

# A New Bulk and Nanostructure Supramolecular Compound $[\text{Co}(\text{dipic})_2\text{Mn}(\text{O}_2)]_n$ , Synthesis and Crystal Structure

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**Abstract:** The nano and bulk structure polymer  $[\text{Co}(\text{dipic})_2\text{Mn}(\text{O}_2)]_n$  (where dipic is pyridine-2,6-dicarboxylic acid), was synthesized by sonochemical method and reflux process respectively. The bulk structure was characterized using single-crystal x-ray diffraction (SC-XRD). The crystal structure of this polymer, which was synthesized using a reflux approach, was found to be a binuclear coordination polymer. In this structure, the cobalt center achieves hexa-coordination by coordinating with two deprotonated dipicolinate groups, acting as tridentate chelating ligands. Manganese center achieves tetra-coordination with four  $\mu$ -carboxylate oxygen from the dipic ligand of  $\text{Co}(\text{dipic})_2$ . The nanostructure of this polymer was characterized using scanning electron microscopy (SEM), x-ray powder diffraction (XRD) and FT-IR spectroscopy and compared with bulk structure polymer.

**Keywords:** Sonochemical method, Nano-sized polymer, Crystal structure, Bulk polymer, Binuclear complex

## Introduction

Nanomaterials have broad applications in a variety of fields because of their unusual and size dependent optical, magnetic, electronic and chemical properties<sup>1,2</sup>. Nanoparticles are characterized by an extremely large surface to volume ratio and their properties are determined mainly by the behavior of their surface<sup>3,4</sup>. The applications of nanoparticles are well known in the fields of cosmetics and pharmaceutical products, coatings, electronics, polishing, semiconductors and catalysis and the design and preparation of novel nanomaterials with tunable physical and chemical properties remains a growing area. There are a range of methods of producing nanosized materials including radiation methods<sup>5</sup>, thermal decomposition<sup>6</sup>, vapor deposition<sup>7</sup>, reduction in micro emulsions<sup>8</sup> and chemical reduction methods<sup>9</sup>. However most of these techniques tend to be expensive and time-consuming. An alternative method, simple and cost effective, is the use of sonochemistry<sup>10</sup>.

Sonochemical synthesis has proven to be a useful technique for generating novel materials with unusual properties and environment-friendly. The sonochemical effects of ultrasound arise from acoustic cavitation, *i.e.*, the formation, growth and implosive collapse of bubble generates localized hot spots through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. In this way, sonochemical synthesis allows the major control of crystalline structure, size and morphology of particles<sup>11-15</sup>. Thus, with (sonochemical synthesis) it was possible to prepare large amounts (>90% yield) of pure anatase phase nanoparticles with the choice of a suitable precursor and appropriated experimental conditions. Additionally, with ultrasonic radiation assisted synthesis the time span involved is only 30-60 min<sup>16</sup>. This method allows the preparation of large amounts of anatase phase in a very short time period and also successive reactions can be performed simultaneously. Sonochemistry is a promising preparation method that may resolve the problems arising from the conventional synthesis methods. Furthermore, this method can save energy and time and thus reduce the cost of final products. The synthesis is rapid and reproducible compared to the conventional methods, mentioned previously<sup>17</sup>.

## Experimental

All synthetic experiments were performed at room temperature. The water was distilled and deionized. Cobalt(II) nitrate hexahydrate, manganese(II) nitrate tetrahydrate, iron(III) nitrate nonahydrate, pyridine-2,6-dicarboxylic acid and sodium hydroxide were obtained and used as received from Aldrich Chemical Co. FT-IR spectra were recorded as KBr pellets on a FT-IR JASCO 460 spectrophotometer. The x-ray data were collected on an STOE-IPDS 2T diffractometer, equipped with a graphite monochromator and thus Mo K $\alpha$  radiation ( $\lambda=0.71073$ ) was used. The morphology of bulk and nanostructure polymer were studied by scanning electron microscopy technique (SEM) using a VEGA\\TESCAN-XMU. Phase analysis of the bulk and nano structure were evaluated by X-ray diffraction (XRD) using Cu-K $\alpha$  radiation between 0°-50°(2 $\theta$ ) with a step size of 0.02°/s recorded on a diffractometer model X Pert MPD. The XRD graph, for single crystal (bulk), was prepared using Mercury software. Ultrasonic generators were carried out on ultrasonic equipment (maximum 300 W at 20 kHz).

### *Synthesis single crystal [Co(dipic)<sub>2</sub>Mn(O)<sub>2</sub>]<sub>n</sub> as bulk structure polymer*

To an aqueous solution, containing an equimolar mixture of metal nitrate, 10 mL of Co(II) nitrate hexahydrate (0.290 g, 1.0 mmol) and manganese(II) nitrate tetrahydrate (0.251 g, 1.0 mmol), in the presence of iron(III) nitrate nonahydrate as catalyst, pyridine -2,6-dicarboxylic acid (0.334 g, 2.00 mmol) was added, and thereafter, an aqueous solution (10 mL) of sodium hydroxide (0.160 g, 4.0 mmol), was also added drop wise with continuous stirring at room temperature for 3 h. Solution filtered off and left to evaporate in beaker in air at room temperature, After 5 days, red crystals of [Co(dipic)<sub>2</sub>Mn(O)<sub>2</sub>]<sub>n</sub> were formed. 57% yield based on metal nitrates.

### *Sonochemical synthesis of [Co(dipic)<sub>2</sub>Mn(O)<sub>2</sub>]<sub>n</sub> as nanostructure polymer*

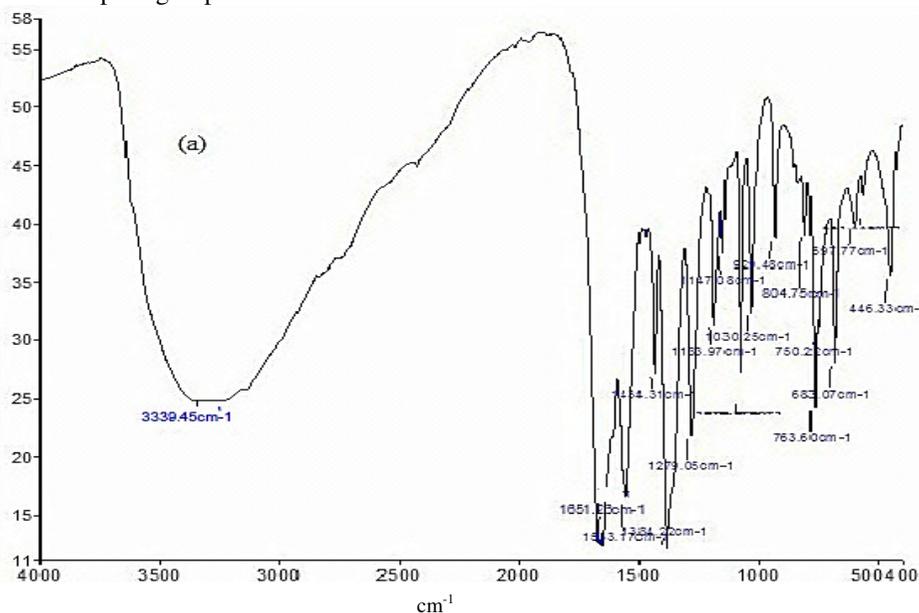
To prepare the nanostructure of [Co(dipic)<sub>2</sub>Mn(O)<sub>2</sub>]<sub>n</sub> by sonochemical process, 10 mL aqueous solution of cobalt(II) nitrate hexa-hydrate (0.1 M) and manganese(II) nitrate tetrahydrate (0.1 M) in the presence of iron(III) nitrate nonahydrate, under the ultrasonic irradiation, (10 mL) aqueous solution of pyridine-2,6-dicarboxylic acid (0.2 M) and (10 mL) of sodium hydroxide (0.4 M) was added in drop wise manner under high-density ultrasonic probe, operating at 20 kHz with a maximum power output of 300 W for 1 hour. The obtained precipitates were filtered off and then dried in air.

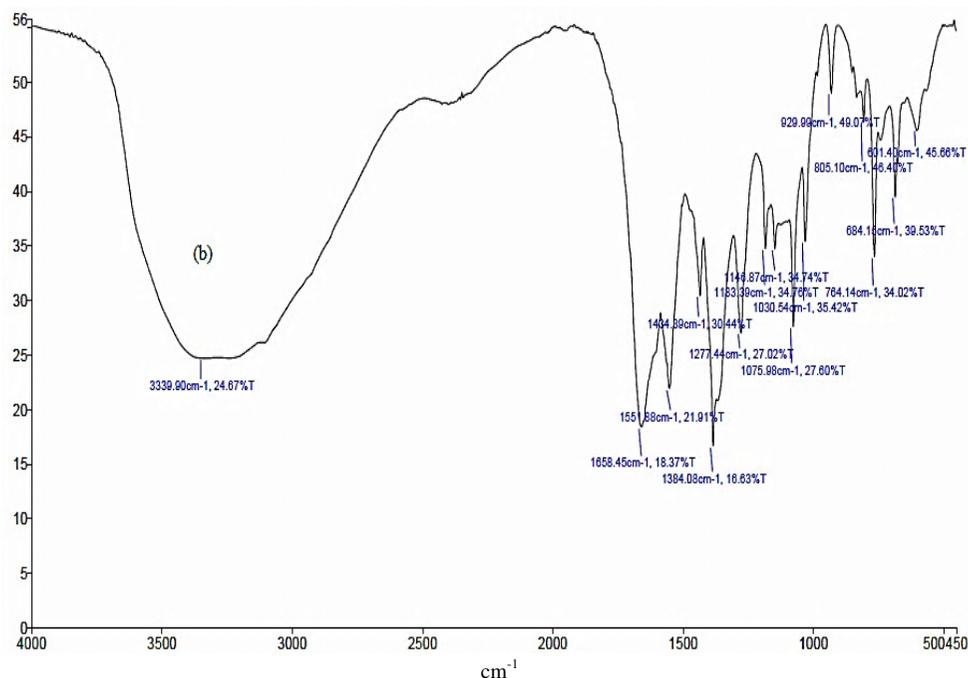
## Results and Discussion

The reaction of pyridine-2,6-dicarboxylic acid as ligand and aqueous solution of NaOH with cobalt(II) nitrate hexahydrate and manganese(II) nitrate tetrahydrate results in the formation of  $[\text{Co}(\text{dipic})_2\text{Mn}(\text{O})_2]_n$ . In this study role Fe is catalyst and association for nuclear Co and Mn for preparation polymer structure. The nano-sized of polymer, was synthesized using the ultrasonic method at an ambient temperature and atmospheric pressure. The single crystals (bulk) of this polymer that suitable for x-ray crystallography, were synthesized by reflux approach. The Structure of bulk and nano-sized polymer,  $[\text{Co}(\text{dipic})_2\text{Mn}(\text{O})_2]_n$ , compared by FT-IR, x-ray diffraction (XRD) graph, scanning electron microscopy technique (SEM).

The FT-IR spectrum of the bulk polymer  $[\text{Co}(\text{dipic})_2\text{Mn}(\text{O})_2]_n$  (Figure 1a), shows broad absorption bands at  $3339\text{ cm}^{-1}$  assigned to the asymmetric and symmetric  $\nu(\text{H}_2\text{O})$  stretching vibration of the coordinated and lattice water molecules. The stretching vibrations asymmetric  $\nu_{\text{as}}(\text{COO})$  and symmetric  $\nu_{\text{s}}(\text{COO})$  of the dipicolinate carboxylate groups were observed at  $1660, 1553\text{ cm}^{-1}$  for  $\nu_{\text{as}}(\text{COO})$  and  $1434, 1384$  and  $1279\text{ cm}^{-1}$ , for  $\nu_{\text{s}}(\text{COO})$ , respectively. This polymer as nanostructure shows broad absorption bands at  $3339\text{ cm}^{-1}$ , for symmetric and asymmetric stretching vibration of coordinated and lattice water  $\nu(\text{H}_2\text{O})$  and  $1658, 1551\text{ cm}^{-1}$  for asymmetric stretching vibrations of  $\nu_{\text{as}}(\text{COO})$  and  $1434, 1384$  and  $1277\text{ cm}^{-1}$  for  $\nu_{\text{s}}(\text{COO})$  respectively (Figure 1b).

The crystallography data collections and structure refinement are listed in Table 1. Bond lengths, bond angles are listed in Table 2. Figure 2 shows the ORTEP diagram for unit part of  $[\text{Co}(\text{dipic})_2\text{Mn}(\text{O})_2]_n$ . The x-ray single crystal, showed that in the structure of complex  $[\text{Co}(\text{dipic})_2\text{Mn}(\text{O})_2]_n$ , the  $\text{Mn}^{\text{II}}$  center, achieves tetra-coordination by coordinating with four  $\mu$ -carboxylate oxygen O of dipicolinate ligand from  $[\text{Co}(\text{dipic})_2]^{2-}$ . The cobalt ion in  $[\text{Co}(\text{dipic})_2]^{2-}$  achieves six-coordination by coordinating with two deprotonated dipicolinate groups, acting as tridentate chelating ligands. The title polymer, crystallized in the monoclinic space group Cc.





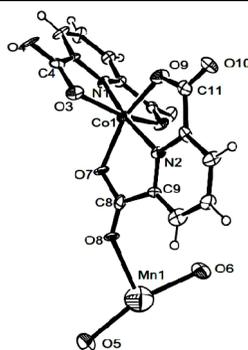
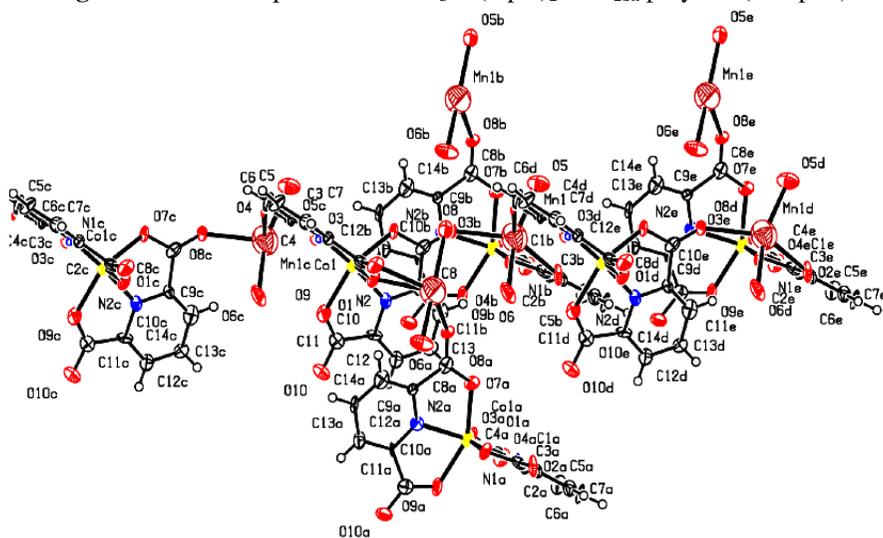
**Figure 1.** FT-IR spectra of  $[\text{Co}(\text{dipic})_2\text{Mn}(\text{O})_2]_n$  as (a) bulk, (b) nano-structured produced by sonochemical method.

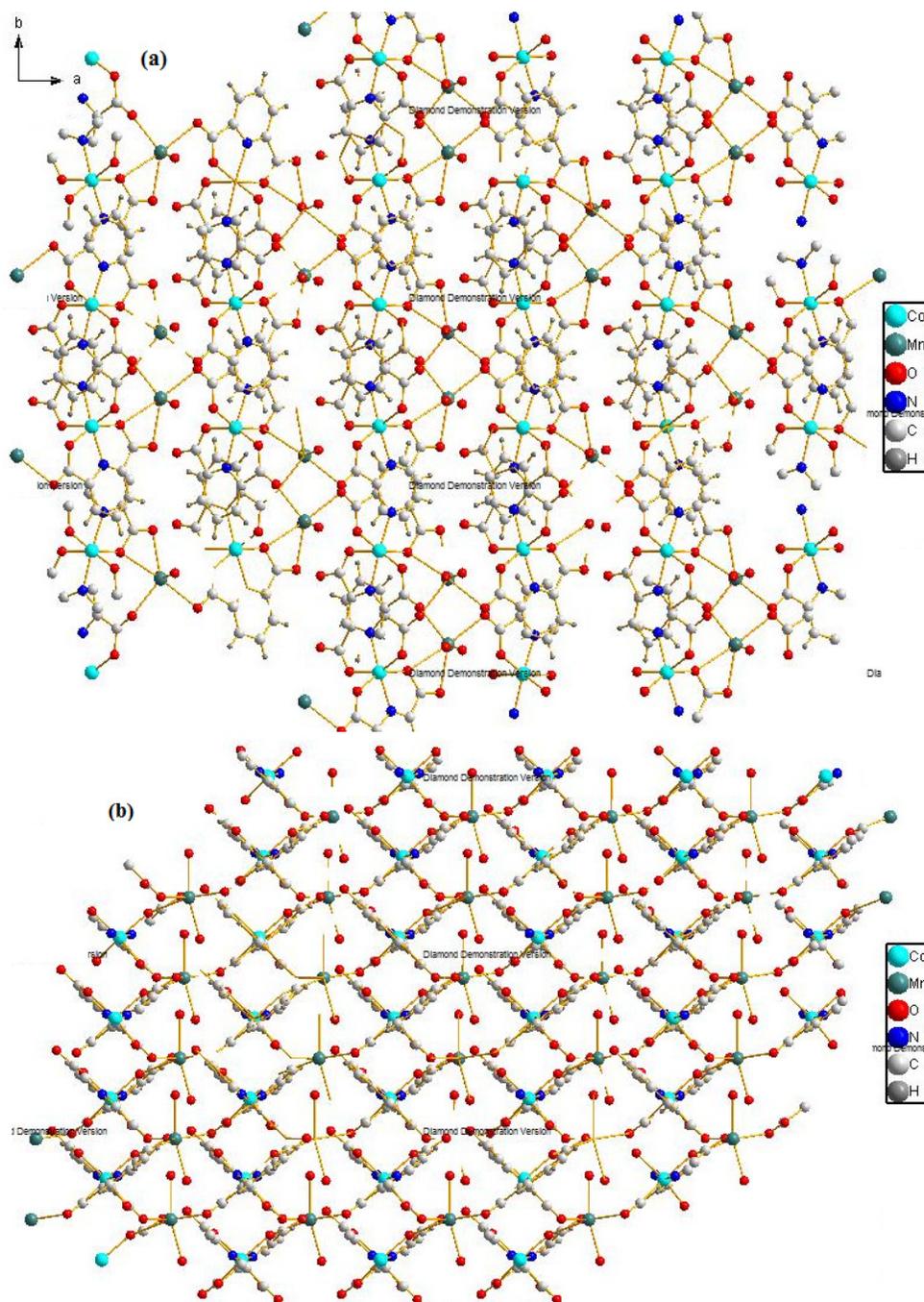
**Table 1.** Crystallographic data and data-collection parameters for  $[\text{Co}(\text{dipic})_2\text{Mn}(\text{O})_2]_n$

Formula	$\text{C}_{14}\text{H}_6\text{CoN}_2\text{MnO}_{10}$
Formula weight	476.08
Temperature (K)	293
Wavelength ( $\text{\AA}$ )	0.71073
Crystal system	Monoclinic
Space group	Cc
$a$ ( $\text{\AA}$ )	14.948(3)
$b$ ( $\text{\AA}$ )	12.460(3)
$c$ ( $\text{\AA}$ )	8.6697(17)
$\alpha$ ( $^\circ$ )	90
$\beta$ ( $^\circ$ )	93.18(3)
$\lambda$ ( $^\circ$ )	90
$V$ ( $\text{\AA}^3$ )	1612.26(60)
$Z$	4
$\rho_{\text{calc}}$ ( $\text{g}/\text{m}^3$ )	1.957
$\mu$ (Mo $K\alpha$ ) ( $\text{mm}^{-1}$ )	2.011
$F(000)$	944
Theta range for data collection	2.7, 25.0
R(int)	0000
R1, wR2	0.1157, 0.3086

**Table 2.** Selected bond lengths (Å) and angles (°) for  $[\text{Co}(\text{dipic})_2\text{Mn}(\text{O})_2]_n$ 

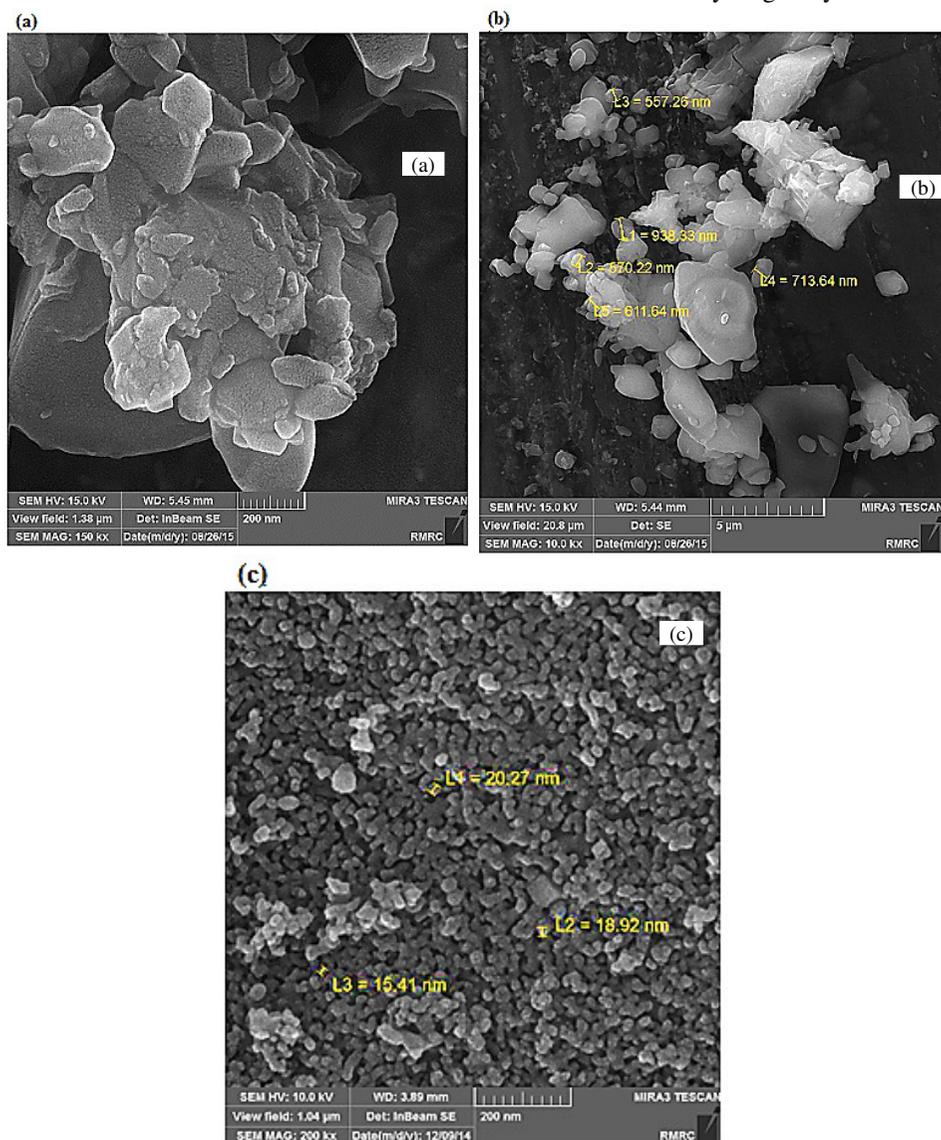
Bond lengths		Bond lengths	
Co(1)–O(1)	2.035(16)	Co(1)–O(3)	2.016(13)
Co(1)–O(7)	2.014(13)	Co(1)–O(9)	2.040(17)
Co(1)–N(1)	2.051(12)	Co(1)–N(2)	2.078(15)
Mn(1)–O(5)	2.338(18)	Mn(1)–O(6)	2.366(18)
Mn(1)–O(2)_b	2.486(15)	Mn(1)–O(4)_d	2.454(15)
Bond angles		Bond angles	
O(1)–Co(1)–O(9)	95.6(6)	O(1)–Co(1)–N(1)	75.7(5)
O(1)–Co(1)–N(2)	93.4(5)	O(3)–Co(1)–O(7)	95.4(5)
O(5)–Mn(1)–O(8)	105.6(6)	O(40_d)–Mn(1)–O(5)	81.4(6)
O(2)_b–Mn(1)–O(5)	86.5(6)	O(40_d)–Mn(1)–O(5)	89.3(6)
O6–Mn1–O(8)	91.6(6)	O(1)_b–Mn(1)–O(6)	106.7(6)
O(2)_b–Mn(1)–O(6)	86.3(6)	O(4)_d–Mn(1)–O(6)	84.5(6)
O(1)_b–Mn(1)–O(8)	84.1(5)	O(2)_b–Mn(1)–O(8)	131.9(6)
O(4)_d–Mn(1)–O(8)	90.7(5)	O(1)_b–Mn(1)–O(2)_	51.2(4)

**Figure 2.** ORTEP representation of  $[\text{Co}(\text{dipic})_2\text{MnO}_2]_n$  polymer (unit part)**Figure 3.** A fragment of the environment of  $[\text{Co}(\text{dipic})_2\text{MnO}_2]_n$

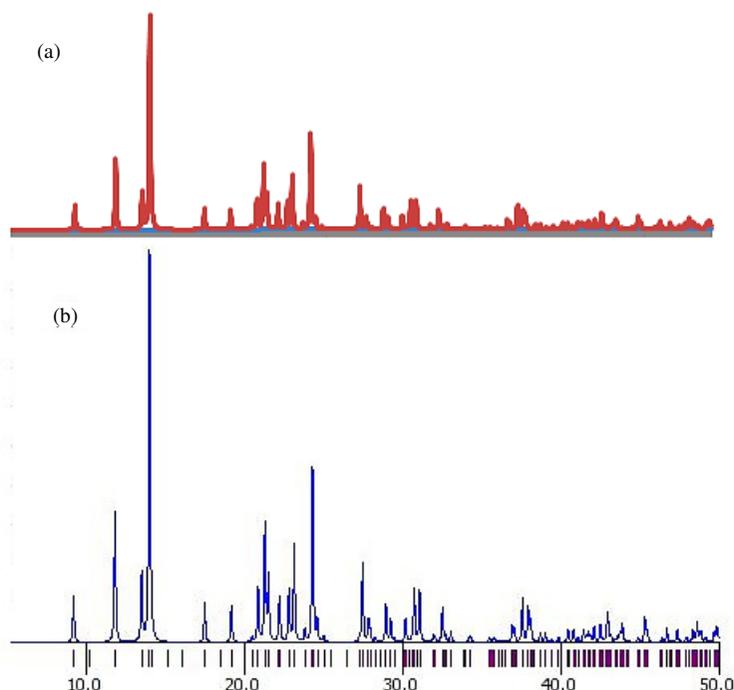


**Figure 4.** The packing of polymer, viewed approximately along (a) *c* and (b) *b* axes. The morphology of polymer synthesized by the sonochemical method and single crystal synthesized by reflux approach was characterized by scanning electron microscopy (SEM).

Figure 5 (a, b) shows the SEM of the bulk polymer prepared by simple mixing of precursors. Figure 5c shows the SEM illustration of the nano-sized polymer prepared by ultrasonic irradiation. These images show, the particles size of bulk is bigger than the sample prepared by a sonochemical method with same concentration of initial reagents. Figure 6a shows the XRD graph of the typical sample of this polymer prepared by sonochemical process, Figure 6b shows the XRD graph from single crystal (bulk) of  $[\text{Co}(\text{dipic})_2\text{Mn}(\text{O})_2]_n$ , prepared using Mercury software. Figures indicate that the structure obtained by the sonochemical irradiation as nano-structures is identical to bulk structure obtained by single crystal.



**Figure 5.** SEM images of  $[\text{Co}(\text{dipic})_2\text{Mn}(\text{O})_2]_n$ : (a, b) of bulk powder prepared via simple mixing of precursors, (c) nano-sized polymer prepared by ultrasonic irradiation



**Figure. 6.** XRD pattern: (a) nano-structure of  $[\text{Co}(\text{dipic})_2\text{Mn}(\text{O})_2]_n$  prepared by sonochemical process, (b) simulated pattern based on single-crystal of polymer

## Conclusion

A new nano-size polymer of  $[\text{Co}(\text{dipic})_2\text{Mn}(\text{O})_2]_n$ , was synthesized using sonochemical irradiation and its crystalline structure (bulk) was synthesized using simple mixing of precursors. This structure was compared by FT-IR spectroscopy, x-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The crystalline structure of bulk structure was characterized using single-crystal x-ray diffraction. The crystalline structure of this compound was found to be a hetero binuclear coordination compound and shows that the coordination number for Mn(II) center is four and for Co(II) center is six.

## Supplementary material

Crystallographic data for the structure reported in the paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1443931. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

## Acknowledgement

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