POSSIBLE SONOCHEMICAL SYNTHESIS OF NANOSIZED PARTICLES MIXED LIGAND METAL COORDINATION POLYMERS DERIVED FROM 1,3-DI(4-PYRIDYL)PROPANE AND BENZIMIDAZOLE

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. For some of them a sonochemical method was used. The compounds were characterized by elemental analysis, FT-IR and electronic spectral studies. Thermogravimetry(TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) were used to study the thermal decomposition steps and to calculate the thermodynamic parameters of the metal coordination polymers. 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 radiation (average size 20-34 nm).

Keywords: Nano-structure, coordination polymers, XRD, SEM and thermal studies.

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 benzimidazolebased 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. Metal complexes of biologically important ligands were sometimes more effective than free ligands [25]. 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 their conversion of some of them into nanostructured by a sonochemical method.

2. Experimental

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 mixing 1,3-di(4-pyridyl)propane (1.5 mmol) dissolved in ethanol (15 ml) with an aqueous alcoholic solution of metal salts of Mn(II) and Cd(II) (1.5 mmol) in 15 ml distilled water, then an ethanolic solution of benzimidazole was added immediately 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 $CaCl_2$.

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 (400-4000 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 700 W. 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 °C min^{-1}. XRD Model PW 1710 control unit Philips, Anode material Cu 40 K.V 30 M.A Optics: Automatic divergence slit. Scanning electron microscope (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:

$$MCl_2 + DPP + BIMZ \xrightarrow[H_2O]{EtOH} \{[M(DPP)(BIMZ)Cl_2(H_2O)].xH_2O\}_n \qquad (1)$$

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

$$Pb(NO_3)_2 + DPP + BIMZ \xrightarrow[H_2O]{EtOH} [Pb(DPP)(BIMZ)(NO_3)_2(H_2O)]_n \qquad (2)$$

The complexes are air stable, insoluble in common organic solvents but soluble in dimethyleformamide (DMF) and dimethylesulphoxide (DMSO). The molar conductivties of the complexes in DMSO at 25 ˚C are in the 32.08-61.62 $\Omega^{-1}cm^2\ mol^{-1}$ 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**	
$\{[Mn(DPP)(BIMZ)Cl_2(H_2O)].H_2O\}_n$ **1**	$C_{20}H_{23}Cl_2MnN_4O_2$ (477.31)	Light-brown	49.66 50.32	5.42 4.86	11.12 11.74	222
$[Co(DPP)(BIMZ)Cl_2(H_2O)]_n$ **2**	$C_{20}H_{21}Cl_2CoN_4O$ (463.28)	Dark-blue	52.08 51.84	4.88 4.57	12.40 12.09	219
$[Cu(DPP)(BIMZ)Cl_2(H_2O)]_n$ **3**	$C_{20}H_{21}Cl_2CuN_4O$ (467.90)	Light-green	51.20 51.33	5.82 4.53	10.01 11.97	205
$[Cd(DPP)(BIMZ)Cl_2(H_2O)]_n$ **4**	$C_{20}H_{21}Cl_2CdN_4O$ (516.76)	White	47.09 46.48	4.72 4.10	10.82 10.84	202
$[Pb(DPP)(BIMZ)(NO_3)_2(H_2O)]_n$ **5**	$C_{20}H_{21}PbN_6O_7$ (664.67)	White	36.95 36.13	3.98 3.19	11.93 12.64	244

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 1600 cm^{-1} in the spectrum of DPP (free ligand) is shifted to a higher wave number (1605-1615 cm^{-1}), indicating participation of this group in the bonding with the metal ions [26]. Furthermore, the IR spectra of the complexes show that υ(C-N) of benzimidazole occurs at 804-815 cm^{-1} [27]. The bands appearing in the range at 3010-3065 cm^{-1} in the spectra of the coordination polymers **1-5** are assigned to νOH of the coordinated water molecules [28], whereas the νOH stretching vibrations of the crystal water molecules are located at 3400 cm^{-1} for the manganese(II) complex **1** [29]. Metal-nitrogen and metal-oxygen bonding are manifested by the appearance of two bands at 418-428 cm^{-1} and 510-518 cm^{-1} regions, respectively [28] (Figure 1). .

Table 2. Infrared spectral data of the coordination polymers.

Compounds	**υ(C=N)**	**υ(C-N)**	**υ(OH) coord.**	**υ(OH) lattice**	**υ(M-N)**	**υ(M-O)**
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

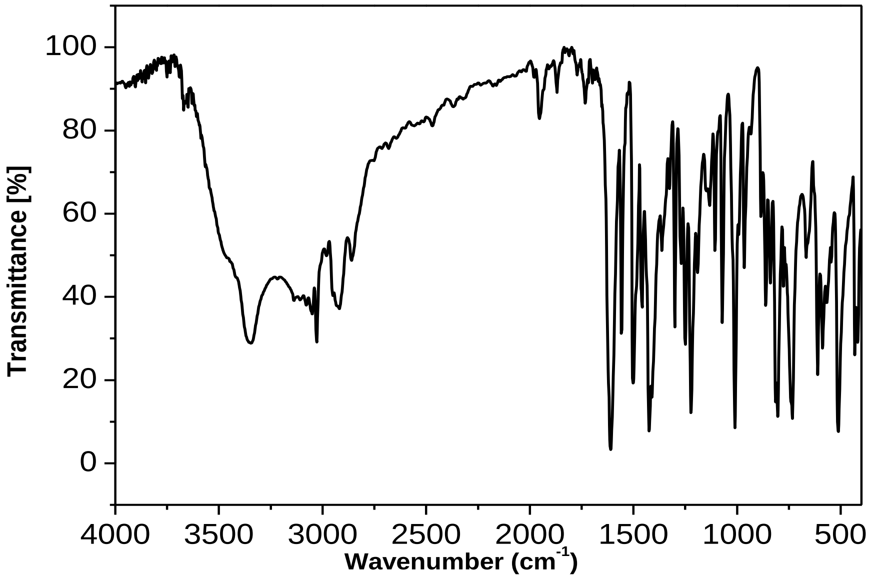


Figure 1. FT-IR spectrum of $\{[Mn(DPP)(BIMZ)(H_2O)Cl_2].H_2O\}_n$ **1**.

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 cm^{-1} and 36,363-39,682 cm^{-1} respectively, which are attributed to the n→π* and π →π* 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 cm^{-1} and at 17,161 cm^{-1}. The magnetic moments for the coordination polymers were measured. The Mn(II) compound gave a value of 5.77 BM [30], in agreement with values reported for octahedral complexes. The cobalt (II) compound exhibits a magnetic moment value of 4.48 BM, in accord with an octacoordination environment around the Co(II) ion [31]. For the copper(II) complex the magnetic moment value of 1.78 BM is in accord with octahedral values for Cu(II) compounds [32]. Based on the forgoing results the suggested structures for 1,3-di(4-pyridyl)propane mixed ligand complexes are shown as follows:

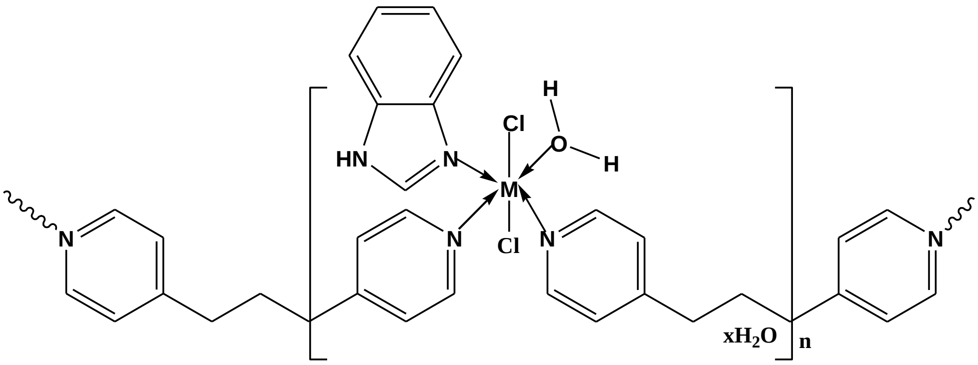


Figure 2. Suggested structure of $\{[M(DPP)(BIMZ)(H_2O)Cl_2].xH_2O\}_n$
M = Mn(II), Co(II), Cu(II) and Cd(II) x = 0 or 1.

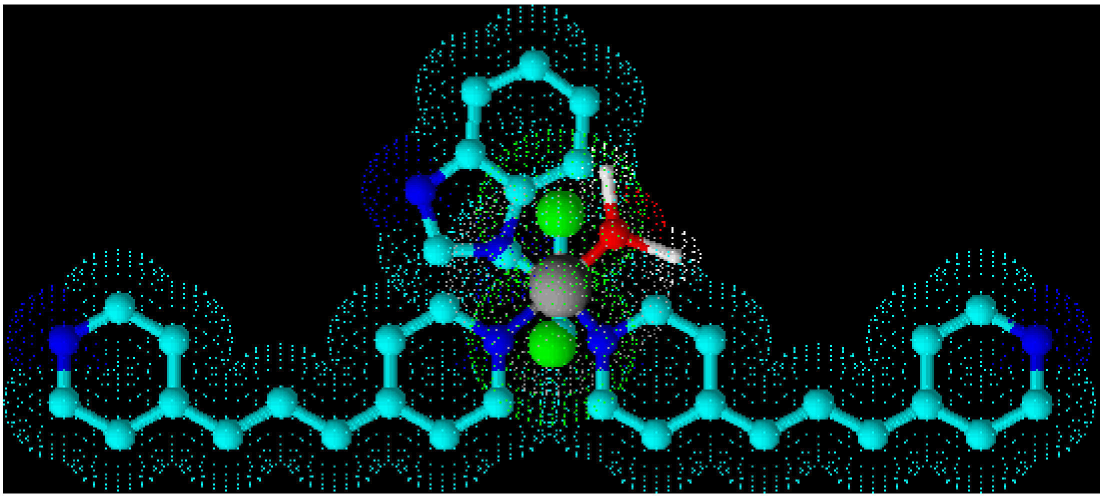


Figure 3. A view of the complete coordination around the metal ions in the coordination polymers

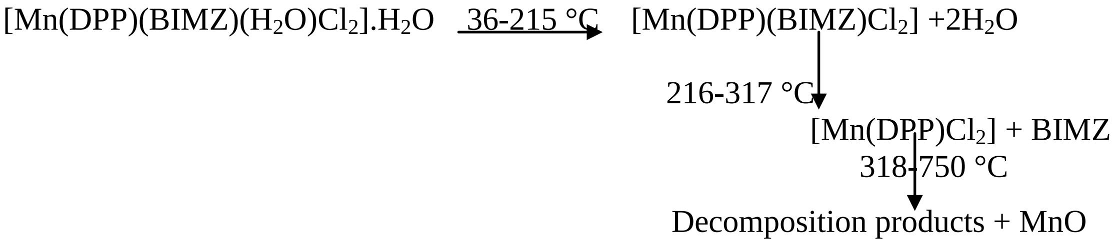
Table 3. Electronic spectral data and magnetic moments of the compounds.

Compound	ν_{max} (cm^{-1})	Assignment	μ_{eff} B.M
Mn(II) **1**	31,250 38,759	n→ π* transition π→ π* transition	5.77
Co(II) **2**	19,920 24,875 38,167	d-d transition n→ π* transition π→ π* transition	4.48
Cu(II) **3**	17,161 25,125 36,363	d-d transition n→ π* transition π→ π* transition	1.78
Cd(II) **4**	34,965 36,496	n→ π* transition π→ π* transition	-
Pb(II) **5**	35,211 39,682	n → π* transition π→ π* transition	-

Thermal analysis

Non-isothermal kinetic analysis for the thermal decomposition of the prepared complexes was carried out using the Coats-Redfern equation [33]. The kinetic parameters were evaluated only for clear out and non-overlapping stages. Kinetic studies were not attempted for decomposition stages, which occur within a very narrow temperature range, resulting in a TG curve too steep for enough data to be collected. Furthermore, some decomposition steps are so small that within the accuracy of the measurements a sufficient number of points from the curve could not be obtained to derive meaningful results for kinetic parameters. The thermal analysis of one of the compounds will be described as a representive example. The thermolysis of $\{[Mn(DPP)(BIMZ)(H_2O)Cl_2].H_2O\}_n$ (Fig. 4 & 5) consists of four decomposition steps, namely at 36-215, 216-317, 318-476 and 477-750 °C. In the first step both the crystal and coordinated water molecules are released (calc. 7.55 %, found 7.17 %). The corresponding DTG midpoint was seen at 65 °C and the corresponding endothermic effect appears at 68 °C. The second step shows a mass loss indicating decomposition of the benzimidazole molecule (calc. 24.75 %, found 26.12 %). This step exhibits a DTG midpoint 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. 56.39 %, found 52.72 %). 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). .



$$\mathrm{[Mn(DPP)(BIMZ)(H_2O)Cl_2].H_2O} \xrightarrow{36\text{-}215\ ^\circ\mathrm{C}} \mathrm{[Mn(DPP)(BIMZ)Cl_2] + 2H_2O}$$

$$\xrightarrow{216\text{-}317\ ^\circ\mathrm{C}} \mathrm{[Mn(DPP)Cl_2] + BIMZ}$$

$$\xrightarrow{318\text{-}750\ ^\circ\mathrm{C}} \text{Decomposition products} + \mathrm{MnO}$$

Scheme 1.

The thermoanalytical data are tabulated in Table 4 and the kinetic parameters and activation parameters were calculated for some of the complexes using Coats-Redfern equation (Table 5).

Table 4. Thermal decomposition data of coordination polymers in dynamic air

Compound	**Step**	**TG/DTG** **Ti**	**Tm**	**Tf**	**Mass Loss(%)**
$\{[Mn(DPP)(BIMZ)(H_2O)Cl_2].H_2O\}_n$	1st	36	65	215	7.17
	2nd	216	254	317	26.12
	3rd	318	422	476	34.30
	4th	477	525	750	18.42
$[Cu(DPP)(BIMZ)Cl_2(H_2O)]_n$	1st	41	62	88	4.29
	2nd	89	160	271	14.67
	3rd	272	289	312	8.90
	4th	313	387	453	10.40
	5th	454	538	750	45.57
$[Cd(DPP)(BIMZ)Cl_2(H_2O)]_n$	1st	33	63	188	2.36
	2nd	189	247	282	24.30
	3rd	283	377	396	11.19
	4th	397	444	488	9.04
	5th	489	617	750	30.05

Ti = Initial temperature.
Tm = Maximum temperature.
Tf = Final temperature.

Table 5. Kinetic parameters and activation parameters ΔH*, ΔS* and ΔG* for the thermal decomposition of $\{[Mn(DPP)(BIMZ)Cl_2(H_2O)].H_2O\}_n$ **1**, $[Cu(DPP)(BIMZ)Cl_2(H_2O)]_n$ **3** and $[Cd(DPP)(BIMZ)Cl_2(H_2O)]_n$ **4** using the Coats-Redfern equation in dynamic air.

		Coats-Redfern equation						
Compound	**Step**	***r***	**n**	**E**	**Z**	**ΔS^***	**ΔH^***	**ΔG^***
1	**1st**	0.9937	0.00	110.4	2.22×10^3	-187.8	104.6	234.4
3	**1st**	0.9999	2.00	56.6	11.46×10^2	-187.0	53.9	114.4
4	**1st**	0.9976	0.00	23.7	4.79×10^2	-198.13	19.41	121.4

E in KJ mol^{-1}, ΔH^* and ΔG^* in $kJmol^{-1}$ & ΔS^* in $kJmol^{-1}K$.

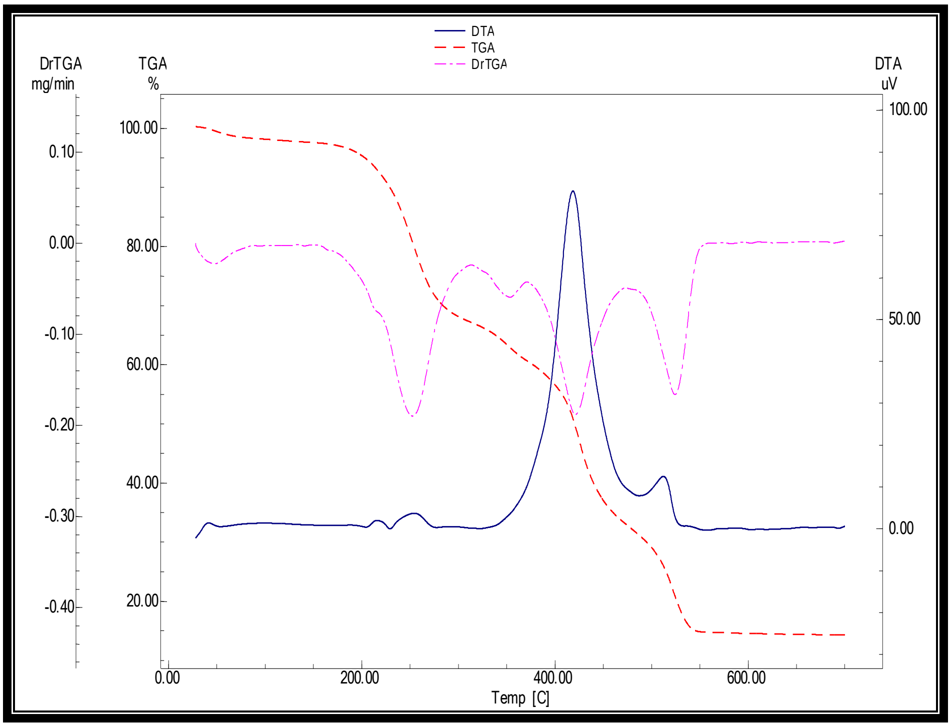


Figure 4. TG, DTG and DTA thermograms of Mn(II) compound in dynamic air.

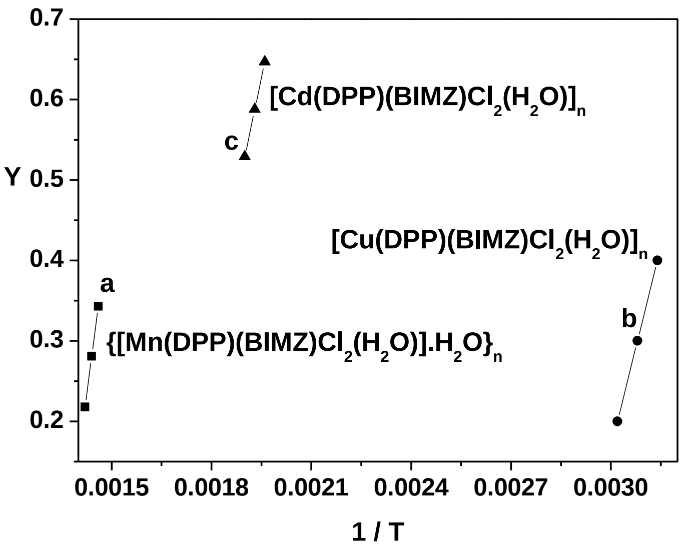


Figure 5. Coats-Redfern plots for a) Mn(II), b) Cu(II) and c) Cd(II) complexes first step in dynamic air.

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 Figure 6). Scherrer's equation (eq.3) was applied to estimate the particle size of the coordination polymers:

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

where K is the shape factor, λ is the X-ray wavelength typically 1.54 Å, β is the line broadening at half the maximum intensity in radians and θ 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 (6). The average size of the particles lies in the range 20-34 nm for Co(II), Cu(II) and Pb(II)compounds.

Table 6. 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	$C_{20}H_{21}CoN_4OCl_2$	$C_{20}H_{21}CuN_4OCl_2$	$C_{20}H_{21}PbN_6O_7$
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(Å3)	901.03	895.10	898.66
Particle size(nm)	20	25	34

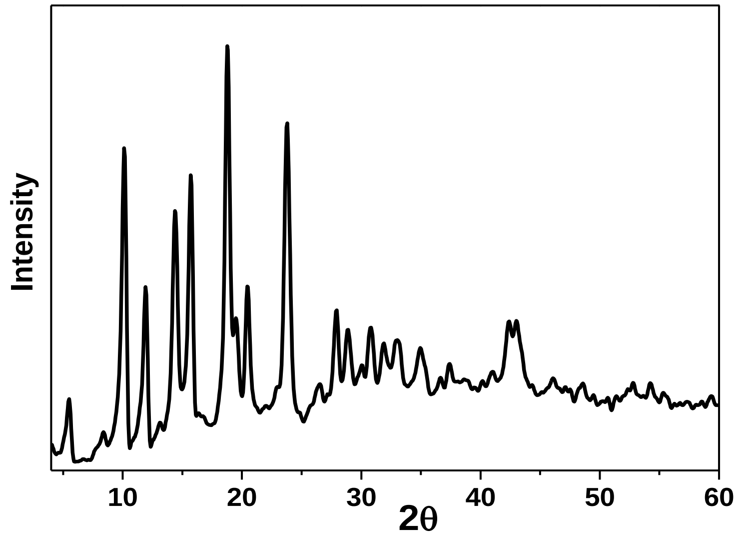


Figure 6. X-ray of $[Cu(DPP)(BIMZ)Cl_2(H_2O)]_n$

Scanning electron microscopy (SEM)

The scanning electron micrograph of the copper(II) ternary coordination polymer prepared by sonication is illustrated in Fig. 7. The micrograph shows the morphology of this nanostructured compound. The nano spheres aggregate to a great extent.

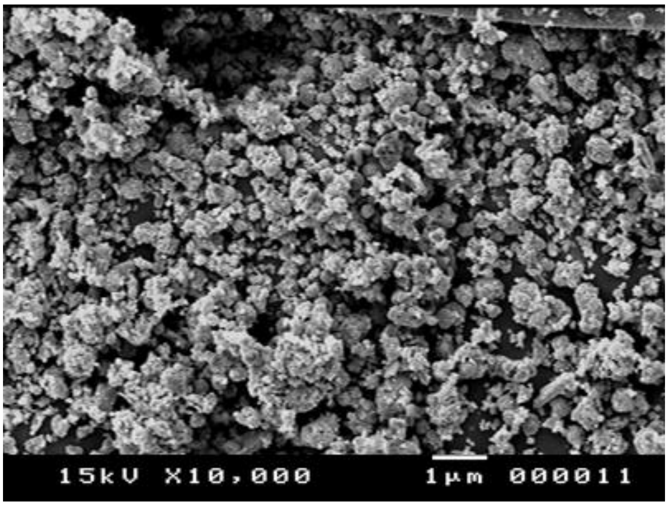


Figure 7. SEM of Cu(II) coordination polymer.

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