

## Ultrasound-Promoted Synthesis and Characterization of Nanoparticles of Coordination Polymer $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$

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### Article history:

Received 3/7/2014

Accepted 5/8/2014

Published online 1/9/2014

### Keywords:

Nanoparticles

Pyridine-2,5-dicarboxylic acid

Sonochemical synthesis

Powder X-ray diffraction

Dynamic Light Scattering

### Abstract

Nanoparticles of coordination polymer  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n \text{H}_2\text{O}$  [ $\text{H}_2\text{pydc}$  = pyridine-2,5-dicarboxylic acid] have been synthesized by sonochemical method and characterized by elemental analysis, infrared spectroscopy, powder X-ray diffraction, scanning electron microscopy, DLS particle size analysis and TGA/DTA. The structure of single crystalline coordination polymer developed from nanosized coordination polymer was determined by X-ray crystallography. The XRPD studies reveal that nanoparticles of coordination polymer  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$  have same structure as that of bulk single crystalline polymer. The coordination polymer possesses a 1-D chain like extended structure with binuclear cobalt(II) nodal unit. The coordination geometry around two cobalt atoms Co(1) and Co(2) can be described as slightly distorted octahedron. The average particle size of nanoparticles calculated by using least square method of Modified Scherrer formula was found ~27 nm. The nanoparticles are composed of polyhedral blocks with definite edges. Dynamic Light Scattering (DLS) measurements show a narrow size distribution. The nanoparticles are thermally stable up to 352 K and thereafter decompose in well defined steps.

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## 1. Introduction

The field of coordination polymers has developed rapidly in recent years because synthesis of coordination polymer offers considerable flexibility and control over structure and properties, thereby offering rare pathways to

rational materials design [1-10]. This flexibility originates from the enormous structural and chemical diversities afforded by molecular systems, features that are less prevalent in many other branches of materials chemistry.

Coordination polymers are organized and sustained by coordinate covalent bonds, supramolecular contacts (such as hydrogen bonds and  $\pi$ - $\pi$  interactions), and nucleophilic interactions [11-13]. Coordination polymers can be rapidly, accurately, and efficiently synthesized from relatively simple units, where the metal ions, multidentate organic ligands, and coordinate bonding are the parameters for directing the self assembly process [14]. Coordination polymers that exhibit micro- and nanoporous behavior have been reported with crystalline structures that are stable upon removal of guest molecules [15-18]. Coordination polymers have promising applications in many aspects such as luminescence, gas storage, selective adsorption and magnetic device [19-21]. Since properties of MOF are controlled by size and shape of framework, the surface area of the materials becomes larger, and the 'quantum size effect' begins to play a significant role when nanometer size range is reached [22-26]. Scaling down these materials to the nanosized has enabled their use in a broad range of applications including catalysis, spin-crossover, templating, biosensing, biomedical imaging, and anticancer drug delivery [27-29]. There are various synthesizing methods for developing nanostructured materials, including gas phase techniques, liquid phase methods, and mixed phase approaches [30-32]. In sonochemistry, molecules undergo a chemical reaction due to the application of powerful ultrasound irradiation (20 kHz–10 MHz). Ultrasound induces chemical changes due to cavitation phenomena involving formation, growth, and instantaneously implosive collapse of bubbles in a liquid, which can generate local hot spots having a temperature of roughly 5000 °C, pressures of about 500 atm and a lifetime of a few microseconds [33]. These extreme

conditions can drive chemical reactions to fabricate a variety of nanocompounds [34-35]. Bang and Suslick have used ultrasound to synthesize nanostructured materials of diverse composition and morphology [32, 36-37]. So far little attention has been given to synthesis of nanosized coordination polymers. The polycarboxylates, have been used to construct coordination frameworks by direct interaction with metal ions to form discrete polynuclear 1-, 2-, and 3-D coordination networks in a variety of coordination modes [38-40]. Pyridinedicarboxylic acids exhibit a variety of bridging modes and a strong tendency to form large, tightly bound metal cluster aggregates. Polymeric structures of pyridinedicarboxylato complexes with transition and lanthanide metals have been reported, in which pyridinedicarboxylates not only chelate but also bridge to form diversified structures [41-43]. In this article, we report a new nanosized coordination polymer of  $\text{Co}^{2+}$  with  $\text{H}_2\text{pydc}$  by sonication method.

## 2. Experimental procedure

All reagents used for the synthesis and analysis were commercially available and used as received. Doubly distilled water was used to prepare aqueous solutions. An ultrasonic processor with thumb-actuated pulser (Sonics make) equipped with a standard probe made of titanium alloy Ti-6 Al-4V operating at 20 kHz with a maximum power output of 130W was used for the ultrasonic irradiation. IR spectra from 4000 to 400  $\text{cm}^{-1}$  were recorded on a spectrophotometer using KBr discs. Thermal analysis was performed on a was carried out on Mettler Toledo TGA/SDTA 851e in Nitrogen atmosphere with a heating rate at heating rate of 10 °C  $\text{min}^{-1}$ . The simulated X-ray powder diffraction (XRPD) pattern based on single-crystal data was

prepared using Mercury software. XRPD measurements were performed using a Bruker

**Table 1.** Crystal data and structure refinement for  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$

Crystal description	block shaped
Crystal color	pink
Crystal size	0.36 x 0.32 x 0.28 mm
Empirical formula	$\text{C}_{14}\text{H}_{22}\text{Co}_2\text{N}_2\text{O}_{16}$
Formula weight	592.19
Radiation, wavelength	Cu $K\alpha$ , 1.54180 Å
No. of molecules per unit cell	2
Unit cell dimensions	a = 7.0508(4) b = 8.9261(5) c = 9.6205(6) Å $\alpha = 91.701(5)^\circ$ $\beta = 99.838(5)^\circ$ $\gamma = 108.010(5)^\circ$
Crystal system	triclinic
Space group	P-1
Unit cell volume	565.14(6)
No. of molecules per unit cell	2
Temperature	150(2) K
Absorption coefficient	1.560 mm <sup>-1</sup>
F(000)	318
Scan mode	w/q scan 565.14(6)
$\theta$ range for entire data collection	$3.09 < \theta < 25.00^\circ$
Range of indices	h = -8 to 8, k = -10 to 10, l = -9 to 9
Reflections collected/unit cell	4248 / 1986
Reflections observed ( $I > 2\sigma(I)$ )	1898
$R_{\text{int}}$	0.0291
$R_{\text{sigma}}$	0.0213
Structure determination	direct methods
Refinement	full-matrix least-squares on $F^2$
No. of parameters refined	198

AXSD8 X-ray diffraction spectrometer with monochromated Cu-K $\alpha$  radiation and SEM using ZEISS EVO Series Scanning Electron Microscope EVO 50 with gold coating. Particle size was determined by the dynamic light scattering (DLS) technique using a Zetasizer Nano ZS 90, Malvern make.

Single crystal X-ray structural studies of the compound  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$  were performed on a CCD Agilent Technologies

(Oxford Diffraction) SUPER NOVA diffractometer. Data were collected at 150(2) K using graphite-monochromated Cu  $K\alpha$  radiation ( $\lambda_\alpha = 1.54180 \text{ \AA}$ ). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on  $F$ . The positions of all the atoms were obtained by direct methods [44]. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally  $1.2U_{eq}$  of their parent atoms. The crystal and refinement data are summarized in Table 1, and selected bond distances and bond angles are shown in Table 2.

**Table 2.** Selected bond distance (Å) and angle (°) data for compound  $\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$  (e.s.d.'s are given in parentheses).

Co(1)-O(1)	2.073(2)
Co(1)-O(5)	2.109(2)
Co(1)-N(1)	2.126(3)
Co(2)-O(2)	2.082(2)
Co(2)-O(7)	2.084(2)
Co(2)-O(6)	2.104(2)
O(1)-C(1)	1.272(4)
O(2)-C(1)	1.249(4)
O(3)-C(6)	1.258(4)
O(4)-C(6)	1.252(4)
O(1)-Co(1)-O(1) <sup>#1</sup>	180.00(13)
O(1)-Co(1)-O(5)	91.25(9)
O(1) <sup>#1</sup> -Co(1)-O(5)	88.75(9)
O(1)-Co(1)-O(5) <sup>#1</sup>	88.75(9)
O(5)-Co(1)-O(5) <sup>#1</sup>	180.0
O(1)-Co(1)-N(1)	79.13(9)
O(1) <sup>#1</sup> -Co(1)-N(1)	100.87(9)

O(5)-Co(1)-N(1)	88.03(10)
O(5) <sup>#1</sup> -Co(1)-N(1)	91.97(10)
O(1) <sup>#1</sup> -Co(1)-N(1) <sup>#1</sup>	79.13(9)
N(1)-Co(1)-N(1) <sup>#1</sup>	180.00(15)
O(2) <sup>#2</sup> -Co(2)-O(2)	180.0
O(2) <sup>#2</sup> -Co(2)-O(7)	91.64(9)
O(7)-Co(2)-O(7) <sup>#2</sup>	88.36(9)
O(2) <sup>#2</sup> -Co(2)-O(6) <sup>#2</sup>	93.70(9)
O(2)-Co(2)-O(6) <sup>#2</sup>	86.30(9)
O(7)-Co(2)-O(6) <sup>#2</sup>	89.49(10)
O(7) <sup>#2</sup> -Co(2)-O(6) <sup>#2</sup>	90.51(10)
C(7)-N(1)-C(2)	118.3(3)
C(2)-N(1)-Co(1)	112.1(2)
O(2)-C(1)-O(1)	125.9(3)
O(2)-C(1)-C(2)	116.8(3)
O(3)-C(6)-O(3)	125.1(3)
O(4)-C(6)-C(5)	117.9(3)
O(3)-C(6)-C(5)	117.0(3)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z #2 -x,-y,-z-

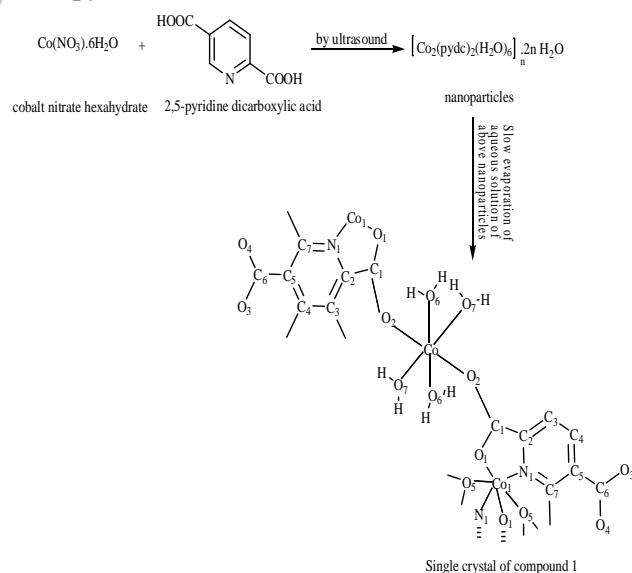
To prepare nanoparticles of coordination polymer of  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$  a 5 mL aqueous solution of cobalt nitrate hexahydrate (0.75 mmol  $\text{L}^{-1}$ , 0.2182 g) was positioned in a high density ultrasonic probe. Aqueous solution of pyridine-2, 5-dicarboxylic acid was prepared by dissolving (1.5 mmol  $\text{L}^{-1}$ , 0.2506 g) of acid in 5 mL aqueous solution of NaOH (0.04 g, 1 mmol  $\text{L}^{-1}$ ). The pH of solution was adjusted between 4-5. The solution of pyridine-2, 5-dicarboxylic acid was added dropwise to the solution of cobalt nitrate hexahydrate while sonicating the reaction mixture. The reaction mixture was sonicated for one hour at room temperature. The pink coloured precipitates were obtained after aging for 1h. The precipitates formed were filtered off, washed with water, and dried in air (yield = 0.34 g ~74% based on cobalt nitrate hexahydrate). Elemental Anal. Calc. (%) for  $\text{Co}_2\text{N}_2\text{C}_{14}\text{H}_{22}\text{O}_{16}$ : Co, 19.90; C, 28.39; H, 3.74; N,

4.73. found (%): Co, 20.0; C, 28.35; H, 3.70; N, 4.78.

In order to isolate single crystal of  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$ , the pink colour precipitates were dissolved in minimum distilled water in a beaker and left to evaporate. After 10 days pink slit-shaped crystal were formed, washed with water and dried in air. Calc. (%) for  $\text{Co}_2\text{N}_2\text{C}_{14}\text{H}_{22}\text{O}_{16}$ : Co, 19.90; C, 28.39; H, 3.74; N, 4.73. found (%): Co, 20.0; C, 28.35; H, 3.70; N, 4.78.

### 3. Results and discussion

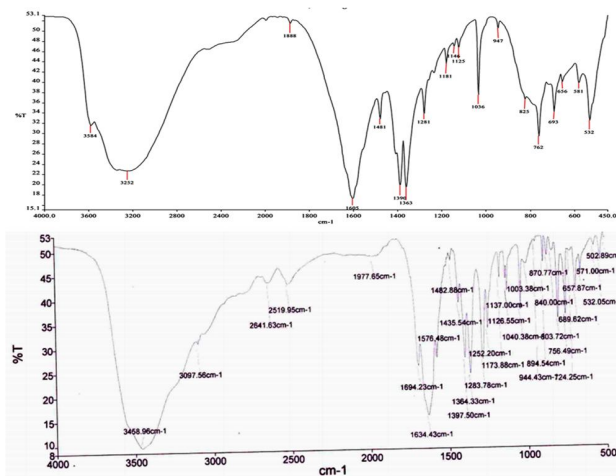
Nanoparticles of 1-D coordination polymer  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$  (**1**) were obtained by the reaction of pyridine-2,5-dicarboxylate with cobalt nitrate hexahydrate by sonochemical method. Single crystals of **1** were obtained by slow evaporation of aqueous solution of the nanoparticles. Scheme 1 gives an overview of the method used for the synthesis of nanoparticles of  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$  (**1**).



**Scheme 1.** Overview of method for synthesis of nanoparticles of  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$

The infrared spectrum of nanosized coordination polymer  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$  (**1**) prepared

by sonochemical method and that of single crystal are shown in (Fig. 1) with suitable matches with slight differences.

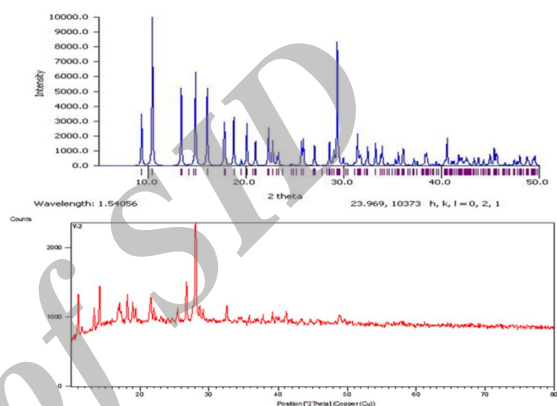


**Fig. 1.** FTIR spectra of (a) single crystal and (b) nanoparticles of  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$

The main bands in the infrared spectrum of  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$  showed indicative vibration bands of carboxylate groups and water molecules. Broad bands in the high energy band region at  $3458\text{ cm}^{-1}$  and  $3252\text{ cm}^{-1}$  are attributed to  $\nu(\text{O-H})$  of coordinated and lattice water molecules. Sharp bands at  $944\text{ cm}^{-1}$  and  $657\text{ cm}^{-1}$  are assigned to rocking  $\rho_r(\text{H}_2\text{O})$  and wagging  $\rho_w(\text{H}_2\text{O})$  modes of coordinated water molecules respectively. Sharp and strong bands at  $1634\text{ cm}^{-1}$  and  $1397\text{ cm}^{-1}$  are assigned to asymmetric  $\nu_{\text{as}}(\text{COO})$  and symmetric  $\nu_{\text{s}}(\text{COO})$  stretching modes of carboxylate group. The  $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$  is 237 suggesting that carboxylate group is not bonded to a single cobalt metal ion in a symmetrical bidentate chelating mode. This is confirmed by single crystal XRD study of the coordination polymer. The carboxylate group is bonded to two cobalt metal ions in a bridging mode. The in-plane  $\delta(\text{OCO})$  vibration mode appears as sharp band at  $756\text{ cm}^{-1}$  whereas sharp band at  $1482\text{ cm}^{-1}$  is assigned to  $\nu(\text{C=N})$  of pyridine ring. The bands for  $\delta(\text{C-H})$  appear at  $1364$

and  $840\text{ cm}^{-1}$ . The non-ligand bands at  $571\text{ cm}^{-1}$  and  $532\text{ cm}^{-1}$  are attributed to  $\nu(\text{Co-O})$  and  $\nu(\text{Co-N})$  bands respectively.

The XRPD pattern of a typical sample of nanoparticles of **1** prepared by sonochemical process is shown in (Fig. 2). The simulated XRPD pattern from single-crystal X-ray data of coordination polymer **1** is also shown for comparison.



**Fig. 2.** XRPD pattern of (a) single crystal and (b) nanoparticles of  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$

Acceptable matches, with slight differences in  $2\theta$ , were observed between experimental and simulated XRPD patterns. This indicates that the compound obtained by the sonochemical process as nanoparticles has molecular structure identical to that of crystalline polymer grown from aqueous solution of nanoparticles. Significant broadening of the peaks in XRPD pattern of nanoparticles indicates that the particles obtained by sonochemical process are of nanometer dimensions. There are no peaks of impurities detected in the XRPD pattern, indicating the high purity of as obtained sample. Diffraction peaks with slight variation in line width ( $\beta$ ) were observed at  $2\theta$  values  $14.37^\circ$ ,  $17.83^\circ$ ,  $19.65^\circ$ ,  $22.76^\circ$ ,  $26.62^\circ$ ,  $28.03^\circ$ ,  $29.57^\circ$ ,  $32.06^\circ$ ,  $38.61^\circ$ ,  $46.19^\circ$  and  $53.19^\circ$ . Different parameters used for calculating

particle size using least square method of Modified Scherrer formula [45] are shown in Table 3.

$$\ln \beta = \ln K \lambda / L + \ln 1 / \cos \theta$$

where  $L$  is the average crystallite size,  $\lambda = 1.5418 \text{ \AA}$  for Cu-K $\alpha$ ,  $\beta$  is the half maximum peak width and  $\theta$  is the diffraction angle in degrees. Fig. 3 indicates linear plot of  $\ln \beta$  vs.  $\ln(1/\cos\theta)$ , the intercept obtained at -5.2313. The average crystallite size was found 27.42 nanometres.

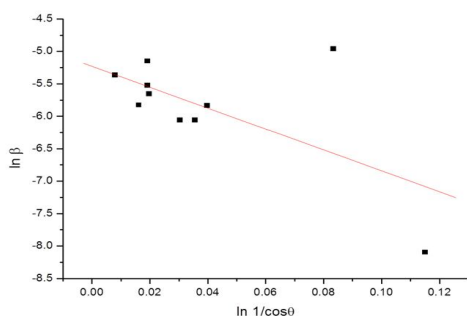


Fig. 3. Linear plot of modified Scherrer equation

Table 3. Different Parameters for calculating average crystallite size from Modified Scherrer equation

2 $\theta$	FWHM( $\beta$ )	$\ln \beta$	$\ln 1/\cos\theta$
14.37	0.2676	-5.366	0.079
17.83	0.2007	-5.654	0.019
19.65	0.1673	-5.825	0.016
22.76	0.2342	-5.525	0.019
26.62	0.3346	-5.149	0.019
28.03	0.1338	-6.059	0.030
29.57	0.1338	-6.059	0.035
32.06	0.1673	-5.835	0.039
46.19	0.4015	-4.960	0.083
53.19	0.4896	-8.095	0.115

An ORTEP view of coordination polymer  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$  is shown in Fig. 4. The coordination polymer possesses a 1-D chain-like extended structure with binuclear cobalt(II) nodal unit. The coordination polymer crystallized in the triclinic  $P-1$  space group, and asymmetric unit consists of one cobalt atom, one pyridine-2,5-

dicarboxylate dianion, three coordinated water, and two lattice water molecules (Fig. 4). The coordination geometry around cobalt atom Co(1) and Co(2) can be described as slightly distorted octahedron (Fig. 5).

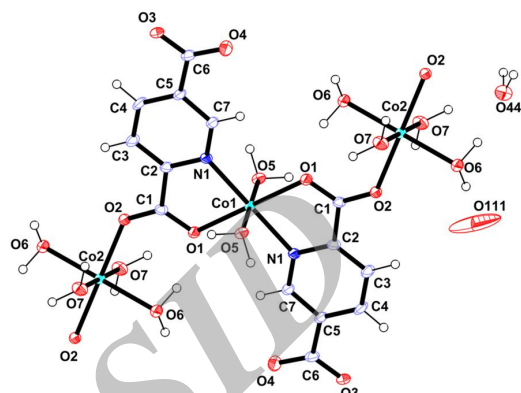


Fig. 4. ORTEP of coordination polymer  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$  with displacement ellipsoids drawn at 50% probability

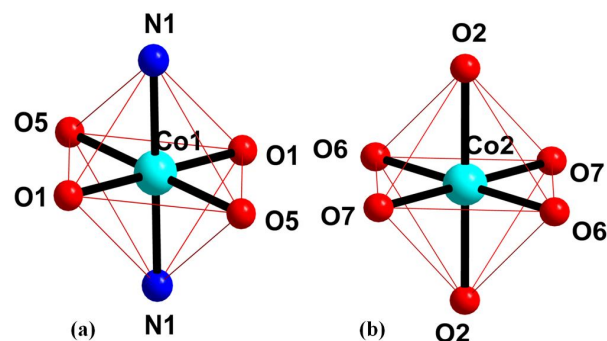
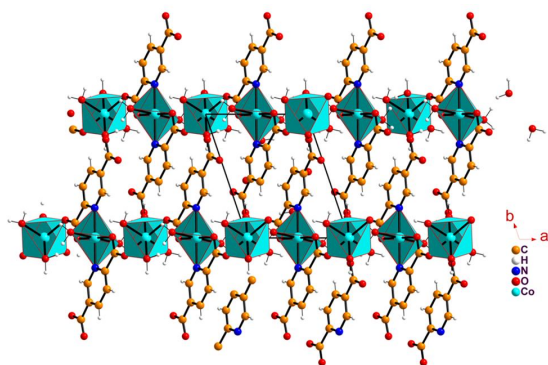


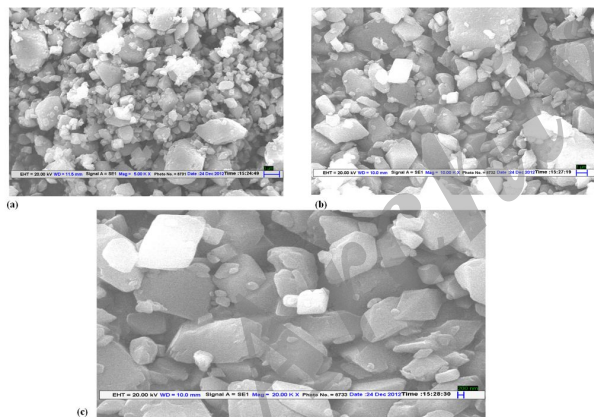
Fig. 5. Distorted octahedral view around Co(II) ions in  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$

The polymer expansion of  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$  is shown in Fig. 6. The crystal structure of crystalline coordination polymer developed from nanoparticles is identical to bulk crystalline polymer obtained by hydrothermal synthesis in an autoclave in our laboratory and reported earlier [46].



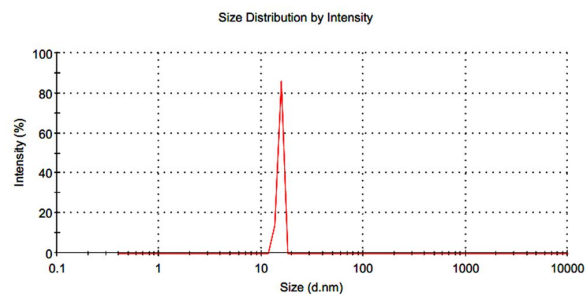
**Fig. 6.** Polymer expansion of  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$  when viewed along c-axis

Fig. 7 (a), (b), (c) show the morphology of nanoparticles prepared by sonochemical method. The nanoparticles are composed of polyhedral blocks with definite edges, and size about 15-30 nm.



**Fig. 7.** (a) Low magnification (b) Medium magnification (c) High magnification SEM images of nanoparticles of  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$ .

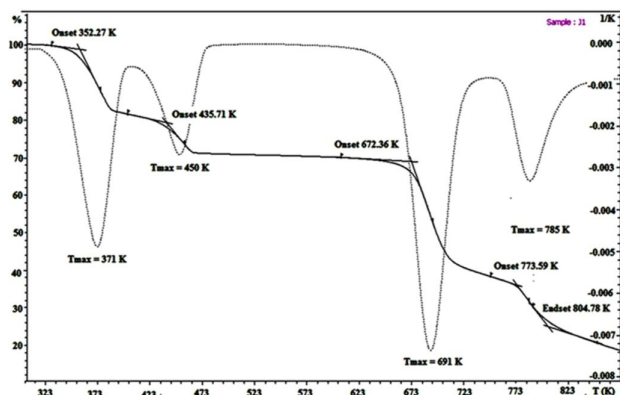
We also determined the particle size of nanoparticles of **1** by DLS method. DLS measurements show mean particle size of 25 nm (Fig. 8) for **1** with narrow size distribution.



**Fig. 8.** Particle size of nanoparticles of  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$  by DLS technique

Fig. 9 shows the heat stability of the nanoparticles of coordination polymer  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$  **1**. The thermal decomposition behavior (TGA/DTA) was investigated in nitrogen atmosphere from from 273 to 873 K at a heating rate of  $10 \text{ K min}^{-1}$ . The nanoparticles of coordination polymer are stable up to 352 K. The first decomposition step has onset from 352 K and end set at 423 K. This involves loss of 18% corresponding to loss of six water molecules. The DTA curve has a sharp endothermic peak at 371 K indicating the loss of six water molecules. The intermediate, having residual weight of 82%, is stable upto 435 K. The second decomposition has onset from 435 K and end set at 473 K. This involves loss of 10% from nanoparticles corresponding to loss of two more water molecules along with a molecule of carbon monoxide. The DTA curve shows a corresponding endothermic peak at 450 K. The residual weight at 473 K is 72%. This intermediate remains stable upto 673 K. The third decomposition has onset at 673 K with steep weight loss occurring up to 723 K followed by gradual weight loss up to 873 K. This involves 43% weight loss corresponding to decomposition of ligand molecule. Two endothermic peaks in DTA curve at 691 K and 785 K appear during decomposition, indicating loss of ligand molecule. The residual weight at 873 K is

28 % (calculated 28.23 %) which corresponds to formation of two molecules of CoO as end product.



**Fig. 9.** TGA-DTA curves of nanoparticles of  $[\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$

#### 4. Conclusion

Nanoparticles of coordination polymer  $\text{Co}_2(\text{pydc})_2(\text{H}_2\text{O})_6]_n \cdot 2n\text{H}_2\text{O}$  were synthesized by sonochemical method. The coordination polymer possesses a 1-D chain like extended structure with binuclear cobalt(II) nodal units. The mean particle size of nanoparticles obtained by XRPD is 27 nm. SEM images show that nanoparticles are composed of polyhedral blocks with definite edges. The nanoparticles are thermally stable up to 352 K.

#### Acknowledgment

We gratefully acknowledge the support of Sophisticated Analytical Instrumentation Facility, Panjab University for XRPD and FTIR study. We also thank Department of Textile, IIT Delhi for electron microscope facility. We also thank DMSRDE Kanpur for thermal study TGA/DTA. Authors are grateful to Dr. Shaikh M. Mobin, Incharge, Sophisticated Instrumentation Centre (SIC), Indian Institute of Technology Indore (IITI), M. P., India for single crystal X-ray diffraction study.

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