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Syntheses, Structures and Photoluminescence Properties of Zinc (II) and Cadmium (II) Metal Complexes Constructed from 3,4-Pyridinedicarboxylic Acid and Aromatic Diimines

Alka Srivastava*, Krishna Srivastava and Jagdish Prasad

Nanoscience and Electrochemical Research Laboratory, Department of Chemistry,
University of Allahabad, Allahabad-211002 (U. P.), INDIA
Email: alka23srivastava@gmail.com

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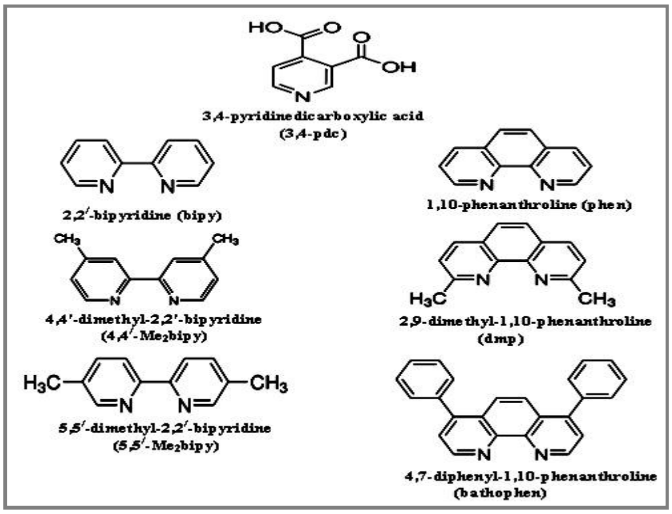
ABSTRACT

Some mixed-ligand complexes of zinc(II) and cadmium (II) $[Zn_3(pdc)_3(bipy)]$ **(1)**, $[Zn_2(pdc)_2(4,4'\text{-}Me_2bipy)_2]$ **(2)**, $[Zn_2(pdc)_2(5,5'\text{-}Me_2bipy)_2(H_2O)_2].(H_2O)_2$**(3)**, $[Zn_2(pdc)_2(phen)_2].4H_2O$ **(4)**, $[Zn_2(pdc)_2(dmp)_2].\ 2H_2O$**(5)**$[Cd_3(pdc)_3(bipy)(H_2O)_4]$ **(6)**, $[Cd_3(pdc)_3(4,4'\text{-}Me_2bipy)(H_2O)_2]$ **(7)**, $[Cd_3(pdc)_3\ (5,5'\text{-}Me_2bipy)(H_2O)_2]$ **(8)**, $[Cd_3(pdc)_3(phen)(H_2O)_3].H_2O$ **(9)**, $[Cd_3(pdc)_3(dmp)(H_2O)_4]$ **(10)** *and* $[Cd(pdc)(bathophen)]$ **(11)** *have been synthesized by hydrothermal method in 3:1:1 metal-to-ligand molar ratio. The newly synthesized complexes have been characterized by elemental analyses (C, H, N), thermogravimetric (TGA/DTG/DTA) analyses, FTIR-spectra, photoluminescence spectra, and powder X-ray diffraction analyses (PXRD).*

Graphical Abstract



Keywords: Mixed-ligand Zn (II) and Cd (II) complexes, 3,4-pyridinedicarboxylic acid, Diimines, Photoluminescence, Thermogravimetry.

INTRODUCTION

The design and synthesis of metal-organic coordination polymers have drawn considerable attention due to a wide range of diversity in their structures, physical and chemical properties and their technological and potential applications as functional materials [1-11]. One of the most challenging research fields in modern chemistry is the design and synthesis of multifunctional compounds and materials with predictable structures and properties. In the 1970s, A.F. Wells[12] focused on the overall structures of inorganic compounds and abstracted crystal structures in terms of their topology by reducing them to a series of points of a certain geometry that are linked to a fixed number of other points. The final structures can thus be described either as polyhedra or as infinite networks. In the early 1990s, R. Robson [13] developed and extrapolated Wells' work into the realm of metal-organic compounds and coordination supramolecular chemistry. In order to design the targets with the different structural features and potential functions, an important step is selection and synthesis of the nodes including mono-, biand poly-nuclear structural units. Different metal ions may exhibit different coordination geometries. Synthesis of desired coordination polymers is still a great challenge for the chemists due to its great dependence on reaction conditions such as temperature, pressure, time, pH, metal to ligand ratio, counter anions, solvents etc. that may alter the nature of the coordination polymers [14-19]. Metal-organic coordination complexes have been successfully designed and synthesized by judicious choice of metal ions and linkers in which metal ions (and/or metal clusters) functioning as nodes and organic ligands or linkers as bridges [20-24].

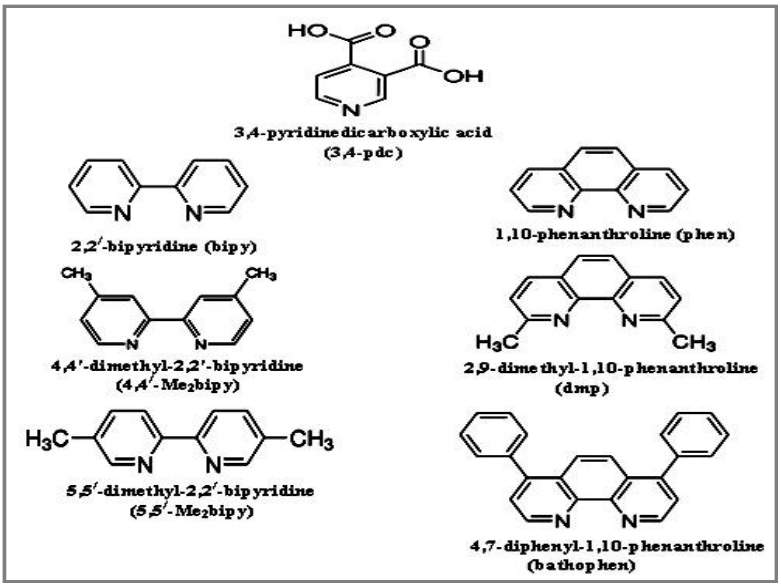
Coordination polymers exhibit a wide range of infinite zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) frameworks with various interesting structural features, resulting from ligand coordination to the metal ions and supramolecular interactions such as hydrogen bonding, aromatic π-π stacking interactions, dipole-dipole interactions as well as van der Waals forces [25-29]. The hydrogen bond, as one type of ubiquitous noncovalent weak interaction, plays an important role in molecular recognition and crystal engineering owing to its unique bond intensity and directionality. Currently, crystal engineering utilizing hydrogen bonding synthons containing a functional inorganic cluster is drawing much attention of researcher's because it affords a rational and reproducible route to design and construct functional supramolecular materials containing luminescent, electronic, or magnetic units [30, 31].

The versatility of metal-organic chemistry offers a unique opportunity to construct multifunctional materials based on the assembly of molecular building blocks. Such an approach can lead to the design of coordination polymers with intriguing architectures and potential applications [32]. Particular attractive is the ability of organic moiety to diversify structural arrangements associated with the wide ranging properties of transition metals (e.g. magnetic and optical properties, electronic conductivity and ferro electricity) [33]. In this regard, much attention has been devoted to the deliberate design and control of self-assembly infinite coordination networks via selecting the chemistry structures of ligands [34]. Among these, the employment of symmetrical ligands is a successful paradigm owing to their high symmetry and structural predictability [35]. Nevertheless, incorporation of unsymmetrical ligands in such a system is relatively recent. Although important progress has been made in the construction of coordination polymers by applying unsymmetrical ligands [36], further research for them is still an especially attractive target, thus allowing the construction of an almost infinite number of new molecule-based entities. Pyridine-3,4-dicarboxylic acid (H_2pdc), as a member of them, has been less studied up to now. Of the relatively few structurally characterized complexes which exit to date [37], all are constructed from PDC and linear ligands.

Pyridinedicarboxylic acids (pdcs) have been widely used as organic ligands to the construction of metal organic coordination polymers (MOCPs) or metal organic frameworks (MOFs), which is of intense interests in recent years[38-43]for their potential application in molecular sieve, optoelectronics, magnetism, chemical sensors and so on [44]. This type of ligands combines the advantages of both organic multi-carboxylic acid and aromatic compound. In coordination compounds, the multi-carboxylic acids as ligands always show varieties of coordination modes for transition metal complexes. The compounds with aromatic rings such as pyridine, 2,2'- bipyridine, 1,10-phenanthroline and their interrelated derivatives can be used as the antenna for energy absorption in photo luminescent materials [**45, 46**]. A fascinating supramolecular architecture can easily be achieved via the combination of carboxylate ligands with other ligands having N-donor chelating bipyridine moiety. 2,2'-bipyridine and its derivatives are frequently used for the synthesis of low dimensional molecular architectures [**47-51**], which can be further extended to high dimensional supramolecular architectures via supra molecular interactions.

On the other hand, polynuclear d^{10} metal (Cu(I), Ag(I), Au(I), Zn(II) and Cd(II) complexes have attracted extensive interest in recent years in that they not only exhibit appealing structures but also possess photo luminescent properties [**52**].

Thus, keeping in mind the above mentioned importance and properties a successful attempt has been made for synthesizing twelve mixed-ligand zinc(II) and cadmium(II) complexes, taking 3,4-pyridinedicarboxylic acid (3,4-pdc) as a primary ligand while diimines, where diimines= bipyridyl (bipy), 4,4'-dimethyl-2,2'-bipyridyl (4,4'-Me_2bipy), 5,5'-dimethyl-2,2'-bipyridyl (5,5'-Me_2bipy), 1,10-phenanthroline (phen),2,9-dimethyl-1,10-phenanthroline (dmp) and 4,7-diphenyl-1,10-phenanthroline (bathophen) as secondary ligands (Scheme 1). These complexes are formulated as: $[Zn_3(pdc)_3(bipy)]$ **(1)**, $[Zn_2(pdc)_2(4,4'\text{-}Me_2bipy)_2]$ **(2)**, $[Zn_2(pdc)_2(5,5'\text{-}Me_2bipy)_2(H_2O)_2].(H_2O)_2$**(3)**, $[Zn_2(pdc)_2(phen)_2]$. $4H_2O$ **(4)**, $[Zn_2(pdc)_2(dmp)_2]$. $2H_2O$ **(5),** $[Cd_3(pdc)_3(bipy)(H_2O)_4]$ **(6)**, $[Cd_3(pdc)_3$ $(4,4'\text{-}Me_2bipy)$ $(H_2O)_2]$ **(7)**, $[Cd_3(pdc)_3(5,5'\text{-}Me_2bipy)(H_2O)_2]$ **(8)**, $[Cd_3(pdc)_3$ (phen) $(H_2O)_3]$. H_2O **(9)**, $[Cd_3(pdc)_3$ $(dmp)(H_2O)_4]$ **(10)** and [Cd(pdc)(bathophen)] **(11)**. These complexes were synthesized by hydrothermal method at100°C±0.5^{0}C by heating the reaction mixture in aqueous medium for 72 h.



Scheme 1. Structures of 3,4-pdc and aromatic diimines ligands.

MATERIALS AND METHODS

Material and physical measurements: Metal salts, i.e., zinc sulphate, cadmium nitrate and organic ligands 3,4-pyridinedicarboxylic acid (3,4-pdc) and aromatic diimines viz; 2,2'-bipyridyl (bipy), 4,4'-dimethyl-2,2'-bipyridyl (4,4'-Me_2bipy), 5,5'-dimethyl-2,2'-bipyridyl (5,5'-Me_2bipy), Phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (dmp) and 4,7-diphenyl-1,10-phenanthroline (bathophen) were purchased from Sigma Aldrich Chemicals Pvt. Ltd., New Delhi and were used as such. Ethanol was purchased from Bengal Chemicals, Kolkata, India. All experimental operations were performed in air. Elemental analyses (C, H, N) were performed on a EURO VECTOR EA 3000 ELEMENTAL ANALYSER. FTIR spectra were recorded in the range 450-4000cm^{-1} on a Agilent Cary 630 FTIR Spectrometer using a KBr pellet. Thermal Gravimetric Analysis (TGA) was performed under an nitrogen atmosphere with a heating rate of 10°C/min using a EXSTAR TG/DTA 6300 analyzer. Room temperature photoluminescence spectra were recorded on aPerkin Elmer LS-45 Fluorescence Spectrometer and Powder X-ray diffraction patterns (PXRD) were taken on a Rigaku SmartLab X-ray diffractometer.

Synthesis of Zn(II) and Cd(II) mixed-ligand complexes: Eleven mixed-ligand complexes of zinc (II) and cadmium (II) with disodium salt of 3,4-pyridinedicarboxylic acid (3,4-pdc) and diimines, (where diimines= bipyridyl (bipy), 4,4'-dimethyl-2,2'-bipyridyl (4,4′-Me$_2$bipy), 5,5'-dimethyl-2,2'-bipyridyl (5,5′-Me$_2$bipy), phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (dmp) or 4,7-diphenyl-1,10-phenanthroline (bathophen)) have been synthesized conventionally by refluxing the reaction mixture of metal salts Zn(II)(3 mM, 862.62 mg); or Cd(II) (3 mM, 925 mg) dissolved in 30 mL water, 3,4-pdc (1 mM, 212 mg) dissolved in 30 mL water and diimines (2,2'-bipy 1 mM, 156.19 mg, 4,4´-Me$_2$bipy, 1 mM, 184 mg, 5,5´-Me$_2$bipy, 1 mM, 184 mg, Phen, 1 mM, 198 mg, dmp, 1 mM, 217.27 mg or bathophen, 1 mM, 332 mg) dissolved in 30 mL ethanol.Added the solution of 3,4-pdc in Zn(II) or Cd(II) solution and after that the solution of a diimine was added in the above mixed solution in a round bottom flask and refluxed this solution mixture on water bath for 72 hours. Filtered the precipitate, washed it with alcohol and dried at room temperature, white colour powders of complexes **1-11** were obtained in 9% , 26.7%, 26.6%, 28.8%, 25.3%, 12.8%, 14%, 14.9%, 15.4%, 44.5% and 16.72% yield, respectively.

RESULTS AND DISCUSSION

Elemental analyses: Elemental analyses (C, H, N) were performed on a Euro Vector Ea 3000 Elemental analyzer and the data is given in table 1.

Vibrational studies: The FTIR spectra of complexes **1-11** indicated the characteristic bands due to coordinated carboxylate anion. A broad band in the region of 3200-3600 cm^{-1} can be attributed to the presence of hydroxyl ν_{OH} ion. The carboxylate stretching vibration (ν_{COOH}) for free 3,4-pdc ligand was observed at 1717 cm^{-1}. But the band for ν_{COOH} disappeared when pdc is coordinated to Zn (II) and Cd (II) metal ion. In addition all the Zn (II) and Cd (II) complexes exhibited an asymmetric $\nu_{as}(COO^-)$ and symmetric $\nu_s(COO^-)$ carboxylate stretching vibrations observed at 1576 and 1385 cm^{-1}, 1576 and 1382 cm^{-1}, 1581 and 1385 cm^{-1}, 1577 and 1385 cm^{-1}, 1522 and 1382 cm^{-1}, 1525 and 1384 cm^{-1} , 1525 and 1385 cm^{-1} , 1564 and 1384 cm^{-1} , 1564 and 1384 cm^{-1} , 1557 and 1385 cm^{-1} and 1562 and 1385 for complexes **1**, **2**, **3**, **4**, **5**, **6, 7, 8, 9, 10** and **11** respectively. The difference between asymmetric and symmetric carboxylate stretching frequencies ($\Delta = \nu_{as}(COO^-) - \nu_s(COO^-)$) is often used to correlate the carboxylate coordination mode [**53-54**]. The difference of asymmetric to symmetric stretching frequency comes out to be is less than 200 cm^{-1}, confirms the bidentate coordination mode of the carboxylate group in these complexes [**55**]. In addition, all the complexes show sharp and medium bands at 668 cm^{-1} attributed to pyridyl vibration [**56**] and at 3019 cm^{-1} assigned to aromatic ν_{CH} [**56**]. The vibrational study of complex **3** to **11** reveals a broad band at 3435 cm^{-1}, which simply indicates the presence of water molecule. Furthermore in complexes **3**, **6**, **7**, **8**, **9** and **10** the presence of water in coordination [**56**] is further supported by the bands at 846 and 772 cm^{-1}. The presence of pyridine ring is confirmed by the medium band at 1060 cm^{-1} in all the Zn(II) and Cd(II) mixed-ligand complexes [**56**]. The FT-IR spectra of complexes **4** and **10** showed two sharp and strong bands in the region 853 and 757 cm^{-1} which was assigned to $\nu_{C=N}$ of phenanthroline ring [**57**]. Finally for the complexes **1** to **11**, the ν(Cu-N) bands appear in far IR region 600 to 400 cm^{-1}, which supports the coordination of both 2,2'-bipyridyl, 1,10-phenanthroline and its derivative through their N-donor atoms with the zinc and cadmium atoms in their corresponding complexes [**58-60**].

Table 1. C, H, N data for complexes **1** to**11**

Complexes	C%		H%		N%	
	Calculated	Found	Calculated	Found	Calculated	Found
$[Zn_3(pdc)_3(bipy)]$ **(1)**	43.880	42.784	2.00	1.802	8.257	8.541
$[Zn_2(pdc)_2(4,4'\text{-}Me_2bipy)_2]$ **(2)**	54.972	54.798	3.616	4.484	10.126	10.277
$[Zn_2(pdc)_2(5,5\text{-}'Me_2bipy)_2(H_2O)_2].(H_2O)_2$ **(3)**	56.968	55.620	5.053	5.214	10.719	9.719
$[Zn_2(pdc)_2(phen)_2].4H_2O$ **(4)**	51.038	50.694	3.356	3.915	9.401	9.882
$[Zn_2(pdc)_2(dmp)_2].\ 2H_2O$**(5)**	55.170	54.876	3.721	4.014	9.195	9.404
$[Cd_3(pdc)_3(bipy)(H_2O)_4]$ **(6)**	30.069	29.197	2.356	2.408	6.599	5.141
$[Cd_3(pdc)_3(4,4'\text{-}Me_2bipy)(H_2O)_2]$ **(7)**	31.61	30.285	2.370	2.225	6.648	5.252
$[Cd_3(pdc)_3(5,5\text{-}'Me_2bipy)(H_2O)_2]$ **(8)**	31.423	30.368	2.370	2.120	6.640	5.256
$[Cd_3(pdc)_3(phen)(H_2O)_3].H_2O$ **(9)**	31.503	29.956	2.304	2.401	6.452	6.992
$[Cd_3(pdc)_3(dmp)(H_2O)_4]$ **(10)**	31.714	29.928	2.605	2.320	6.290	5.210
$[Cd(pdc)(bathophen)]$ **(11)**	55.997	54.716	3.115	3.700	6.886	6.499

Thermal analyses: Thermal stability of complexes was studied in the range of 30-1000°C by controlling the heating rates 10°C/min. The simultaneous TG/DTG/DTA curves in nitrogen atmosphere of all the complexes are shown in figure 1 to 3.

The TGA curve of **complex 1** showed that chemical decomposition starts at about 377°C and ends around 493°C with a weight loss of 62.5% corresponding to the expulsion of organic components. After that the remaining weight of 34.3% (Calcd. 34.77%) corresponds to ZnO residue. In this complex the DTG curve displays two peaks at 442°C and 475°C and the DTA curve displayed one exothermic peak at 474°C (Figure 1).

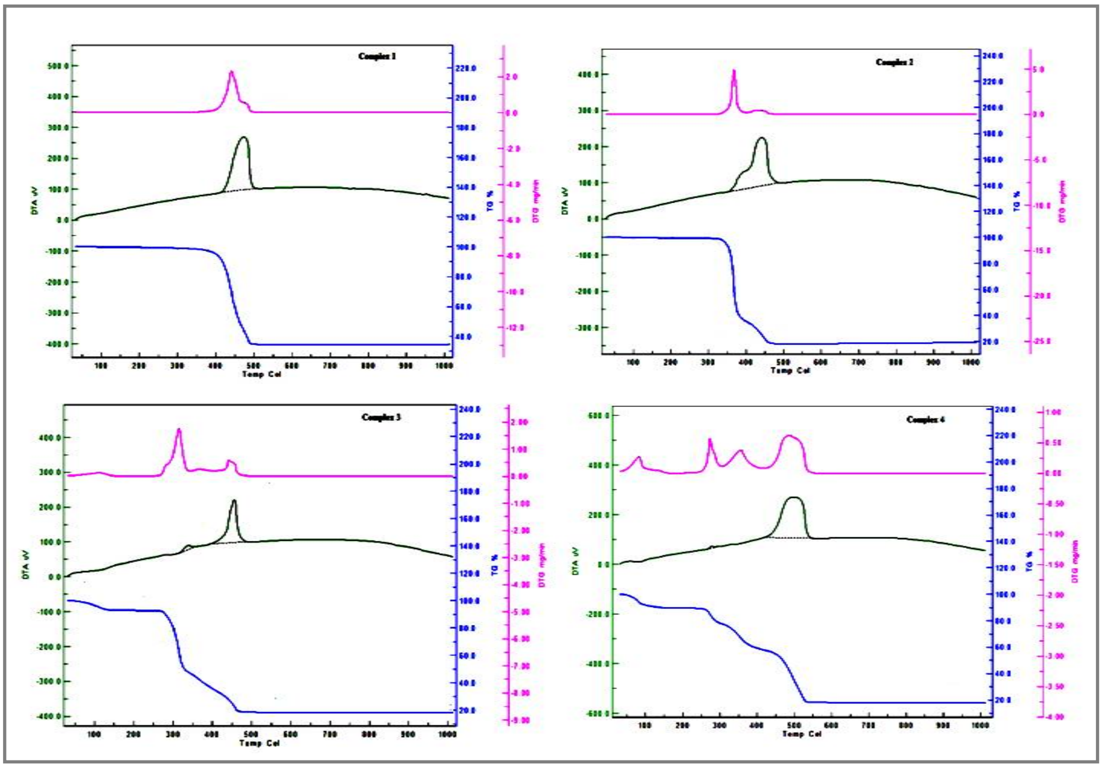


Figure 1. TG/DTA/DTG curves of complexes 1-4.

Complex 2 showed two step thermogram curve (Figure 1). The complex is stable upto 200°C, which indicating that the absence of lattice and coordinated water molecules. Above 332°C, the loss is continuous in the two stages. In the first stage of thermal dehydration of the complex takes place in between 332-400°C with DTG peak observed at 367°C and DTA peak observed at 394°C and the second stage of the decomposition takes place in between 400-468°C with DTG peak observed at 442°C and DTA peak observed at 443°C corresponding to the removal of organic ligands. Above 468°C, the complex was converted into ZnO residue 18.8% (Calcd. 19.63%).

The TGA of **complex 3** showed a first weight loss of 3.5% in the temperature range 100-200°C, corresponding to the loss of two lattice and two coordinated water molecules per formula unit (Figure 1). Subsequent to this there was no obvious weight loss occurs upto 260°C. The second weight loss starts at about 270°C to 331°C to give a total weight loss of 42.8% corresponding to the loss of 5,5'-dimethyl-2,2'-bipyridine ligand with DTG peak obtained at 340°C which clearly showed that an unstable intermediate are also formed during this decomposition step. The third weight loss occurs from 331°C to 467°C (30.3%) with DTG peak obtained at 443°C and DTA peak at 457°C corresponds to the loss of pdc ligand. In this complex the overall mass loss observed was 82% and it was compared with theoretical mass loss value which was found correct. The end product estimated as was ZnO 18% residue (Calcd. 18.05%).

The decomposition of **complex 4** takes place in four steps (Figure 1**)**. In the first step of thermal dehydration, i.e. upto 100°C with mass loss of 8.3% corresponds to the removal of four lattice water molecules and DTG peak obtained at 83°C. in the second and third step of thermal degradation which occurs in in the temperature range 248-300°C and 300-400°C and their corresponding DTG peak obtained at 274°C and 356°C, this range corresponds to the decomposition of phenanthroline ligand and observed mass loss was recorded as 10.8% and 19%. The fourth step was the decomposition of pdc ligand in the temperature range 400°C to 537°C with DTG peak observed at 487°C (41% weight loss). The remaining weight of 17.9% (Calcd. 18.21%) corresponds to the percentage of Zn and O components indicating that the final product was ZnO.

The thermogravimetric decomposition of **complex 5** occurred in four steps **(**Figure 2). The thermal dehydration of this complex in the first stage which accounts for a mass loss of 4.3% was attributed to the loss of two lattice water molecules in the temperature upto 100°C with DTG peak observed at 87°C. After that the complex was stable upto 200°C, indicating that the coordinated water molecules were not present in this complex. In the second and third stages which occur in the temperature range 313-400°C and 400-500°C with DTG peak at 329°C and 364°C corresponds to the decomposition of 2,9-dimethyl-1,10-phenanthroline ligand with total mass loss of 41.1%. The fourth step was the decomposition of pdc ligand in the temperature range 500 to 600°C with DTG peak observed at 546°C with mass loss of 35.3%. The final residual product appears to be ZnO above 600°C as shown by the 18.7% residue (Calcd. 17.81%).

The TGA curve of **complex 6** exhibits two continuous weight loss steps (Figure 2**)**. The first weight loss starts at about 100°C and ends at 192°C to give a total weight loss of 6.4% corresponding to the loss of four coordinated water molecules with DTG peak observed at 184°C and endothermic DTA peak observed at 161°C clearly indicating the phase change during this degradation step. The second weight loss of 49.8% occurred between 300°C and 476°C with DTG obtained at 391°C and exothermic DTA curve obtained at 416°C corresponding to the removal of organic components. The remaining weight of 41.8% corresponds to the percentage of Cd and O components indicating that the final product was CdO (Calcd. 40.31%).

The thermogravimetric decomposition of **complex 7** showed three step decomposition (Figure 2). This complex is stable upto 100°C, indicating that the lattice water molecule was not present in this complex. In the first stage of thermal dehydration of the complex took place in a two steps i.e. from temperature 100°C to 184°C and from 184°C to 300°C (4.3%) with phase change indicated by the endothermic DTA peak at 179°C. The two water molecules were removed in this step. In the second and third stage the total weight loss of 52.4% occurred between 300°C to 400°C and 400°C to 464°C with sharp exothermic DTA peak at 412°C. the maximum rate of mass loss was indicated by DTG peak at 389°C corresponding to the removal of organic ligands. The end product eastimated was CdO residue 42.8% (Calcd. 43.39%).

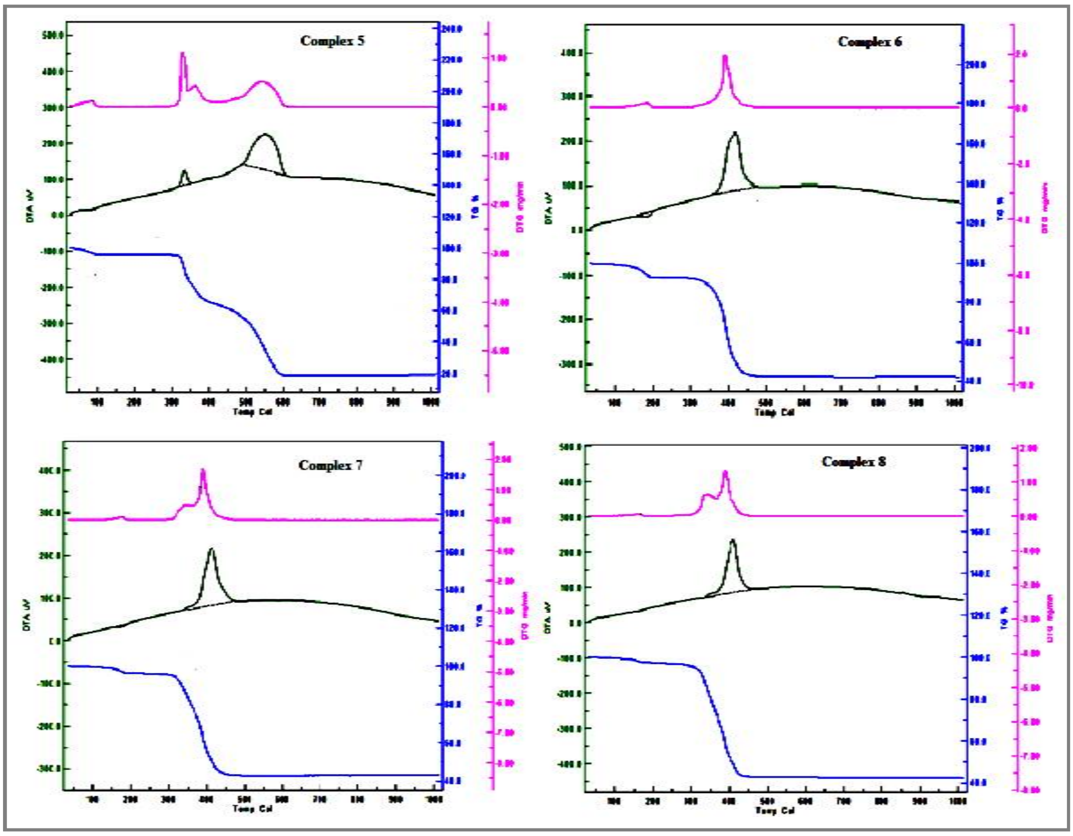


Figure 2. TG/DTA/DTG curves of complexes 5-8.

The TGA of **complex 8** showed three continuous weight loss step (Figure 2). In the first step, the decomposition of complex occurred in two stages i.e. between 100°C to 173°C and 173°C to 300°C with total mass loss of 3.8% with DTG peak observed at 164°C which corresponds to the expulsion of two coordinated water molecule. In the second and third step the total weight loss of 52.7% occurred between 300°C to 399°C and 399°C to 444°C with DTG peak obtained at 341°C and 389°C corresponds to the removal of organic components. The residue was CdO 42.2% (Calcd. 43.39%).

The thermogram of **complex 9** shows three step decomposition process (Figure 3). In the first step upto 100°C with mass loss of 1.5% corresponds to the removal of one lattice water molecule. In the second step that is in between 100 to 175°C with mass loss of 5.4% corresponds to the removal of three water molecules. The broad DTG peak observed at 160°C and endothermic DTA peak was observed at 162°C. The third stage was the decomposition of organic ligands in the temperature range 300°C to 469°C with DTA peak obtained at 393°C and407°C and DTG curve obtained at 379°C, the mass loss was 49.2%. Above 500°C the complex was converted into CdO residue 43.00% (Calcd. 41.88%).

The TGA of **complex 10** exhibit two continuous weight loss steps (Figure 3**)**. The first weight loss starts at 99.8°C to 220°C to give a total weight loss of 5.3% with DTG peak observed at 209°C and endothermic DTA peak obtained at 209°C corresponding to the loss of four coordinated water molecule. The second weight loss of 51.3% occurred between 300°C and 491°C with DTG peak observed at 386°C corresponding to the removal of organic components. The remaining weight of 41.4% corresponds to the percentage of Cd and O components indicating that the final product was CdO.

In **complex 11**, the TGA curve shows that the complex is stable upto 200°C. After that the chemical decomposition starts at about 300°C and ends around 665°C with a weight loss of 75.2% corresponding to the removal of 4,7-diphenyl-1,10-phenanthroline and 3,4-pyridinedicarboxylic acid ligands. The remaining weight of 23.8% corresponds to the CdO residue. In this complex the DTG curve displayed three peaks at 355°C, 572°C and 624°C and the DTA curve displayed two distinct exothermic peaks at 575°C and 621°C (Figure 3).

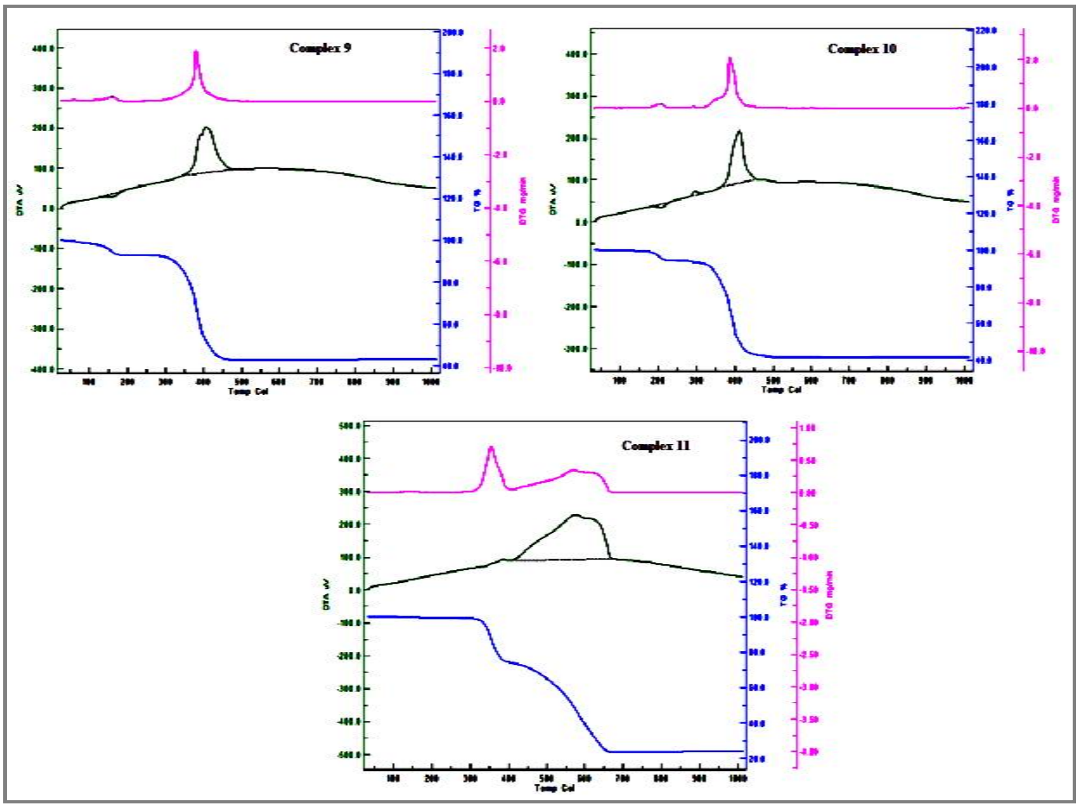


Figure 3. TG/DTA/DTG curves of complexes 9-11.

Photoluminescent properties: The liquid state photoluminescent spectra of the complexes**1**, **2**, **4** and **9** at room temperature are shown in figure 4. The luminescent spectra of complexes **1**, **2**, **3**, **6**, **7**, **8** and **11** are almost similar, i.e., exhibit two intense emission maxima at 460 and 472 nm for complexes**1**, **3** and **6** upon excitation at 353 nm, 412 and 434 nm for complex **2** and **11** upon excitation at 353 nm for **2** and 378 nm for the complex **11**, 410 and 432 nm for complexes **7** and **8** upon excitation at 364 nm. According to the literature [61], the peaks at 412 and 434 nm would be assigned to the emission of ligand to metal charge transfer while the peaks at 460 and 472 nm would be attributed to the intraligand emission from the 2,2'-bipyridine ligand [62, 63]. It is known that the free 2,2'-bipyridine molecule displayed a weak luminescence at 530 nm in the solid state at room temperature. The blue shift and luminescent enhancement of the emission at 460 and 472 nm compared to that of free 2,2'-bipyridine molecule may be due to the chelation of the 2,2'-bipyridine ligand to the metal ion, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay of the intraligand emission excited state[64, 65]. On the other hand the luminescent spectra of the complexes **4** and **5** exhibit an intense luminescence with an emission maxima at 436 nm upon excitation at 353 nm. This emission at 436 nm can be attributed to the intra ligand emission from the 3,4-pdc ligand [66, 67]. Free 3,4-pdc exhibit a weak luminescence at 490 nm in the solid state at room temperature. The enhancement and blue shift (from 490 nm to 436 nm) of the emission of the 3,4-pdc ligand in complexes 4 and 5 compared to that of free 3,4-pdc may be attributed to the coordination bond between the pdc ligand and the Zn(II) metal, which increases the rigidity of the ligand and reduces the loss of energy by radiation less decay of the intra ligand emission excited state [68, 69]. The emission spectra of complexes **9** and **10** in the liquid state at room temperature were shown in figure 4. It can be observed that an intense emission occur at 400 nm for complex 6, 10 and 11 upon excitation at 353 nm, 365 nm and 378 nm respectively. In order to understand the nature of emission bands of these three complexes, we analyzed the photo luminescent property of 3,4-pdc ligand and found that the strongest emission peak for 3,4-pdc ligand is about 370 nm, which is attributed the л*→n transition [70]. Therefore, the emission at 400 nm may not be related to the л*→n of the ligand. In addition similar emission bands have been observed previously for other d10 metal organic polymers with either photo luminescent or non photo luminescent ligands, such as [Zn(mpa)(phen)]n [71], $[Cd_3(tma)_2(H_2O)_2].2H_2O$ [72], $Cd_3tma_2.dabco.2H_2O$ [73] and $[Cd_3(pydc)_2(OH)_2(H_2O)_2]_n$ [74]. Thus according to the above literature, the emission band at 400 nm might be attributed to the ligand-to-metal charge transfer (LMCT). These observations indicate that the condensed polymeric complexes **9** and **10** may be excellent candidates for potential photoactive materials.

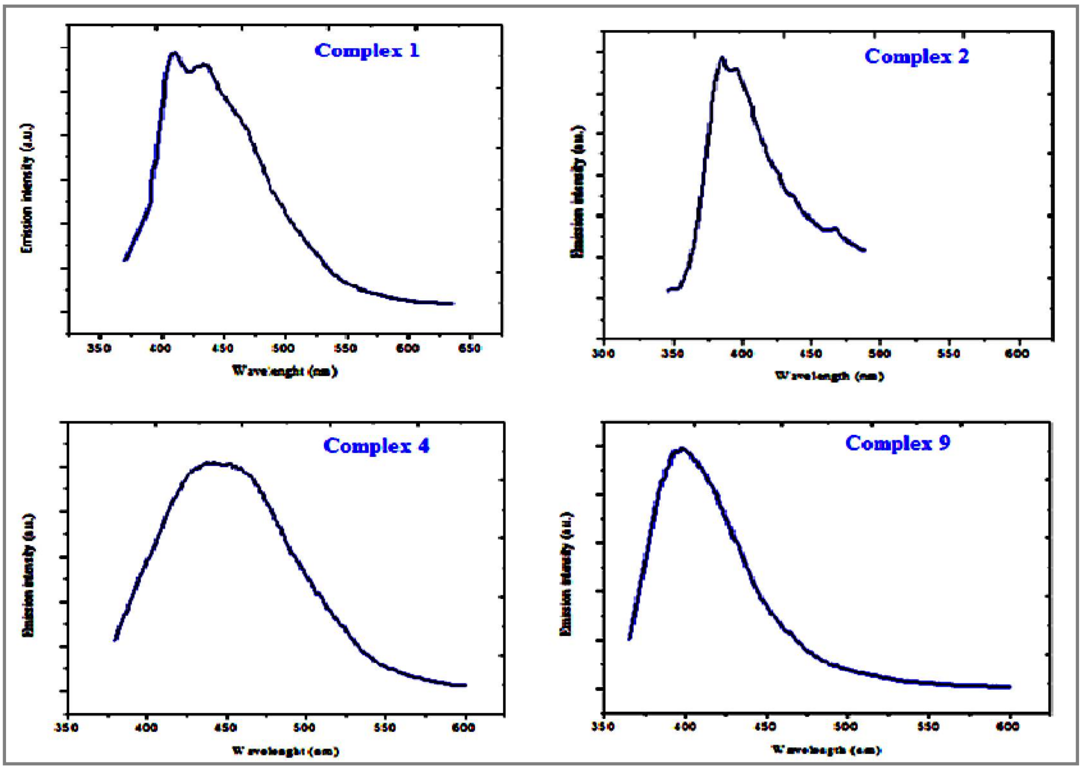


Figure 4. Liquid-state emission spectra of complexes **1**, **2, 4** and 9.

Powder x-ray diffraction analysis: Powder X-ray diffraction data of all the complexes were collected on a Rigaku Smart Lab X-ray diffractometer. Powder X-ray diffraction (PXRD) method is a popular technique, which has been used for the investigations of molecular and crystal structures [75], qualitative recognition of different complexes [76], quantitative resolution of chemical moiety [77, 78] measuring the degree of crystallinity [79], isomorphous substitutions [80], stacking faults [81], polymorphisms [76], phase transitions [82], particle sizes [83] etc. In powder complexes, diffracted beams are typically come from the sample that reflects its structural physico-chemical features. Thus powder X-ray diffraction method can analyze structural characteristics with other uncertainties of a wide range of materials such as inorganic catalysts, superconductors, biomolecules glasses, polymers and so on [84]. The XRD pattern of the complexes **1** to **11** showed well defined crystalline peaks indicating that all the complexes are amorphous in nature. The Powder XRD for complexes **1, 2, 6** and **8**are given as figure 5 and the molecular structures of coordination polymers **1-1** are given as (Figure 6-8).

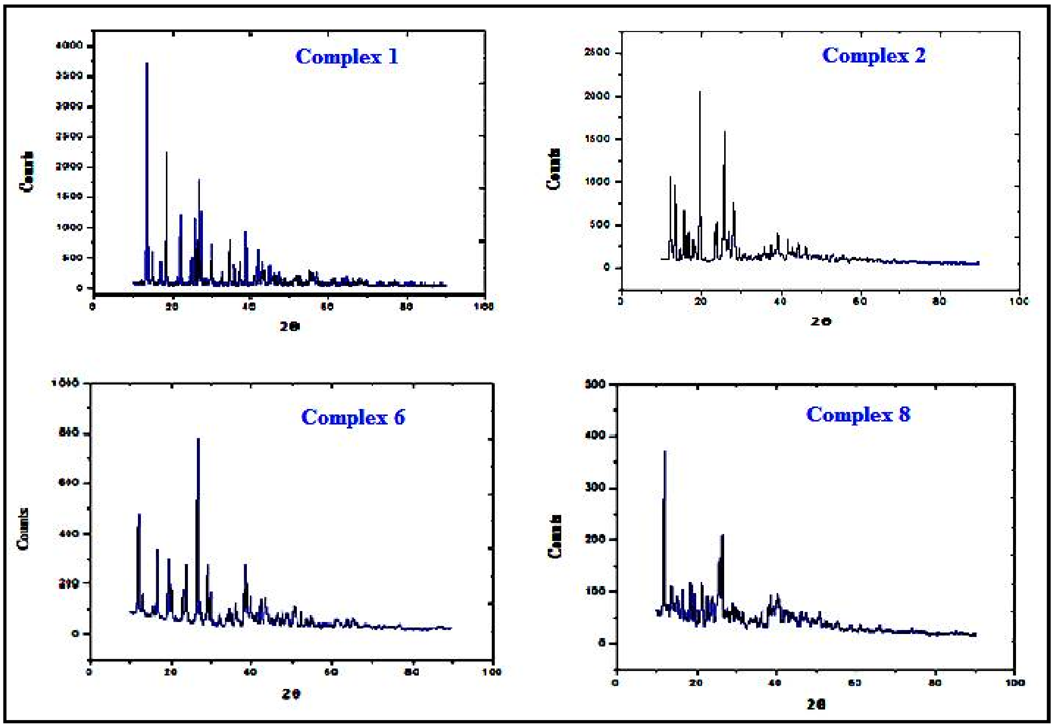


Figure 5. PXRD Pattern of complexes **1**, **2, 6 and 8.**

Proposed Structures of the Newly Synthesized Zn (II) and Cd (II) Mixed-Ligand Coordination Polymers

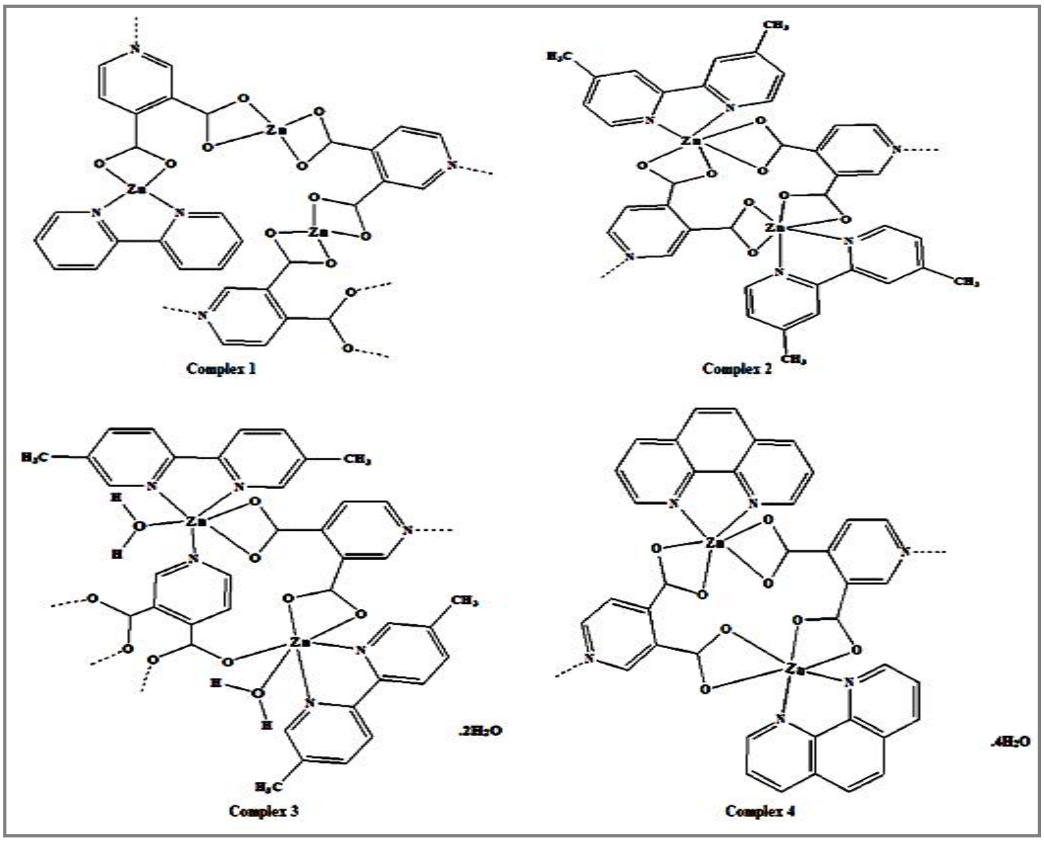


Figure 6. Proposed structures of Zn(II) mixed-ligand coordination polymers 1-4

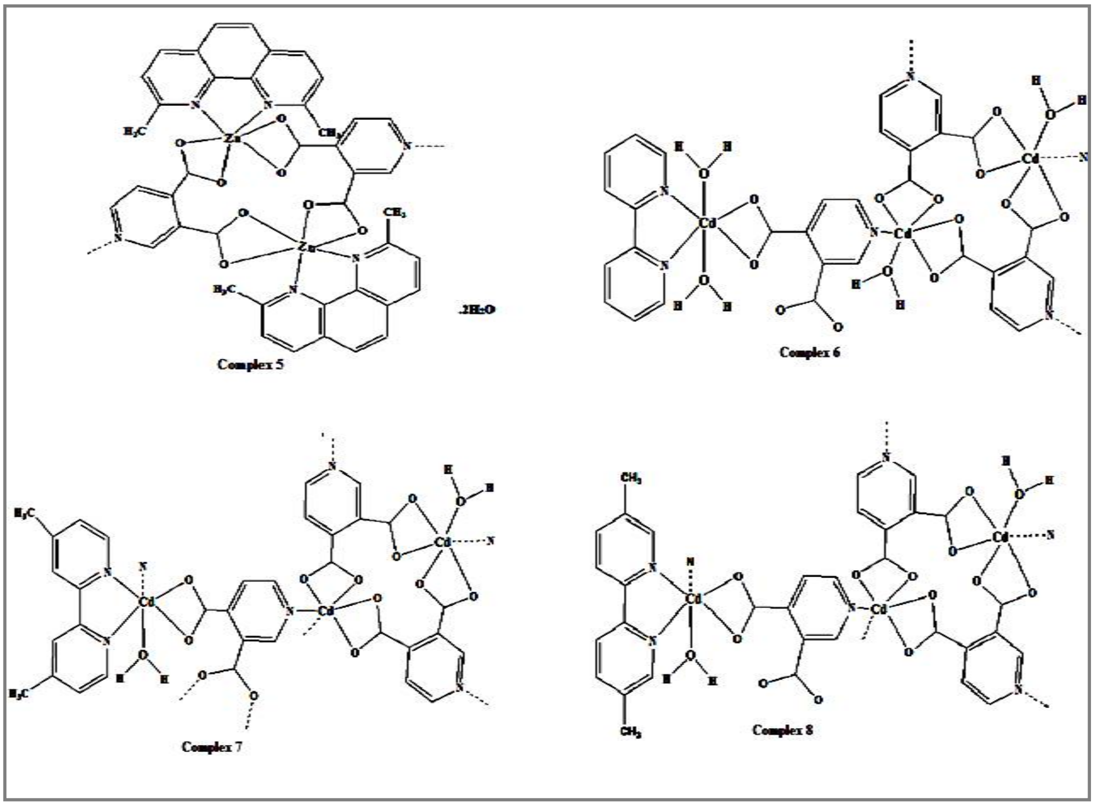


Figure 7. Proposed structures of Zn(II) (5) and Cd(II) (6-8) mixed-ligand coordination polymers.

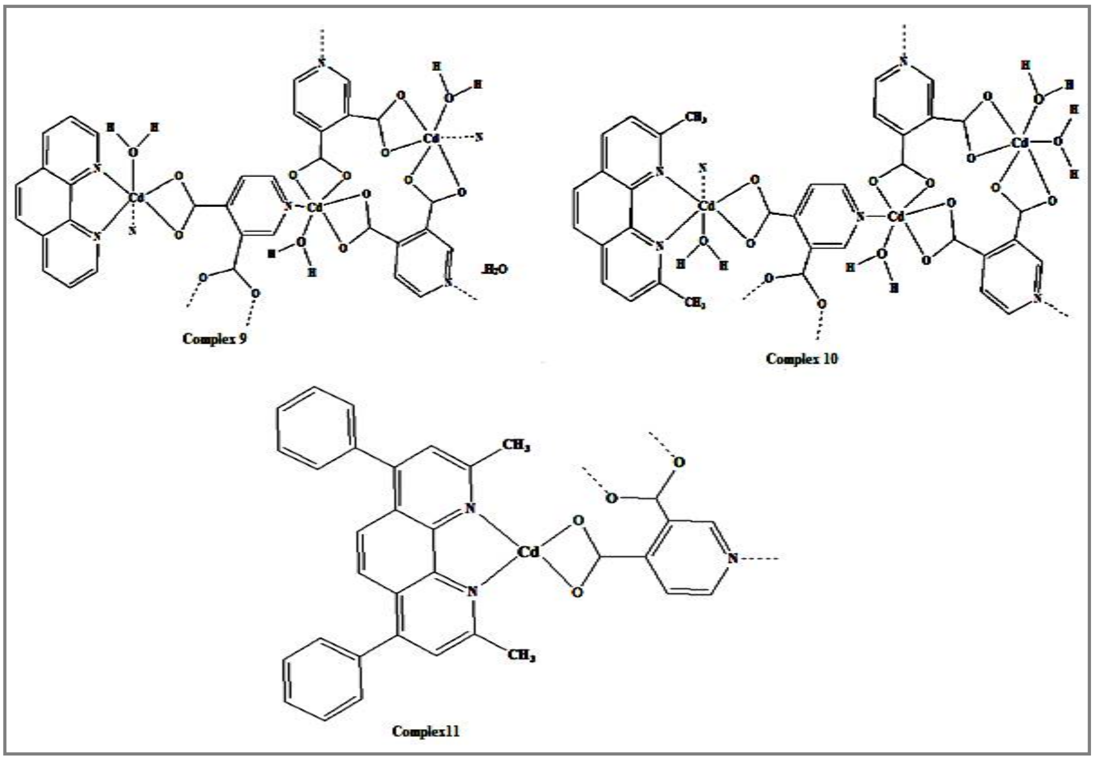


Figure 8. Proposed structures of Cd(II) mixed-ligand coordination polymers 9-11.

APPLICATION

The strong photoluminescence properties of all the newly synthesized Zn (II) and Cd (II) Mixed-Ligand Coordination Polymers shows that they may be excellent candidates for potential photoactive materials.

CONCLUSION

In this paper, some mixed-ligand metal-organic coordination polymers of Zn(II) and Cd(II) with 3,4-pyridinedicarboxylic acid (3,4-pdc) and aromatic diimines where diimines= 2,2'-bipy, 4,4'-Me_2bipy, 5,5'-Me_2bipy, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline (dmp) and 4,7-diphenyl-1,10-phenanthroline (bathophen) were hydro-/solvothermally synthesized and were structurally characterized by Elemental analyses, thermal analyses, FT-IR spectra, photoluminescence spectra and Powder X-ray diffraction analyses (PXRD). Infrared spectra suggested that the starting acid H_2pdc was completely deprotonated and coordinated to the metal centers through carboxylate O in bidentate fashion and one nitrogen from the pyridine ring. On the basis of Powder X-ray diffraction analysis it is concluded that all the complexes were polycrystalline/amorphous in nature. TGA results show that the complexes **1**, **2** and **11** were more stable and did not show any change upto 200°C indicating that the hydrated and coordinated water molecules were not present in the complexes. Furthermore, the strong photoluminescence properties of all the complexes indicate that they may be excellent candidates for potential photoactive materials.

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