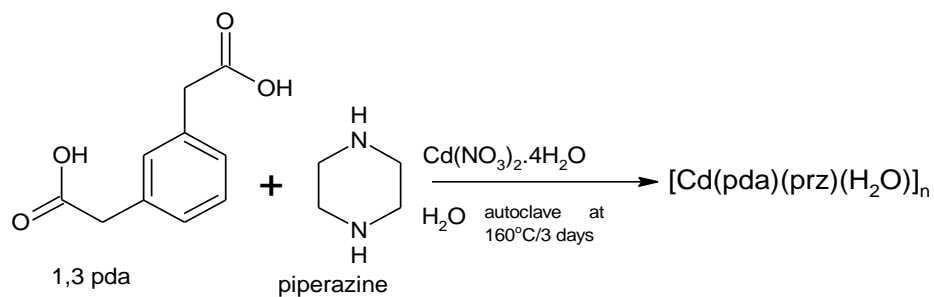
Single crystal X-ray diffraction analysis was carried out and it revealed that 1p, 2p, 2m have a monoclinic crystal system and 2p has orthorhombic crystal system. 1p has  $C2/c$  space group, 2p has  $C2221$ , 1m has  $P2_1/c$  and 2m  $P2_1$  space group. 2p and 2m has 3D coordination framework. IR studies shows the similar spectra for all compounds. It shows no absorption band around  $1700\text{ cm}^{-1}$  as there is complete deprotonation of carboxylic group of the ligand. All compounds show bands in the region  $3300\text{ cm}^{-1}$ - $3400\text{ cm}^{-1}$  assigned for water molecule. It shows strong absorption in the range of  $1638\text{ cm}^{-1}$ - $1640\text{ cm}^{-1}$  for asymmetric vibration and at  $1390\text{ cm}^{-1}$  for symmetric vibration. Luminescent studies showed enhanced ligand-centered luminescence.

- Four coordination polymers,  $[Zn(pda)(bpy)(H_2O)]_n \cdot nH_2O$ ,  $[Cd(pda)(prz)(H_2O)]_n$ ,  $[Co_3(u_3-OH)_2(pda)(pyz)_n \cdot 2nH_2O]$  and  $[Pr_2(pda)_3(H_2O)_2]_n$  ( $H_2pda$ = 1,3-phenyldiacetic acid,  $bpy$ =4,4'-bipyridine,  $prz$ =piperazine and  $pyz$ =pyrazine) were synthesized hydrothermally by Jin- Zhong Gu et al in the year 2011. Hydrothermal synthesis were carried out at  $160^\circ\text{C}$  for 3 days.

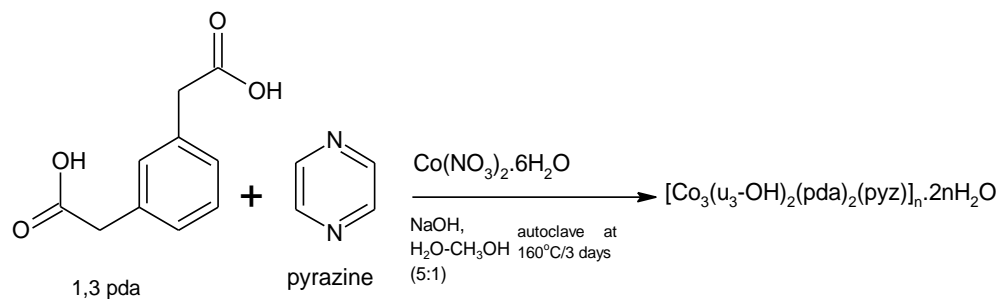
1)



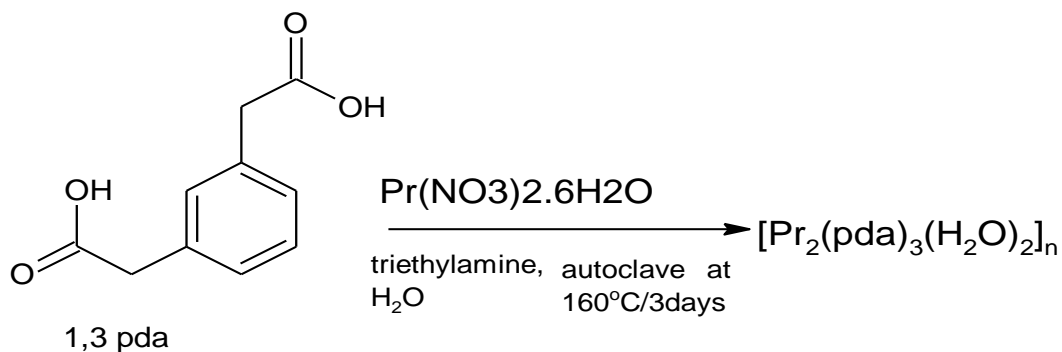
2)



3)



4)



Single crystal X-ray analysis were carried and it revealed that complex 1,2 crystallizes in the triclinic crystal system having P-1 space group. Both complex forms the distorted octahedral geometry. complex 1 generates the 1D wheel like chain structure and complex 2 forms 1D ladder-like chain which is further extended into a 3D metal-organic supramolecular framework. Complex 3 crystallizes in the monoclinic crystal system having P2/c space group and shows distorted octahedral geometry and generates 2D sheet which is further extended to 3D supramolecular

framework. Complex 4 crystallizes in the triclinic crystal system having P-1 space group. This complex forms distorted tricapped trigonal prism geometry and generates 3D MOF. X-ray powder diffraction measurement were carried out which revealed that synthesized materials of compound are homogeneous.

Thermal gravimetric analysis (TGA) were carried out for all the complexes at the rate of 10°C/min under nitrogen atmosphere and showed that 3D complex 4 is more stable than 1D complex 1, 2 and 3. Photoluminescent properties were studied for complex **1** and **2** at room temperature. complex 1 showed red shift due to ligand to metal charge transfer(LMCT). Complex 2 shows intense blue luminescence due to intraligand fluorescence emissiion. Magnetic properties were studied for complexes **3** and **4**, and showed antiferromagnetic interactions between the nearest metal ion.

## CHAPTER 2

### EXPERIMENTAL SECTION

#### Materials and method

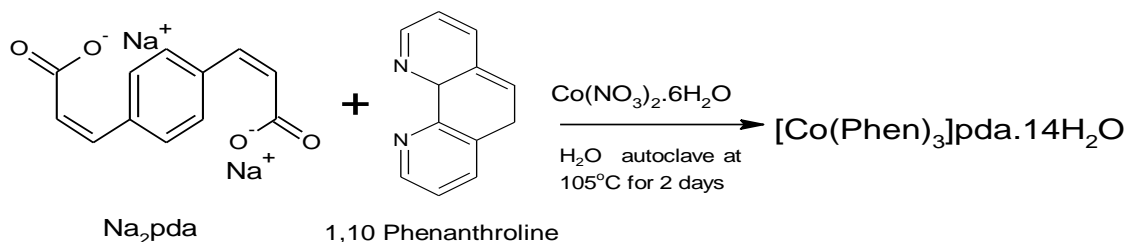
##### Preparation of disodium salt of phenylenediacrylic acid (Na<sub>2</sub>pda)

20 mL of distilled water was taken in a 250mL beaker and kept for heating on hot plate with magnetic stirrer. Once water started boiling to this hot solution 0.655g (3mM) of phenylenediacrylic acid was added and stirred for some time. To this 0.504g (6mM) of sodium bicarbonate was added pinch wise till the pH was maintained to 7 and kept for stirring. Solution was allowed to evaporate to dryness which yielded to give pale yellow powder.

#### Synthesis: Hydrothermal method

##### Preparation of [Co(phen)<sub>3</sub>]pda.14H<sub>2</sub>O

Aqueous solutions of cobalt nitrate hexahydrate (1mMole,0.29g), disodium salt of 1,4-phenylenediacrylic acid(Na<sub>2</sub>pda) (1mMole,0.26g) and 1,10-phenanthroline(3mMole,0.6g) was made by dissolving in 3ml of distilled water separately. Aqueous solution of Na<sub>2</sub>pda and 1,10-phenanthroline was added to aqueous solution of cobalt nitrate hexahydrate with constant stirring. This mixture was then sealed into 25mL Teflon lined stainless steel autoclave and heated at 105°C for 48 hours. Brown colour crystals were obtained which were filtered and air dried.



## CHAPTER 3

## INFRARED SPECTRAL ANALYSIS

[Co(phen)<sub>3</sub>]pda.14H<sub>2</sub>O compound was prepared by reacting cobalt nitrate hexahydrate with phenylenediacrylate and 1,10-phenanthroline. Brown crystals were obtained. IR of this was reported and compared with phenylenediacrylic acid (H<sub>2</sub>pda) and 1,10-phenanthroline (1,10-phen).

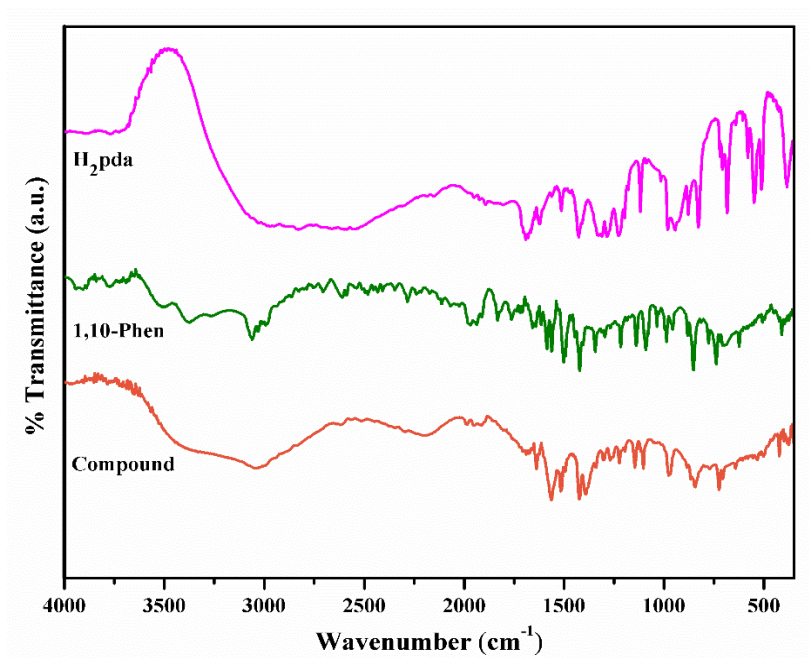


Fig. Comparison of IR spectra of compound with H<sub>2</sub>pda and 1,10-phen.

The IR spectra of carboxylic acid is characterized by strong absorption at 1750-1700 cm<sup>-1</sup> associated with C=O bond and 1300-1200cm<sup>-1</sup> for C-O bond. Whereas Carboxylate ion shows strong Anti-symmetric  $\nu_{as}$  and Symmetric  $\nu_s$  COO<sup>-</sup> stretching absorptions at 1650-1510 and 1400-1280 cm<sup>-1</sup> respectively. For phenylenediacrylic acid (**H<sub>2</sub>pda**) IR spectra showed absorption at 1701cm<sup>-1</sup> which attributed to COOH stretching vibration. Peak at 2500-3000 cm<sup>-1</sup> was observed due to acidic OH stretching vibration. For 1,10-phenanthroline(**1,10-phen**) IR spectra showed peak at 3053 cm<sup>-1</sup> which attributed to aromatic C-H vibration and peak in the range of 1400-1640

$\text{cm}^{-1}$  corresponds to the C=C and C=N. For  $[\text{Co}(\text{phen})_3]\text{pda} \cdot 14\text{H}_2\text{O}$  (**compound**) IR spectra exhibited broad absorption band  $2700\text{--}3500\text{cm}^{-1}$  assigned to O-H stretching vibration of water molecule. IR spectra showed weak absorption at  $1700\text{cm}^{-1}$  due to complete deprotonation of phenylenediacrylic acid ( $\text{H}_2\text{pda}$ ). Peak in the range of  $1400\text{--}1550\text{cm}^{-1}$  were seen due to presence of C=N and C=C stretching vibration which was seen in case of 1,10-phenanthroline.

## THERMAL ANALYSIS

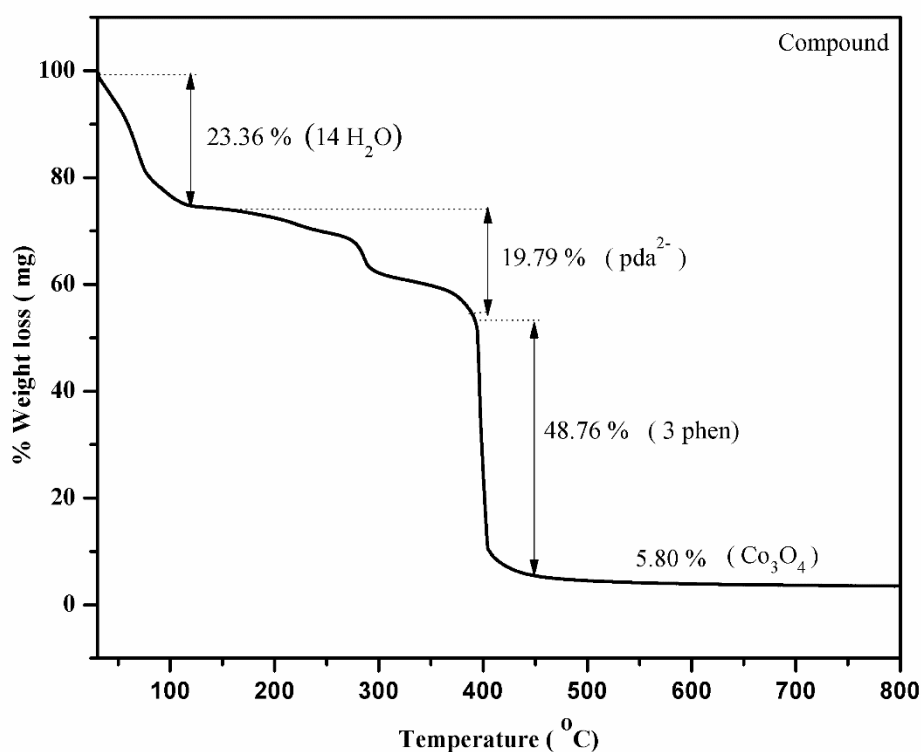


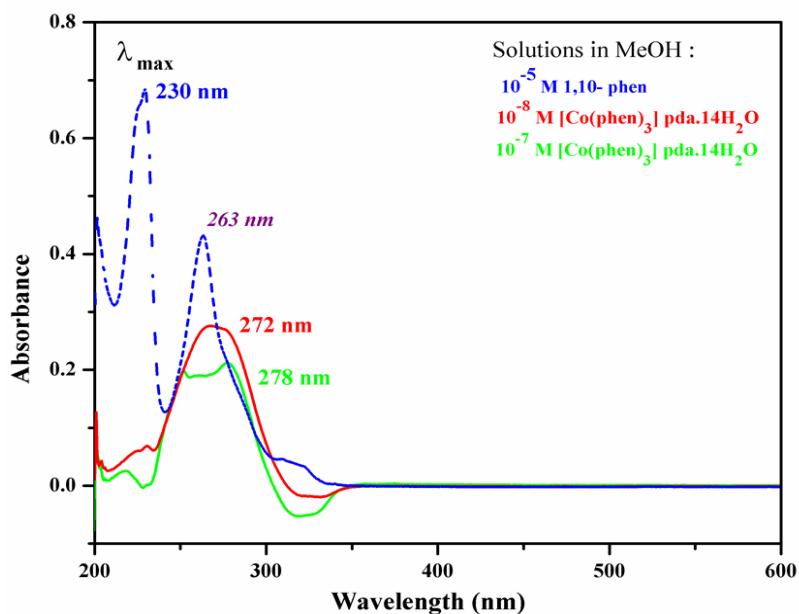
Fig.

The Thermogravimetric analysis(TG) of the compound  $[\text{Co}(\text{phen})_3]\text{pda} \cdot 14\text{H}_2\text{O}$  shows that at temperature around  $110^\circ\text{C}$  it was seen that there was 23.36% weight loss which indicated the presence of 14  $\text{H}_2\text{O}$  molecules. At temperature around  $370^\circ\text{C}$  there was 19.79% weight loss which corresponds to the loss of  $\text{pda}^{2-}$ . At temperature above  $450^\circ\text{C}$  there was complete decomposition



of the compound forming  $\text{Co}_3\text{O}_4$  with the weight loss of 48.76% which corresponds to the loss of three phenanthroline ligands.

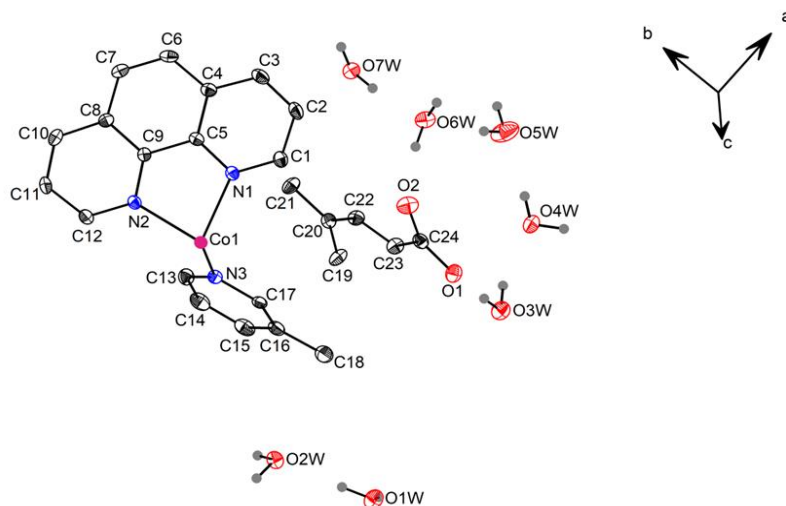
### UV-VISIBLE SPECTRAL ANALYSIS



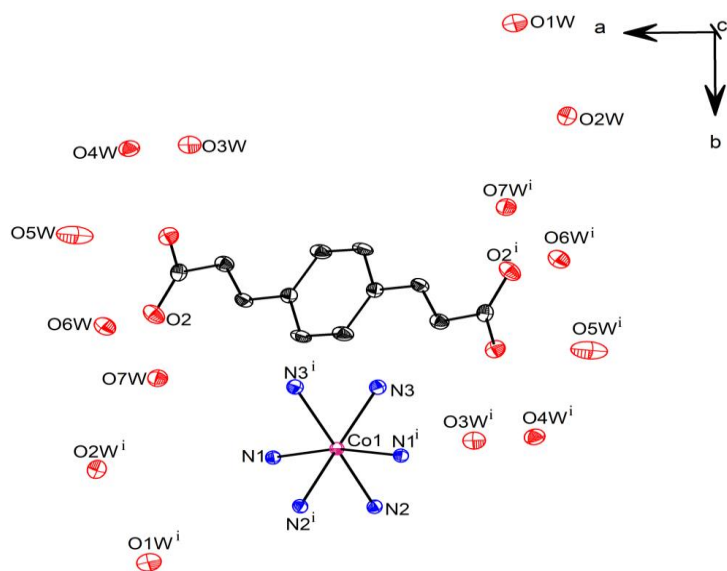
For the complex  $[\text{Co}(\text{phen})_3]\text{pda} \cdot 14\text{H}_2\text{O}$ , two bands were observed having  $\lambda$  value 230nm and 272nm with concentration  $1 \times 10^{-8}\text{M}$  having molar absorptivity value  $\epsilon = 274 \times 10^5 \text{ mol}^{-1}\text{L cm}^{-1}$  and three bands were seen with  $\lambda$  value 217nm, 250nm and 278nm with concentration  $1 \times 10^{-8}\text{M}$  having molar absorptivity  $\epsilon = 214 \times 10^4 \text{ mol}^{-1}\text{L cm}^{-1}$  are of ligand centered and assigned to  $\pi\text{-}\pi^*$  on  $n\text{-}\pi^*$  transition in the pyridine rings of the phenanthroline ligand. This is due to process of dilution. By diluting the complex with more methanol concentration decreases as a result three bands appears for the complex having concentration  $1 \times 10^{-7}\text{M}$  which is not seen in case of complex having concentration  $1 \times 10^{-8}\text{M}$ .

## SINGLE CRYSTAL X-RAY DIFFRACTION STUDIES

### Crystal Structure of $[\text{Co}(\text{phen})_3] \text{pda} \cdot 14\text{H}_2\text{O}$



**Figure.** The asymmetric unit of  $[\text{Co}(\text{phen})_3] \text{pda} \cdot 14\text{H}_2\text{O}$  showing the atom labelling scheme.



**Figure:** X-ray crystal structure of  $[\text{Co}(\text{phen})_3] \text{pda} \cdot 14\text{H}_2\text{O}$ . The N-atoms of phen are depicted without the C-atom rings for clarity. (H atoms are omitted for clarity).

**Table.** Crystallographic parameters for [Co(phen)<sub>3</sub>] pda·14H<sub>2</sub>O

Chemical formula	C <sub>48</sub> H <sub>60</sub> CoN <sub>6</sub> O <sub>18</sub>
Formula weight	1067.95 g mol <sup>-1</sup>
Crystal system	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>
Temperature(K)	100(2)
Wavelength (Å)	0.71073
Unit cell dimensions	a= 23.1091(13) Å, α=90° b= 12.1077(5) Å, β= 111.410(2) ° c= 19.7428(10)Å, γ=90°
Volume (Å <sup>3</sup> )	5142.8(4)
Z	4
Density (g/cm)	1.379
Absorption coefficient (mm <sup>-1</sup> )	0.412
F(000)	2244

The X-ray Single Crystal structure of the above said compound revealed a [Co(phen)<sub>3</sub>]<sup>2+</sup> cationic moiety, charge balanced by pda<sup>2-</sup> and the presence of fourteen solvate water molecules, which was formulated as given by [Co(phen)<sub>3</sub>] pda.14H<sub>2</sub>O.

The single-crystal data revealed that the Co(II) coordination complex crystallizes in the monoclinic system with C2/c space group. The asymmetric unit is composed of half a Co(II) unit, one and a half phen unit, half  $\text{pda}^{2-}$  and seven water molecules. The Co(II) ion adopts a distorted octahedral geometry being ligated by two N-atoms each from the three phen rings (Co-N 2.1208(18), 2.125(2) and 2.1376(19) Å). The acidic linker,  $\text{H}_2\text{pda}$  is completely deprotonated and acts as a counter balancing dianion to Co(II). Furthermore, the  $\text{pda}^{2-}$  moiety exhibits H-bonding interactions with the solvate water molecules.

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