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# Possible Sonochemical Synthesis of Nanosized Particles Mixed Ligand Metal Coordination Polymers Derived from 1,3-Di(4-pyridyl)propane and Benzimidazole

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## Authors' contributions

*This work was carried out in collaboration between all authors. Author AAMA designed the study, wrote the protocol, and wrote the first draft of the manuscript. Authors MAG and AAMA managed the literature searches, analyses of the study, discussed the spectroscopy analysis and author MSAF managed the experimental process. Authors AAMA and BMAZ managed the thermal, X-ray and SEM. All authors read and approved the final manuscript.*

Original Research Article

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## ABSTRACT

Nanosized mixed ligand Mn(II), Co(II), Cu(II), Cd(II) and Pb(II) coordination polymers derived from 1,3-di (4-pyridyl) propane (DPP) and benzimidazole (BIMZ) were synthesized. The compounds were characterized by elemental analysis, FT-IR and electronic spectral studies. The thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) were used to study the thermal decomposition steps. The scanning electron microscope SEM photographs and particle size calculations from the powder XRD data indicate the nano-sized nature of three compounds prepared under ultrasonic irradiation (average size 20-34nm).

**Keywords:** Nano-structure; coordination polymers; XRD; SEM; thermal studies.

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## 1. INTRODUCTION

Coordination polymers are organic–inorganic hybrid compounds formed by self-assembly of discrete molecular building blocks. The synthesis of metal coordination polymers is often guided by the quest to understand how molecules can be organized and how functions can be achieved. Many attempts were made to prepare variety of transitional metal complexes using different spacers and their properties were physically and chemically determined [1-10]. Pyridyl groups are widely incorporated in compounds employed as antidepressant, insecticidal, pharmaceuticals, herbicidal and plant growth regulating agents [11-20]. The flexible nitrogen ligand 1,3-di(4-pyridyl)propane was used in the construction of coordination polymers that can show a wide range of interesting topologies as chains, ladders, grids and adamantoid networks [21]. A considerable number of metal benzimidazole complexes including Mn, Fe, Co, Cu, Cd, Pd, Pb and Pt were reported [22-24]. Metal complexes containing benzimidazole based ligands were the subject of intensive researches not only owing to their rich coordination chemistry, but also due to a number of established and potential application areas e.g. production of efficient orange light emitting devices (OLEDs), with enhanced stability and efficiency. This article focuses on the synthesis and characterization of five new Mn(II), Co(II), Cu(II), Cd(II) and Pb(II) coordination polymers with 1,3-di(4-pyridyl)propane and benzimidazole as well as on conversion of some of them into nanostructured compounds by a sonochemical method.

## 2. EXPERIMENTAL

### 2.1 Material and Methods

All reagents and solvents for the synthesis and analysis were commercially available and were used as received. The complexes were prepared by stirring 1,3-di(4-pyridyl)propane (1.5mmol) dissolved in ethanol (15ml) with an aqueous alcoholic solution of metal salts of Mn(II) and Cd(II) (1.5mmol) in 15ml distilled water, then an ethanolic solution of benzimidazole was added to the above mixture in the molar ratios 1:1:1 for M: DPP: BIMZ. The same procedure was applied for the coordination polymers of Co(II), Cu(II) and Pb(II) but under ultrasonic irradiation. The complexes were precipitated after stirring for 1 h. They were filtered and washed with ethanol and then dried over anhydrous  $\text{CaCl}_2$ .

### 2.2 Physical Measurements

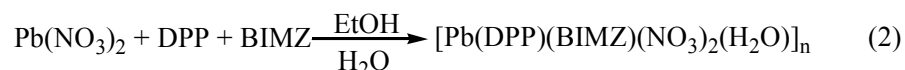
Elemental analyses (carbon, hydrogen and nitrogen) were performed using Analyischer Funktionstest Vario El Fab-Nr.11982027 elemental analyzer. Infrared spectra were recorded as KBr disks ( $400\text{-}4000\text{cm}^{-1}$ ) with a FT-IR spectrophotometer model (Thermo-Nicolet-6700 FTIR) and the electronic spectra were obtained using a Shimadzu UV-2101 PC spectrophotometer. The sonication experiments were performed on sonicator type Q 700, 20 kHz, output 700W. Magnetic susceptibility measurements were done on a magnetic susceptibility balance of the type MSB-Auto. The conductance was measured using a conductivity Meter model 4310 JENWAY. Thermal studies were carried out in dynamic air on a Shimadzu DTG 60-H thermal analyzer at a heating rate  $10^\circ\text{Cmin}^{-1}$ . XRD Model PW 1710 control unit Philips, Anode material Cu 40 kV, 30 M.A Optics: Automatic divergence slit was used. Scanning electron microscope was of the type JEOL JFC-1100E ION SPUTTERING DEVICE, JEOL JSM-5400LV SEM. SEM specimens were coated with gold to increase the conductivity.

### 3. RESULTS AND DISCUSSION

The reactions of manganese (II), cobalt(II), copper(II), cadmium(II) and lead(II) with 1,3-di(4-pyridyl)propane and benzimidazole proceed readily to form the corresponding mixed ligand coordination polymers. The following equations illustrate these reactions:



M = Mn(II), Co (II), Cu (II) or Cd(II), x = 0 or 1.



The complexes are air stable, insoluble in common organic solvents but soluble in dimethylformamide (DMF) and dimethyl sulphoxide (DMSO). The molar conductivities ( $10^{-3}$  M) of the complexes in DMSO at 25°C are in the 32.08-61.62  $\Omega^{-1}\text{cm}^2 \text{mol}^{-1}$  range indicating the non-electrolytic nature of the compounds. The compositions of the compounds are supported by elemental analysis Table 1.

**Table 1. Colors, elemental analysis and melting points of the compounds**

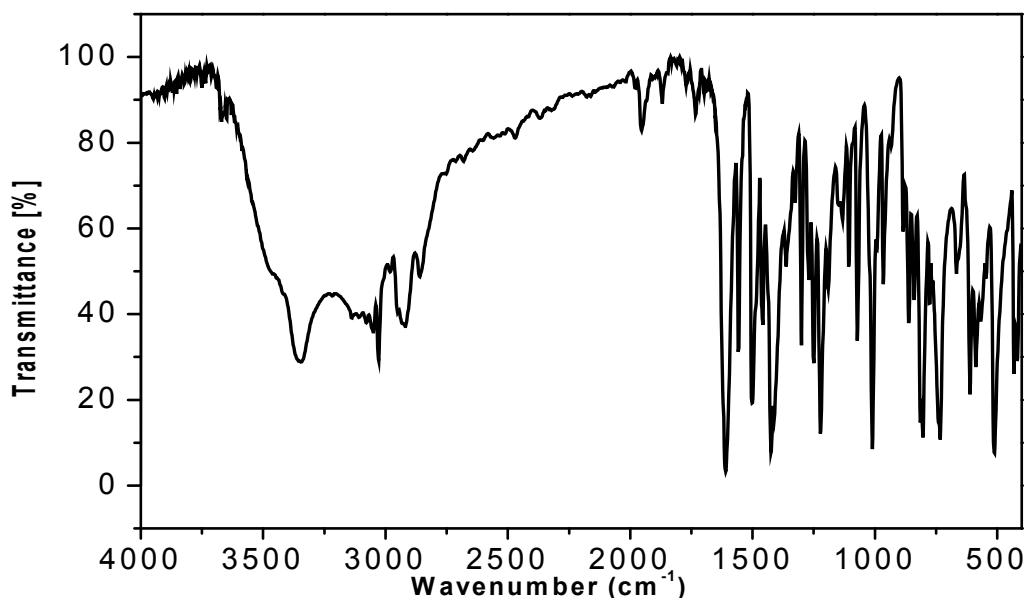
Compound	M. F. (M.Wt)	Color	Found (Calcd. %)			m.p.°C (Decom.)
			C	H	N	
{[Mn(DPP)(BIMZ)Cl <sub>2</sub> (H <sub>2</sub> O)]·H <sub>2</sub> O} <sub>n</sub> <b>1</b>	C <sub>20</sub> H <sub>23</sub> Cl <sub>2</sub> MnN <sub>4</sub> O <sub>2</sub> (477.31)	Light- brown	49.66 50.32	5.42 4.86	11.12 11.74	222
[Co(DPP)(BIMZ)Cl <sub>2</sub> (H <sub>2</sub> O)] <sub>n</sub> <b>2</b>	C <sub>20</sub> H <sub>21</sub> Cl <sub>2</sub> CoN <sub>4</sub> O (463.28)	Dark- blue	52.08 51.84	4.88 4.57	12.40 12.09	219
[Cu(DPP)(BIMZ)Cl <sub>2</sub> (H <sub>2</sub> O)] <sub>n</sub> <b>3</b>	C <sub>20</sub> H <sub>21</sub> Cl <sub>2</sub> CuN <sub>4</sub> O (467.90)	Light- green	51.20 51.33	5.82 4.53	10.01 11.97	205
[Cd(DPP)(BIMZ)Cl <sub>2</sub> (H <sub>2</sub> O)] <sub>n</sub> <b>4</b>	C <sub>20</sub> H <sub>21</sub> Cl <sub>2</sub> CdN <sub>4</sub> O (516.76)	White	47.09 46.48	4.72 4.10	10.82 10.84	202
[Pb(DPP)(BIMZ)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O)] <sub>n</sub> <b>5</b>	C <sub>20</sub> H <sub>21</sub> PbN <sub>6</sub> O <sub>7</sub> (664.67)	White	36.95 36.13	3.98 3.19	11.93 12.64	244

#### 3.1 IR Spectra

The main IR frequencies can be seen in Table 2. From the IR spectra it is found that the (C=N) band which appears at 1600cm<sup>-1</sup> in the spectrum of DPP (free ligand) is shifted to a higher wave number (1605-1615cm<sup>-1</sup>), indicating participation of this group in the bonding with the metal ions [25]. Furthermore, the IR spectra of the complexes show that  $\nu$  (C-N) of benzimidazole occurs at 804-815cm<sup>-1</sup> [26]. The bands appearing in the range at 3010-3065 cm<sup>-1</sup> in the spectra of the coordination polymers 1-5 are assigned to  $\nu$ OH of the coordinated water molecules [27], whereas the  $\nu$ OH stretching vibrations of the crystal water molecules are located at 3400cm<sup>-1</sup> for the manganese(II) complex 1 [28]. Metal-nitrogen and metal-oxygen bonding are manifested by the appearance of two bands at 418-428cm<sup>-1</sup> and 510-518cm<sup>-1</sup> regions, respectively [27] (Fig.1).

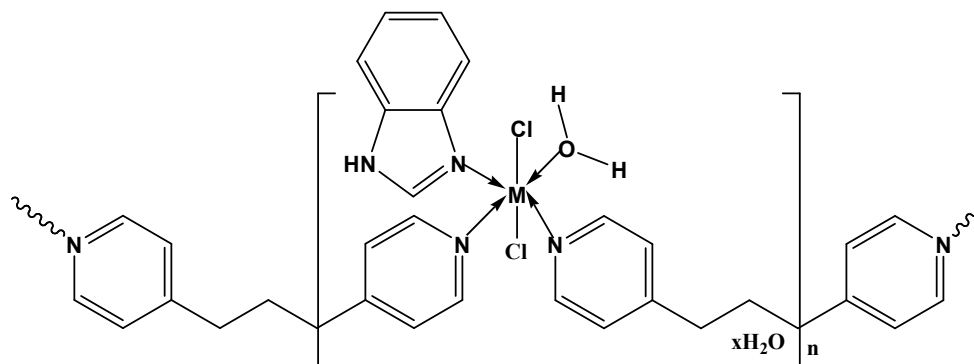
**Table 2. Infrared spectral data of the coordination polymers**

Compounds	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{N})$	$\nu(\text{OH})$ coord	$\nu(\text{OH})$ lattice	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
DPP	1600	798	-	-	-	-
BIMZ	1604	800	-	-	-	-
1	1609	804	3010	3400	425	511
2	1605	806	3051	-	420	514
3	1615	807	3065	-	426	518
4	1613	813	3050	-	428	510
5	1611	815	3032	-	418	514

**Fig. 1. FT-IR spectrum of  $\{[\text{Mn}(\text{DPP})(\text{BIMZ})(\text{H}_2\text{O})\text{Cl}_2]\cdot\text{H}_2\text{O}\}_n$  1**

### 3.2 Electronic Spectra and Magnetic Moments

The UV-Vis spectra of the coordination polymers were recorded in DMSO. The results are shown in Table 3. The spectra display two distinct bands in the ranges 24,875-35,211  $\text{cm}^{-1}$  and 36,363-39,682  $\text{cm}^{-1}$  respectively, which are attributed to the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions within BIMZ and DPP ligands. In the visible spectra, there are characteristic bands related to d-d transitions for Co(II) and Cu(II). In the visible spectra of Co(II) and Cu(II) compounds the d-d bands are observed at 19,920  $\text{cm}^{-1}$  and at 17,161  $\text{cm}^{-1}$ . The magnetic moments for the coordination polymers were measured. The Mn(II) compound gave a value of 5.77 BM [29], in agreement with values reported for octahedral complexes. The cobalt (II) compound exhibits a magnetic moment value of 4.48 BM, in accordance with an octacoordination environment around the Co(II) ion [30]. For the copper(II) complex the magnetic moment value of 1.78 BM is consistent with octahedral values for Cu(II) compounds [31]. Based on the forgoing results the suggested structures for 1,3-di(4-pyridyl) propane mixed ligand complexes are shown as follows (Fig. 2):



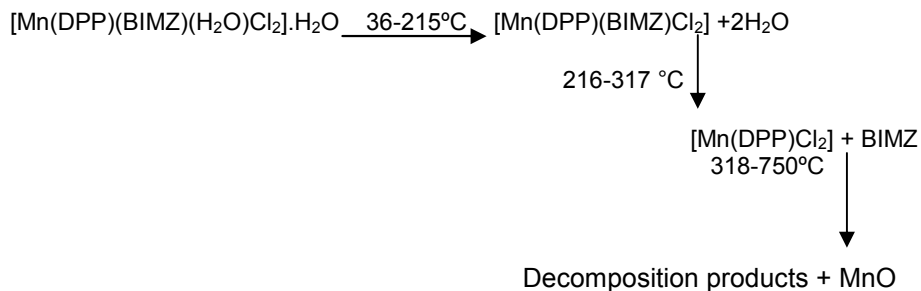
**Fig. 2. Suggested structure of  $\{[M(DPP)(BIMZ)(H_2O)Cl_2].xH_2O\}_n$**   
*M=Mn(II), Co(II), Cu(II) and Cd(II) x=0 or 1.*

**Table 3. Electronic spectral data and magnetic moments of the compounds**

Compound	$\nu_{max}$ (cm <sup>-1</sup> )	Assignment	$\mu_{eff}$ B.M
Mn(II) 1	31,250	$n \rightarrow \pi^*$ transition	5.77
	38,759	$\pi \rightarrow \pi^*$ transition	
Co(II) 2	19,920	d-d transition	4.48
	24,875	$n \rightarrow \pi^*$ transition	
	38,167	$\pi \rightarrow \pi^*$ transition	
Cu(II) 3	17,161	d-d transition	1.78
	25,125	$n \rightarrow \pi^*$ transition	
	36,363	$\pi \rightarrow \pi^*$ transition	
		$\pi \rightarrow \pi^*$ transition	
Cd(II) 4	34,965	$n \rightarrow \pi^*$ transition	-
	36,496	$\pi \rightarrow \pi^*$ transition	
		$\pi \rightarrow \pi^*$ transition	
Pb(II) 5	35,211	$n \rightarrow \pi^*$ transition	-
	39,682	$\pi \rightarrow \pi^*$ transition	
		$\pi \rightarrow \pi^*$ transition	

### 3.3 Thermal Analysis

The thermal analysis of one of the compounds will be described as a representative example. The thermolysis of  $\{[Mn(DPP)(BIMZ)(H_2O)Cl_2].H_2O\}_n$  (Fig. 3) consists of four decomposition steps, in the temperature ranges 36-215, 216-317, 318-476 and 477-750°C. In the first step both the crystal and coordinated water molecules are released (calc. 7.6%, found 7.2%). The corresponding DTG maximum was seen at 65°C and the corresponding endothermic effect appears at 68°C. The second step shows a mass loss indicating evolution of the benzimidazole molecule up to the peak of the DTG curve (calc. 24.8%, found 26.1%). This step exhibits a DTG maximum at 254°C and an exothermic DTA peak at 255 °C. The third and fourth steps are related to decomposition of the rest of the compound (calc. 56.4%, found 52.7%). The DTG curve displays these two steps at 422 and 525°C with corresponding DTA exothermic peaks at 423 and 526°C respectively. The residue could be a manganese (II) oxide (MnO) (calc. 14.86%, found 13.99%) (Scheme 1). The thermoanalytical data are tabulated in Table 4.

**Scheme 1. Thermal decomposition pathways of the Mn(II) complex****Table 4. Thermal decomposition data of coordination polymers in dynamic air**

Compound	Step	TD/DTG			Mass
		Ti	Tm	Tf	Loss (%)
[[Mn(DPP)(BIMZ)(H <sub>2</sub> O)Cl <sub>2</sub> ].H <sub>2</sub> O] <sub>n</sub>	1 <sup>st</sup>	36	65	215	7.2
	2 <sup>nd</sup>	216	254	317	26.1
	3 <sup>rd</sup>	18	422	476	34.3
	4 <sup>th</sup>	477	525	750	18.4
[Cu(DPP)(BIMZ)Cl <sub>2</sub> (H <sub>2</sub> O)] <sub>n</sub>	1 <sup>st</sup>	41	62	88	4.3
	2 <sup>nd</sup>	89	160	271	14.7
	3 <sup>rd</sup>	272	289	312	8.9
	4 <sup>th</sup>	313	387	453	10.4
	5 <sup>th</sup>	454	538	750	45.6
[Cd(DPP)(BIMZ)Cl <sub>2</sub> (H <sub>2</sub> O)] <sub>n</sub>	1 <sup>st</sup>	33	63	188	2.4
	2 <sup>nd</sup>	189	247	282	24.3
	3 <sup>rd</sup>	283	377	396	11.2
	4 <sup>th</sup>	397	444	488	9.0
	5 <sup>th</sup>	489	617	750	30.1

*Ti=Initial temperature. Tf=Final temperature. Tm=Peak temperature*

### 3.3 X-Ray Powder Diffraction of the Coordination Polymers

The X-ray powder diffraction patterns were recorded for the cobalt(II), copper(II) and lead(II) coordination polymers. The diffraction patterns indicate that the compounds are crystalline. The crystal lattice parameters were computed with the aid of the computer program TREOR. The crystal data for the compounds belong to the crystal system triclinic. The significant broadening of the peaks indicates that the particles are of nanometer dimensions (XRD of Cu(II) compound is depicted in Fig. 4). Scherrer's equation (Eq.3) was applied to estimate the particle size of the coordination polymers:

$$D = K\lambda / \beta \cos\theta \quad (3)$$

where  $K$  is the shape factor,  $\lambda$  is the X-ray wavelength typically 1.54 Å,  $\beta$  is the line broadening at half the maximum intensity in radians and  $\theta$  is Bragg angle and  $D$  is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size. The crystal data together with particle size are recorded in Table 5. The average size of the particles lies in the range 20-34nm for Co(II), Cu(II) and Pb(II) compounds.

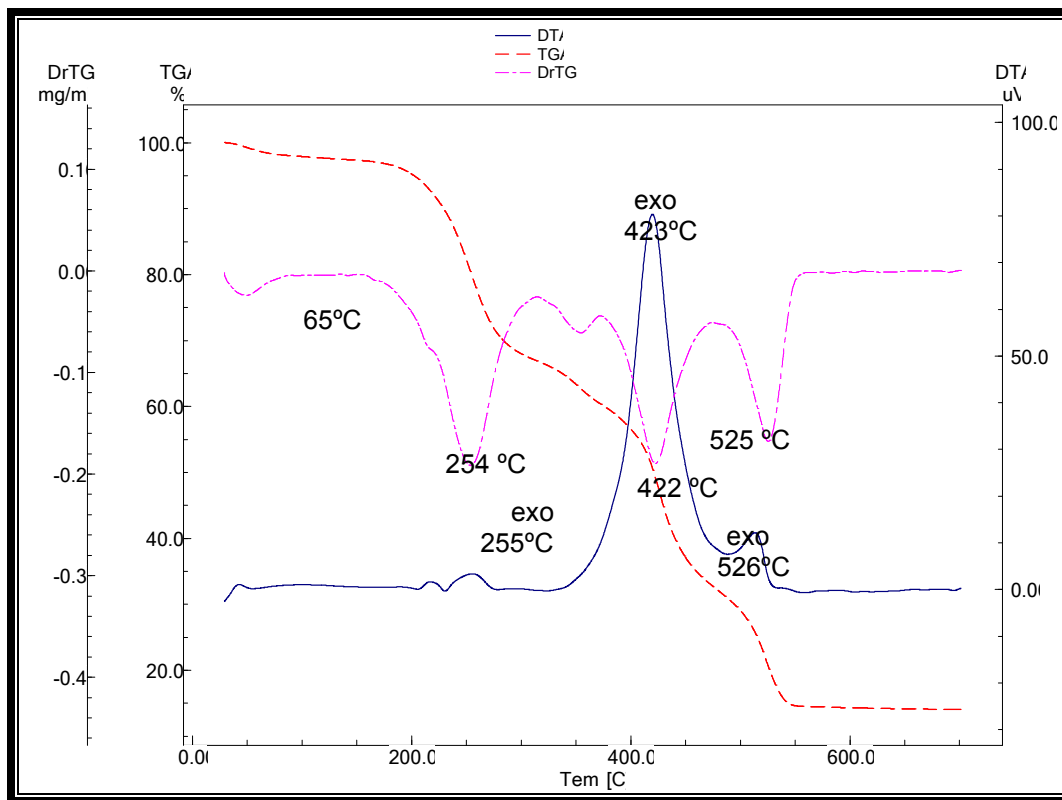


Fig. 3. TG, DTG and DTA thermograms of Mn(II) compound in dynamic air

Table 5. X-ray powder diffraction crystal data of the Co(II), Cu(II) and Pb(II) compounds and their particle size

Parameters	Co(II) compound 2	Cu(II) compound 3	Pb(II) compound 5
Empirical formula	C <sub>20</sub> H <sub>21</sub> CoN <sub>4</sub> OCl <sub>2</sub>	C <sub>20</sub> H <sub>21</sub> CuN <sub>4</sub> OCl <sub>2</sub>	C <sub>20</sub> H <sub>21</sub> PbN <sub>6</sub> O <sub>7</sub>
Formula weight	463.28	467.90	664.67
Crystal system	triclinic	triclinic	triclinic
a (Å)	7.787	6.538	7.086
b (Å)	11.042	7.885	10.131
c (Å)	13.527	20.863	14.890
α (°)	62.172	104.985	58.187
β (°)	95.871	117.942	64.297
γ (°)	117.698	93.906	74.690
Volume of unit cell(Å <sup>3</sup> )	901.03	895.10	898.66
Particle size(nm)	20	25	34

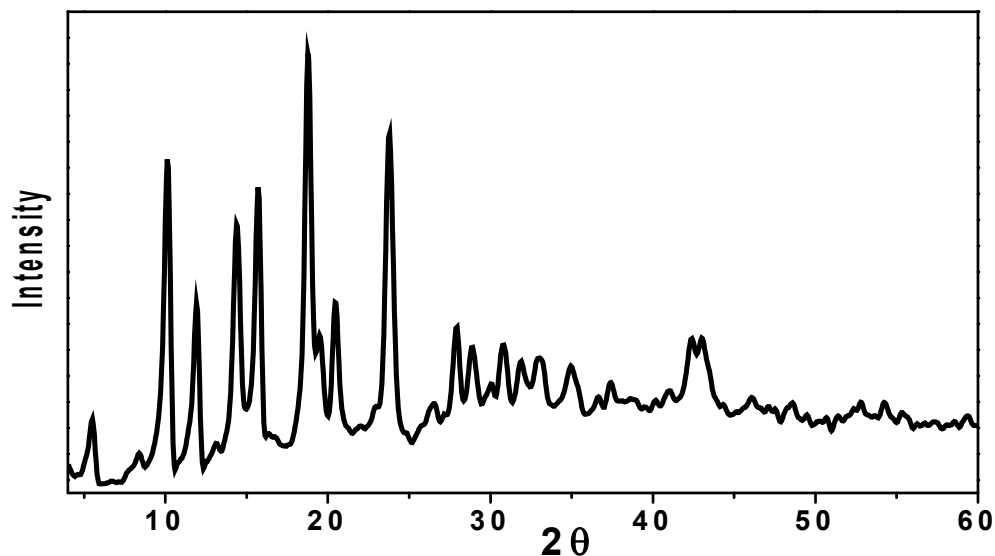


Fig. 4. X-ray of  $[\text{Cu}(\text{DPP})(\text{BIMZ})\text{Cl}_2(\text{H}_2\text{O})]_n$

### 3.4 Scanning Electron Microscopy (SEM)

The scanning electron micrograph of the copper(II) ternary coordination polymer prepared by sonication is illustrated in Fig. 5. The micrograph shows the morphology of this nanostructured compound. The nano spheres aggregate to a great extent.

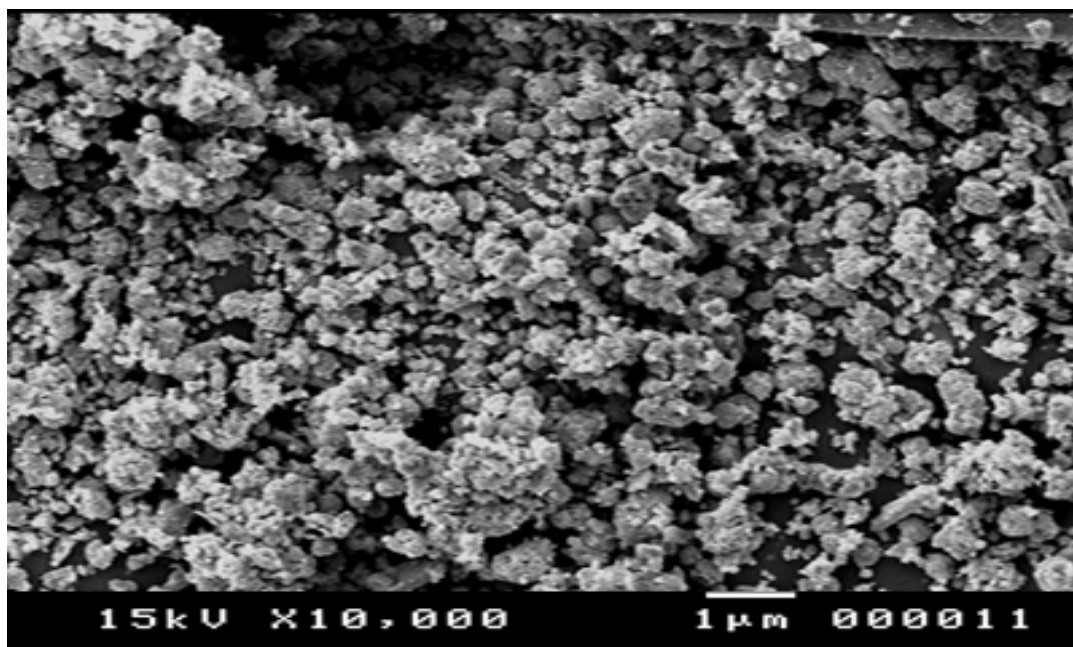


Fig. 5. SEM of Cu(II) coordination polymer



## 4. CONCLUSION

Thus we can conclude that these synthesized mixed ligand coordination polymers of the definite structure possess the ability to form nanosized new supramolecular materials upon ultrasonic irradiation. The compounds are highly crystalline and exhibit high thermal stabilities.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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