



Synthesis and Characterization of Mixed-ligand Copper(II) and Zinc(II) Complexes Involving pyridine-2,5-dicarboxylic acid and 1,3,5-Benzenetricarboxylic acid

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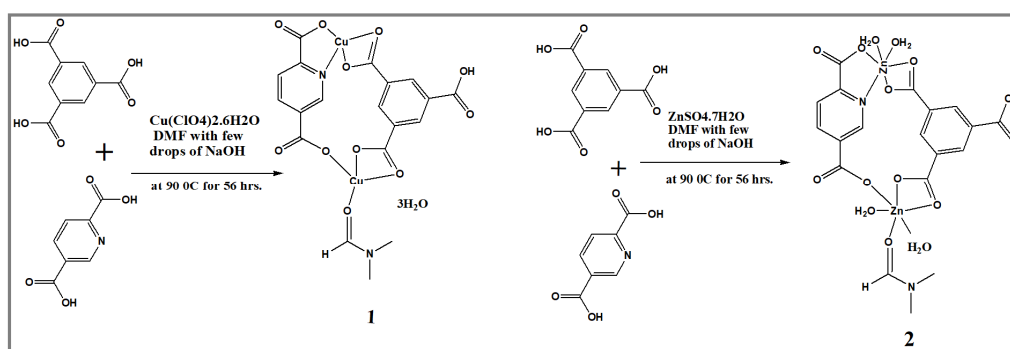
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ABSTRACT

Two mixed-ligand copper(II) and zinc(II) complexes with pyridine-2,5-dicarboxylic acid and 1,3,5-benzenetricarboxylic acid have been synthesized, namely $[\text{Cu}_2(2,5\text{-pdc})(1,3,5\text{-Hbtc})(\text{DMF})].3\text{H}_2\text{O}$ **1** and $[\text{Zn}_2(2,5\text{-pdc})(1,3,5\text{-Hbtc})(\text{DMF})(\text{H}_2\text{O})_4]$ **2** by hydrothermal method in 2:2:1 metal : 2,5-pdc : 1,3,5-btc molar ratio (2,5-pdc = pyridine-2,5-dicarboxylic acid and 1,3,5-btc = 1,3,5-benzenetricarboxylic acid). The synthesized complexes are characterized by elemental (C,H,N), fourier transform infrared (FT-IR), thermogravimetric and powder X-ray diffraction (PXRD) analyses.

Graphical Abstract



Hydrothermal process for the synthesis of Cu(II) and Zn(II) complexes, **1** and **2** and their proposed molecular structures.

Keywords: Cu(II), Zn(II), FT-IR, Thermal analyses, Powder X-ray diffraction (PXRD).

INTRODUCTION

Copper, and other transition metals, are essential for many enzymes, particularly those catalyzing physiologically important reactions. It has strongest ability to form complexes with peptides, proteins, amino acids as well as other organic molecules in the living organisms [1]. It is a biologically relevant

element and many enzymes that depend on copper for their activity have been identified. Cu(II) is a substitutionally labile metal ion, so multidentate ligands are believed to be better than bidentate ligands in keeping the Cu(II) ion chelated in solution. Typically, upon association with dioxygen or hydrogen peroxide these copper complexes are thought to perform reactive intermediates [2]. Examples of copper-containing compounds include electron-transfer (ET) proteins (e.g., azurin, plastocyanin, laccase), oxygen-binding enzymes (e.g., ferroxidase, tyrosinase, ascorbate oxidase), and oxygen transport proteins (hemocyanin) [3].

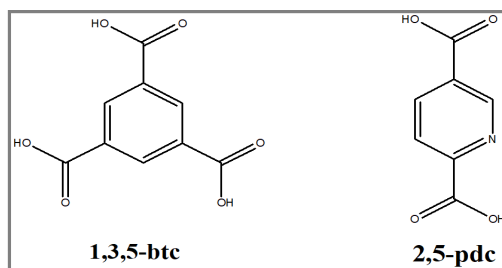
Copper (II)-organic frameworks (Cu-OFs) possess enormous structural diversity due to its flexible coordination sphere around the Cu(II) ion, in combination with steric and packing forces. It is one of the most important transition metal ions, not only because of its relevance as the active-site structure of metalloproteins, but also due to its magnetochemistry [4]. Several Cu(II) complexes, which possess biologically active ligands, demonstrate high nucleobase affinity and nuclease activity and are found to have the potential to serve as anticancer agents [5] and have shown a significant decrease in tumor volume, mitotic and proliferation indices in different types of human cancer cells [6].

Zinc(II) cations, due to its $3d^{10}$ electronic configuration, form complexes with a flexible coordination environment, and geometries of these complexes can vary from tetrahedral to octahedral, and severe distortions of the ideal polyhedra occur easily. Due to the general lability of $3d^{10}$ metal ion Zn(II) complexes, the formation of coordination bonds is reversible which enables metal ions and ligands to rearrange during the process of self-organization to give highly ordered network structures. The blocking or terminal co-ligands, which are usually used along with the bridging ligand to complete the metal-coordination sphere, can alter the supramolecular assembly and consequently the type of structure formed taking advantage of the flexibility of the coordination sphere. Zn(II) chemistry plays an important role in biological systems [7].

The carboxylate ligands can have different coordination modes and each of them may play role in the formation of supramolecular assembly. The compounds having multiple carboxylic acid (-COOH) groups are good synthons for supramolecular architectures and coordination polymers. Carboxylate groups display a variety of binding geometries, such as monodentate-terminal, monodentate-bridging, bidentate-bridging, and chelating, in coordination chemistry and the active sites of metalloenzymes [8]. Pyridine-2,5-dicarboxylic acid (2,5-btc) has important biological function in the metabolism such as enzyme inhibitor, plant preservative and food sanitizer. Pyridine-2, 3-, 2, 4-, 2, 5-, 2, 6-, 3, 4- and 3, 5- dicarboxylic acids exhibit various coordination modes. Pyridine-2,5-dicarboxylic acid (2,5-pdc) is a multifunctional polytopic ligand which can bridge metal centres through different bridging modes with M–N and M–O bonds [9, 10].

1,3,5-benzenetricarboxylic acid (H_3btc) is widely used to construct metal-organic coordination polymers (MOFs) with diverse topology and interesting properties. The star-like (H_3btc) molecule possesses interesting features that are conducive to the formation of versatile coordination structures. Firstly, the multi-carboxylate groups on the benzene ring may be completely or partially deprotonated. Secondly, the ($-COO^-$) groups may not lie in the phenyl ring plane upon coordination to metal ions owing to space hindrance, and as a result, the molecules may connect metal ions in different directions, generating multidimensional architectures [11]. It is important to mention that Krishna and co-workers have investigated the mixed-ligand copper(II)-organic coordination compounds by using 2-aminopyridine-3-carboxylic acid (2-APCA) as a primary ligand while the aromatic diimines, viz., 1,10-phenanthroline (1,10-phen), 2,2'-bipyridine (2,2'-bipy) and 2,9-dimethyl-1,10-phenanthroline (dmp) as secondary ligands in aqueous/nonaqueous media. These complexes, namely [Cu(2-APCA)(bipy)(ONO_2^-)] **1**; [Cu(2-APCA)(phen)(H_2O)](NO_3^-) **2**, and [Cu(2-APCA)₂(dmp)(H_2O)](NO_3^-) **3**. All these complexes **1** to **3** have been characterized by elemental analyses, molar conductance measurements, FT-IR and UV-Visible spectroscopic techniques, room temperature magnetic susceptibility measurements, TGA and DSC of these complexes also done. Molar

conductance measurements have been carried out in DMSO and DMF, complexes **1** and **3** correspond to non-electrolyte and complex **2** represents monocationic nature. The redox properties of the all these complexes were extensively investigated by electrochemical method using cyclic voltammetry (CV). The electrochemical behavior of complex **3**, involving dmp as the secondary ligand is different from rest of two mixed-ligand copper(II) complexes. Based on these studies, a square-pyramidal coordination geometry around the copper(II) ion has been proposed in solid complexes **1** to **3**. In DMSO and DMF solutions, complexes **1**, **2** and **3** possess distorted octahedral geometry due to solvent coordination [12].



Scheme 1. The structures of 1,3,5-benzenetricarboxylic acid (H_3btc) and pyridine-2,5-dicarboxylic acid (pdc), ligands.

This article aims first at compiling these studies related to structural characterization of complexes, $[Cu_2(2,5-pdc)(1,3,5-Hbtc)(DMF)] \cdot 3H_2O$ **1** and $[Zn_2(2,5-pdc)(1,3,5-Hbtc)(DMF)(H_2O)_4]$ **2**. We have investigated these complexes **1** and **2** by using elemental analyses (C,H,N), fourier transform infrared (FT-IR) spectra, thermal analyses (TGA/DTA/DTG) and powder X-ray diffraction (PXRD) analyses to arrive at conclusion regarding their geometrical structure.

MATERIALS AND METHODS

All chemicals and organic solvents used for the synthesis were purchased commercially and used without further purification. Chemicals required are $Cu(ClO_4)_2 \cdot 6H_2O$, $ZnSO_4 \cdot 7H_2O$, pyridine-2,5-dicarboxylic acid and 1,3,5-benzenetricarboxylic acid were purchased from Aldrich and used without further purification. The structures of 1,3,5-benzenetricarboxylic acid (H_3btc) and pyridine-2,5-dicarboxylic acid (pdc), ligands are given in (Scheme 1). All other reagents were commercially available and used as received.

Instrumentation: Elemental analyses (C, H, N) were determined with Euro Vector EA 3000 Elemental Analyzer. IR spectra were recorded with a Thermo Scientific Nicolet iS5 FT-IR spectrophotometer (KBr pellets) in the $4000\sim 600\text{ cm}^{-1}$ region. The thermogravimetric / differential thermal analyzer (TG/DTA) were determined with a EXSTAR TG/DTA 6300 spectrophotometer. Thermal (TGA/DTA/DTG) of complexes was studied in the range of $35\text{-}900^\circ\text{C}$ by controlling the heating rates $10^\circ\text{C min}^{-1}$ in nitrogen atmosphere. The powder X-ray diffraction (PXRD) patterns were recorded and analyzed with Rigaku Smart Lab X-ray diffractometer.

Standard procedure for synthesis of mixed-ligand Cu(II) and Zn(II) complexes, 1 and 2: $Cu(ClO_4)_2 \cdot 6H_2O$ (185 mg, 0.5 mmol), pyridine-2,5-dicarboxylic acid (83 mg, 0.5 mmol) and 1,3,5-benzenetricarboxylic acid (52 mg, 0.25 mmol), each dissolved in 4 mL deionized water, except in the case of 1,3,5-btc where it was dissolved in 2 mL DMF and 4 mL water. Then, these solutions were mixed with each other and sonicated for 15 mins. The mixture was placed in a Teflon-lined Stainless Steel Reactor (Vessel) and put in a computer-controlled oven for hydrothermal reaction at 90°C for 56 hrs, the blue colored precipitate of Cu(II) complex **1** was obtained and filtered. Then it was washed several times with small portions of alcohol/ether and air-dried at room temperature. Zn(II) complex **2** was synthesized following the same procedure as for the complex **1**

Blue colored powder of **1** (yield: 51.6 %; mp 317 °C). anal. calcd. for $C_{19}H_{20}N_2O_{14}Cu_2$ (**1**): C, 36.19; H, 3.17; N, 4.44%; found: C, 31.21; H, 3.72; N, 4.31%. IR data (KBr pellets, cm^{-1}) 3213, 3319, 3363, 3433, 1730, 1633, 1616, 1559, 1369, 833, 725 and 671 cm^{-1} . Colorless needle like solid of **2** was obtained (yield: 52.7%; mp: 350 °C). anal. calcd. for $C_{19}H_{22}N_2O_{15}Zn_2$ (**2**): C, 34.96; H, 3.37; N, 4.29%; found: C, 29.51; H, 4.11; N, 3.13%. IR data (KBr pellets, cm^{-1}) 3350, 3287, 3123, 1729, 1616, 1550, 1429, 1348, 799, 725 and 660 cm^{-1} .

RESULTS AND DISCUSSION

Elemental analyses: The results of elemental analyses (C, H, N) of the complexes **1** and **2** are given in table 1.

Table 1. Analytical data and physical properties of mixed-ligand Cu(II) and Zn(II) complexes **1** and **2**

Complexes	M.W.	Color	M.P. (°C)	Yield (%)	Elemental analyses (%) Calcd. (Found)		
					C	H	N
1	630.00	Sky blue	317	51.2	36.19 (31.21)	3.17 (3.72)	4.44 (4.31)
2	652.00	colorless	350	52.7	34.96 (29.51)	3.37 (4.10)	4.29 (3.13)

FT-IR spectra: The frequencies of the IR absorption bands of the free ligands and complexes **1** and **2** are given in table 2, and their corresponding IR spectra are depicted in (Figures. 1, 2, 3 and 4), respectively. The peak at 3287 cm^{-1} can be attributed to the presence of hydroxyl ion [13]. The carboxylate stretching vibration (ν_{COOH}) for free 2,5-pdc ligand was observed at 1722 cm^{-1} , but the band for ν_{COOH} disappeared when 2,5-pdc is coordinated to Cu(II) ion. It exhibited an asymmetric $\nu_{as}(COO^-)$ and symmetric $\nu_s(COO^-)$ carboxylate stretching vibrations at 1633, 1616 and 1369 cm^{-1} . 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 [14-16]. The difference of asymmetric to symmetric stretching frequency comes out to be more than 200 cm^{-1} , confirming the monodentate coordination mode of the carboxylate group in the complex [17, 18]. It is to be noted that the complex shows sharp and medium bands at 1559, 726, and 671 cm^{-1} , attributed to pyridyl and $\nu(C-N)$ vibration and at 2964 cm^{-1} assigned to aromatic ν_{C-H} stretching mode of vibration [18-20].

Table 2. Characteristic infrared frequencies of free ligands and mixed-ligand Cu(II) and Zn(II) complexes, **1** and **2**

Ligand/ Complex	$\nu(OH)$ Phenolic/ H_2O	$\nu(C=O)$	$\nu(C=N)$	$\nu(C-O)$	New bands
2,5- H_2pdc	3473	1722	1581	1163	-
1,3,5- H_3btc	3423	1722	-	1184	-
1	3640-3213	1616	1559	1115	1359, 833, 725, 671
2	3639-3123	1616	1550	1108	1348, 799, 725, 660

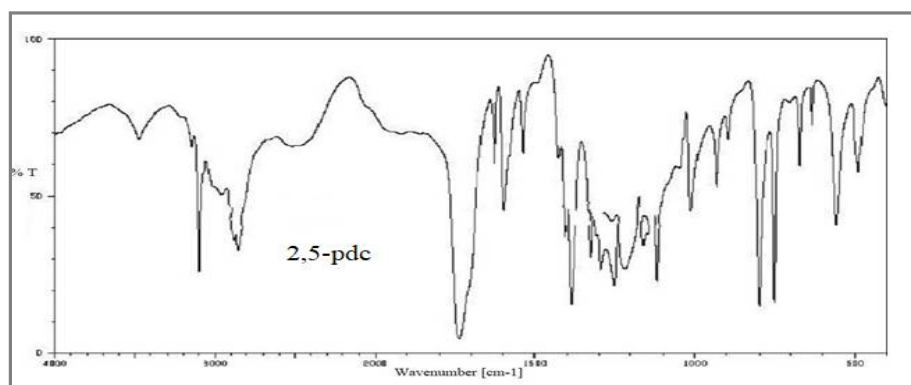


Figure 1. FT-IR spectra of free (non-coordinated) ligand 2,5-pdc.

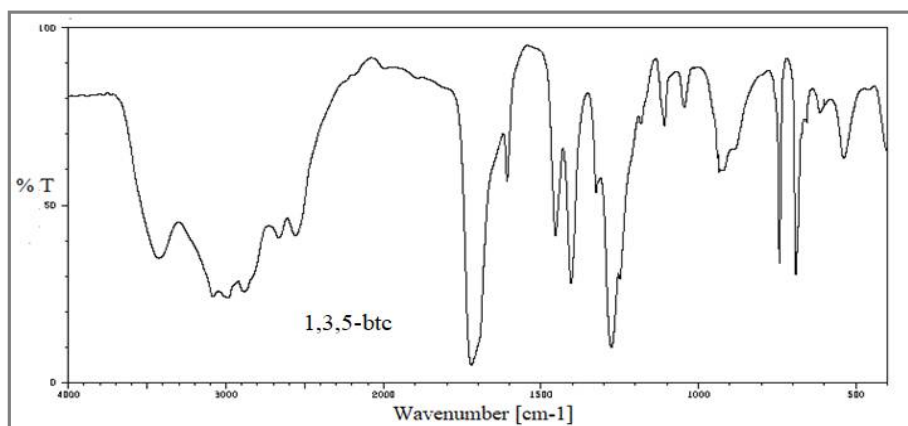


Figure. 2. FT-IR spectra of free (non-coordinated) ligand 1,3,5-btc.

The IR spectra of these complexes, **1** and **2** are almost similar. Peaks at 3123 and 3287 cm^{-1} can be assigned to the presence of hydroxyl ion. An asymmetric $\nu_{\text{as}}(\text{COO}^-)$ and symmetric $\nu_{\text{s}}(\text{COO}^-)$ carboxylate stretching vibrations are observed at 1616 and 1348 cm^{-1} , respectively for complex **2**. The values of ($\Delta = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$) comes out to be more than 200 cm^{-1} for this complex, showing the monodentate coordination mode of the carboxylate oxygen. It is to be noted that this complex also shows sharp and medium bands at 1550, 725, and 660 cm^{-1} , assigned to pyridyl and $\nu(\text{C-N})$ vibration and the peak at 2988 cm^{-1} is assigned to aromatic $\nu_{\text{C-H}}$.

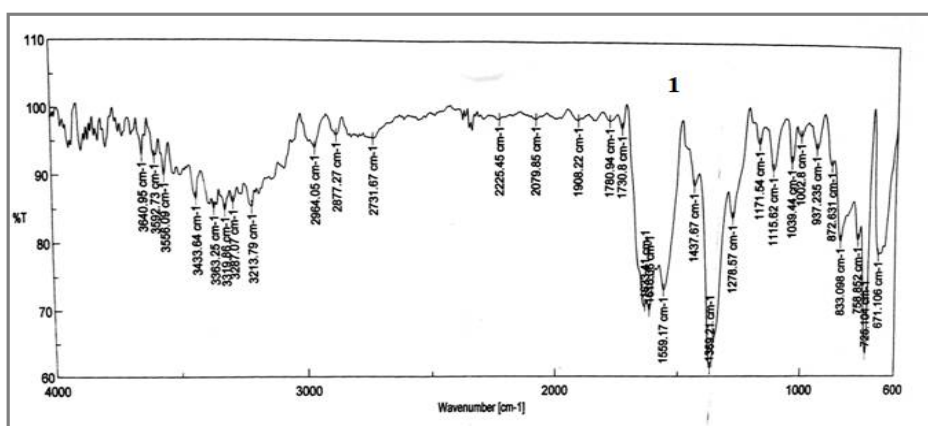


Figure. 3. FT-IR spectra of mixed-ligand Cu(II) complexes, **1**.

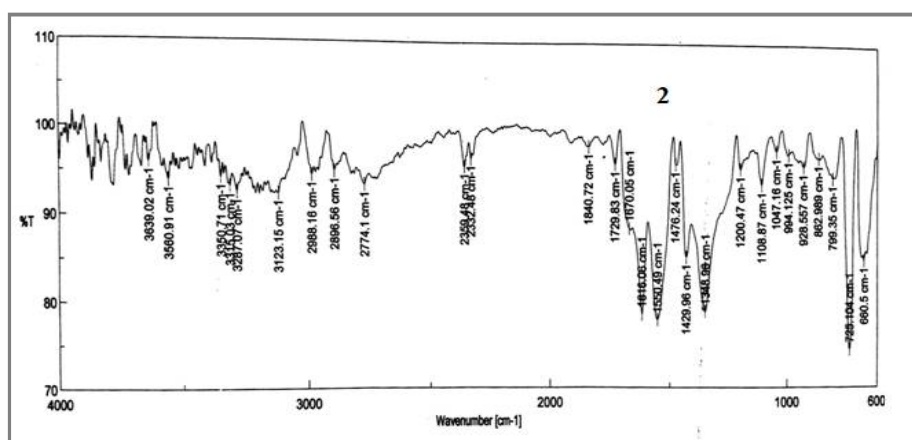


Figure. 4. FT-IR spectra of mixed-ligand Zn(II) complexes, **2**.

Thermal analysis of mixed-ligand complexes 1 and 2: The simultaneous TGA/DTA/DTG curves in nitrogen atmosphere of Cu(II) and Zn(II) complexes, **1** and **2** are shown in (Figure 5 and 6). The thermal stability of complexes were studied in the range of 30-900°C by controlling the heating rates 10°C min⁻¹. Thermo-analytical results of these mixed-ligand Cu(II) and Zn(II) complexes are given in table 3.

Table 3. Thermo-analytical results of mixed-ligand Cu(II) and Zn(II) complexes, **1** and **2**

Complex	Temperature of TGA (°C)	Temperature of DTG	Weight loss (%) calcd. (found)	Assignment
1	up to 100	-	8.57 (6.01)	with loss of 3 lattice water molecules
	up to 190	181	11.42 (9.77)	with loss of DMF molecules
	up to 415	306-382	51.93 (59.84)	with loss of 2,5-pdc and 1,3,5-btc molecules
Residue 1	-	-	25.23 (32.27)	CuO
2	up to 148	104-137	11.04 (10.70)	with loss of coordinated water molecules
	up to 350	258	7.60 (11.17)	with loss of DMF molecule
	up to 479	404-444	57.82 (52.38)	with loss of 2,5-pdc and 1,3,5-btc molecules
Residue 2	-	-	24.97 (29.32)	ZnO

The thermogravimetric decomposition of **complex 1** exhibited three continuous weight loss steps. The first step accounts for a mass loss of 6.01 % (calcd. 8.57 %) was attributed to the loss of lattice water molecules in the temperature upto 100°C. The second step which accounts for a mass loss of 9.77 % (calcd. 11.42 %) was due to the loss of coordinated DMF in the temperature upto 190°C with DTA and DTG curves at 181°C and 181°C. The third step of heating process which occur in the temperature upto 415°C with DTA and DTG curves at 322°C, 406°C and 306°C, 318°C, 382°C, respectively correspond to the decomposition of 2,5-pdc²⁻ and 1,3,5-Hbtc²⁻ anionic ligands with total mass loss of 51.93% (calcd. 59.84%). The end product was estimated as CuO 32.27 % residue (calcd. 25.23%).

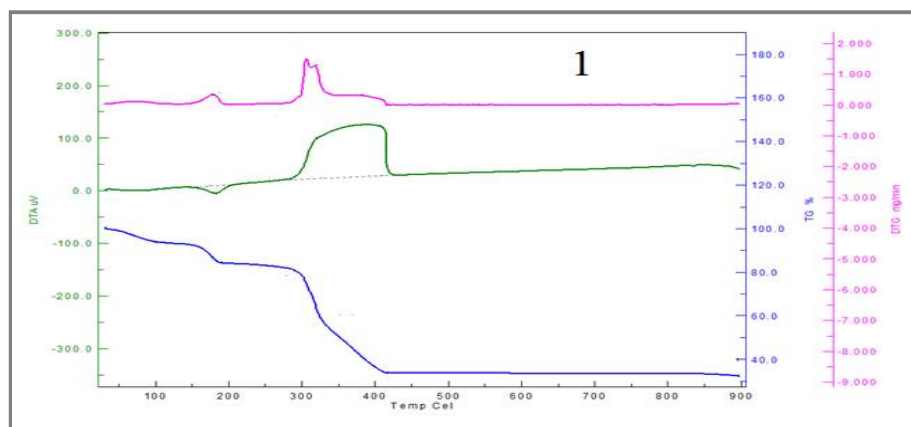


Figure 5. TGA curves of mixed-ligand Cu(II) complexes, **1**.

The thermogravimetric decomposition of **complex 2** also showed three continuous weight loss steps. The first step which accounts for a mass loss of 10.70 % (calcd. 11.04 %) was attributed to the loss of coordinated water molecules in the temperature upto 148°C with TGA and DTG curves at 105°C, 148°C and 104°C, 137°C. The second step which accounts for a mass loss of 7.60 % (calcd. 11.17 %) was due to the loss of coordinated DMF in the temperature upto 350°C with DTA and DTG curves at 260°C and 258°C. The third step of heating process which occur in the temperature upto 479°C with DTA and DTG curves at 418°C, 460°C and 404°C, 444°C respectively correspond to the decomposition of 2,5-pdc and 1,3,5-Hbtc ligands with total mass loss of 52.38% (calcd. 57.82%). The end product was estimated as ZnO 29.32 % residue (calcd. 24.97 %).

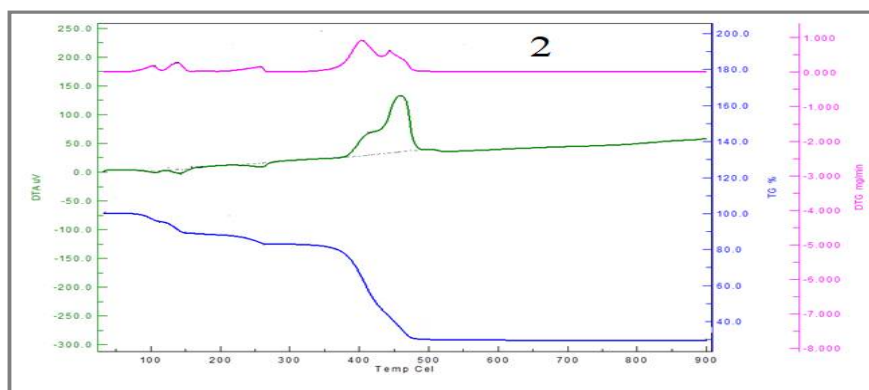
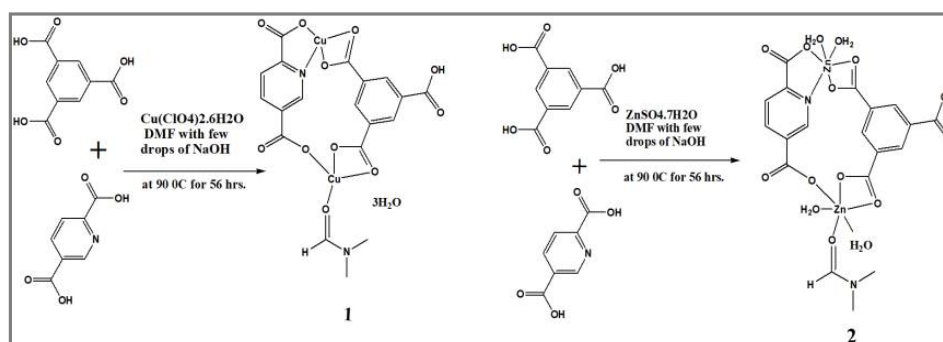


Figure 6. TGA curves of mixed-ligand Zn(II) complexes, 2.

On the basis of experimental results of elemental analyses, IR spectra and thermogravimetric data the chemical formulae and structures of these complexes, are proposed as illustrated in Scheme 2. It is noteworthy that both these complexes are binuclear in structure. In complex 1, both the carboxylate groups of 2, 5-pdc²⁻ anionic ligands are coordinated with O atoms in a monodantate manner. On the other hands, two of the carboxylate groups of 1,3,5-Hbtc²⁻ anionic ligands are coordinated in chelating modes with the two metal centers. Along with Pyridyl N atom with one of the Cu(II) centers (Scheme 2). On the other hand, complex 2 also involves a binuclear structure in which each Zn(II) ion is six-coordinated octahedral structure where two additional coordinated water molecules. It is interesting to note that the mode of coordination of the two ligands involved is similar to that of complex 1 (Scheme2).



Scheme 2. Hydrothermal process for the synthesis of Cu(II) and Zn(II) complexes, 1 and 2 and their proposed molecular structures.

Powder X-ray diffraction (PXRD) analyses: Powder X-ray diffraction data of the complexes 1 and 2 were collected on a RigakuSmart Lab X-ray diffractometer (Figure 7 and 8). The good quality of X-ray diffractograms patterns of copper(II) and zinc(II) complexes indicate high crystallinity of these complexes. The powder diffraction patterns of complex 1 exhibited 12 peaks between 2 theta values of 10-45°. Complex 2 has also shown 9 peaks up to 10-75° of 2 theta values [21, 22]. Most of the literature survey reveals that transition metal complexes generally crystallize with octahedral, tetrahedral or square planar geometry [21].

X-Ray diffractometry is an important technique for structure determination because it is non-destructive, non-contrast, fast and sensitive one. XRD, however, does not provide the quantitative compositional data obtained by the electron microprobe of the textural and qualitative compositional data obtained by SEM. The objective of an X-Ray diffraction measurement is to determine the dimensions and shape of unit cell and to identify the detailed structure of the complex molecule

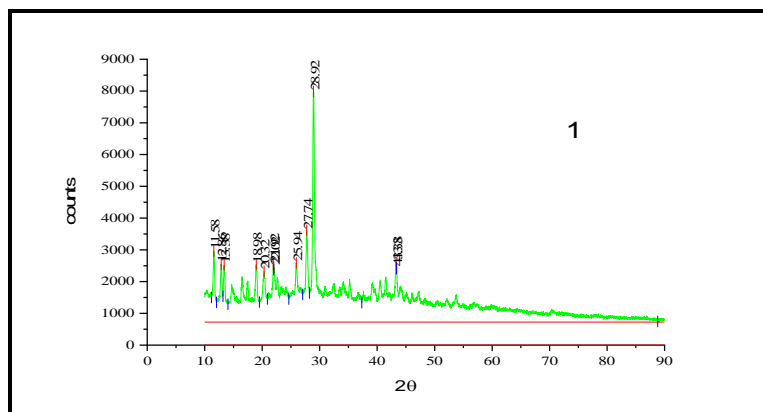


Figure 7. PXRD patterns of mixed-ligand Cu(II) complexes, 1

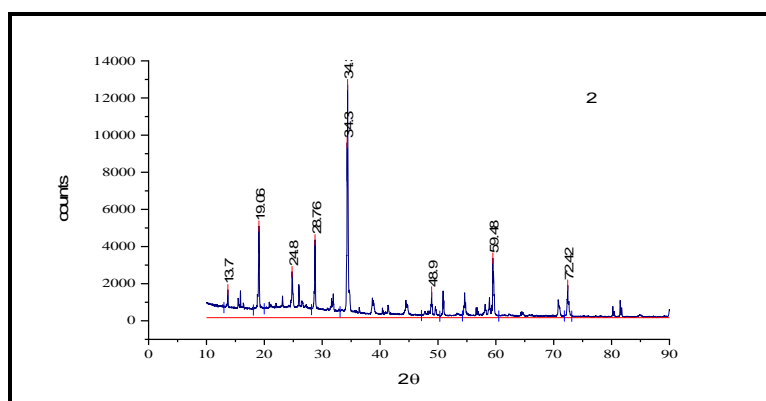


Figure 8. PXRD patterns of mixed-ligand Zn(II) complexes, 2.

Crystallite size and average crystallite size can be estimated from XRD data using the following Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where, D = crystallite size (nm), K = 0.9 (Scherrer Constant), $\lambda = 1.5406$ (m), β = FWHM (Radians), θ = Peakposition (Radians)

Average crystallite size for complexes 1 and 2 are estimated as 193.49 and 656.15 nm, respectively and are given in tables 4 and 5.

Table 4. Crystallite size, D (nm) average value of complex 1

Peak No.	Peak position 2 theta	FWHM	D (nm)	Average value of D (nm)
1	11.58	0.38611	206.8070231	193.49
2	12.86	0.43961	181.856181	
3	13.38	0.40577	197.1252813	
4	18.98	0.50116	160.7175355	
5	20.32	0.71437	112.9785406	
6	21.92	0.27973	289.2747909	
7	22.02	0.87254	92.75511197	
8	25.94	0.82252	99.11336015	
9	27.74	0.44622	183.3822886	
10	28.92	0.34363	238.750381	
11	43.3	0.32355	264.1711082	
12	43.38	0.2898	295.0182028	

Table 5. Crystallite size D (nm) average value of complex 2

Peak No.	Peak position 2 theta	FWHM	D (nm)	Average value of D (nm)
1	13.7	0.17156	466.391036	656.15
2	19.06	0.14772	545.3196629	
3	24.8	0.24198	336.1450358	
4	28.76	0.10663	769.1301148	
5	34.3	0.05553	1497.201606	
6	34.38	0.14264	582.9889298	
7	48.9	0.11197	779.3955664	
8	59.48	0.23615	387.4401135	
9	72.42	0.18186	541.4036249	

APPLICATION

Thermal stability TGA curves showed the chemical decomposition of complexes. It corresponds with the presence of the expulsion of water of hydration (non-coordinated), coordinated water and the organic components takes place in the temperature range 30 to 480°C.

CONCLUSION

In this paper, hydrothermal syntheses, characterization and spectral studies of mixed-ligand Cu(II) and Zn(II) complexes, namely $[\text{Cu}_2(2,5\text{-pdc})(1,3,5\text{-Hbtc})(\text{DMF})].3\text{H}_2\text{O}$ **1** and $[\text{Zn}_2(2,5\text{-pdc})(1,3,5\text{-Hbtc})(\text{DMF})(\text{H}_2\text{O})_4]$ **2** have been investigated. These complexes were characterized by elemental analyses, FT-IR spectra, thermal and PXRD analyses. FT-IR spectra suggested that 2,5-pdc acid was completely deprotonated and coordinated to the metal centers through carboxylate O in monodentate fashion. The appearance of a lower shifted peak at 1607 cm^{-1} and a higher shifted peak at 735 cm^{-1} indicates that the coordination complexes **1** and **2** coordinate to an oxygen atom in the C=O bond. Thermal stability (TGA/DTA/DTG) curves showed the chemical decomposition of complexes. It corresponds with the presence of the expulsion of water of hydration (non-coordinated), coordinated water and the organic components takes place in the temperature range 30 to 480°C.

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