

Contents list available at **IJND**
International Journal of Nano Dimension

Journal homepage: www.IJND.ir

**Sonochemical synthesis and characterization of a nano-sized
Manganese (II) coordination polymer,
[$\{Mn(NCS)_2(4,4' \text{-bipy})(H_2O)_2\}(4,4' \text{-bipy})\}_n$; with
4,4'-Bipyridine (4,4'-bipy) ligand**

ABSTRACT

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Received 17 April 2013

Received in revised form

14 July 2013

Accepted 13 August 2013

A novel nano – sized manganese (II) coordination polymer, [$\{Mn(NCS)_2(L)(H_2O)_2\}(L)_n$], (1) ($L = 4,4'$ -Bipyridine), have been synthesized by a sonochemical process and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), IR spectroscopy and elemental analysis. Direct calcination of the single crystals and nano-sized compound 1 at 400 °C under air atmosphere yields mixture of $K_2Mn_2(SO_4)_3$, MnOS and Mn_3O_4 nanoparticles. Results show that the size and morphology of the $K_2Mn_2(SO_4)_3$, MnOS, Mn_3O_4 nanoparticles depend on the particles size of compound 1. Decrease in the particles size of compound 1 leads to decrease in the particles size of the $K_2Mn_2(SO_4)_3$, MnOS and Mn_3O_4 .

Keywords: Nano-particle; Sonochemical; Coordination polymer; Manganese; Calcination.

INTRODUCTION

Coordination polymers are one of important topic of modern solid state chemistry. Efforts about coordination polymers have been done since last decades to simultaneously exploit the influence exerted by the transition metal ions as well as the organic spacers [1-4]. In general, the type and topology of the product generated from the self-assembly of inorganic metal nodes and organic spacers depend on the functionality of the ligand [5-6] and valences and the geometric needs of the metal ions used. Many attempts have been made to prepare variety of transition metal complexes using different spacers and their structures and properties have been determined [6-9]. Chemists and materials scientists studied metal coordination supramolecular compounds widely, as they exhibit a range of potentially useful applications in molecular adsorption, catalysis, magnetism; luminescence, nonlinear optics, and molecular sensing that are not found in mononuclear compounds [10-12].

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The size and shape of solid materials influence on the chemical and physical properties. This is especially true for materials with morphological features smaller than a micron in at least one dimension, which is commonly called nano-scale materials, or simply nano-materials. By decreasing the size of coordination supramolecular compounds as polymers in nano-size, surface area will increase, therefore, chemical and physical properties of them will change [12-15]. Nano-sized particles of coordination supramolecular materials are fascinating to explore, because they are interesting candidates for applications in gas storage, adsorption and separation science, catalysis, molecular sensing, photonics and magnetic materials. In this study we described a simple method of sonochemical preparation of a nano manganese(II) coordination polymer, $[\{Mn(NCS)_2(L)(H_2O)_2\}(L)]_n$, (1) ($L^- = 4,4'$ -Bipyridine), and the use of this new compound to prepare $K_2Mn_2(SO_4)_3$, MnOS, Mn_3O_4 nanoparticles. Sonochemistry is a new method which molecules react due to powerful ultrasound radiation. These extreme conditions can promote the formation of nano-sized structures, mostly by the instantaneous formation of a plethora of crystallization nuclei [16]. This has been widely used to produce nano-sized structures of a variety of compounds [17]. In recent years many kinds of nano-sized materials have been prepared by this method [18-24].

EXPERIMENTAL

Materials and characterization

All reagents and solvents for the synthesis and analysis were commercially available and used as received. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer of Philips Company with monochromated $MnK\alpha$ radiation. The samples were characterized with a scanning electron microscope (SEM) (Philips XL 30) with gold coating.

Synthesis of $[\{Mn(NCS)_2(4,4'$ -bipy)(H_2O) $_2\}(4,4'$ -bipy)] $_n$

$MnSO_4 \cdot H_2O$ (84.5 mg, 0.5 mmol) and KSCN (97 mg, 1 mmol) were dissolved in 7 mL of H_2O . A 5 ml CH_3OH solution of 4, 4'-bipy (78 mg,

0.5 mmol) was added to the former mixture. After one day, yellow crystals were obtained (30 mg). IR (KBr, cm^{-1}): ν 2000 (NCS). Anal. Found: C, 51.77; H, 3.92; N, 16.84. Calc. for $C_{22}H_{20}N_6MnS_2O_2$: C, 50.87; H, 3.85; N, 16.18%. Crystal data: $a=9.14(1)$, $b=10.272(8)$, $c=7.509(2)$ Å, $\alpha=103.72(4)$, $\beta=95.83(8)$, $\gamma=107.94(8)^\circ$.

Synthesis of nano-sized $[\{Mn(NCS)_2(L)(H_2O)_2\}(L)]_n$, (1) ($L^- = 4,4'$ -Bipyridine), (1) by sonochemical method

To prepare the nanostructure of compound 1 by sonochemical process, we used an ultrasonic bath and the power of 0.138 KW for 1 hour. Ligand (1mmol, 0.169g) and $MnSO_4 \cdot H_2O$ (1mmol, 0.156g) were solved dispersedly in 10 mL water and solution of manganese salt was added to the ligand solution in ultrasonic bath. After 10 min, to the prepared $MnSO_4 \cdot H_2O$ solution and ligand solution, 1 mmol KSCN dissolved in 10 ml of distilled water was added in drop wise manner under the ultrasonic irradiation. The obtained precipitates were filtered, subsequently washed with double distilled water and then dried. IR (KBr, cm^{-1}): \square 2100 (NCS). Anal. Found: C, 51.73; H, 3.9; N, 16.9. Calc. for $C_{22}H_{20}N_6MnS_2O_2$: C, 50.9; H, 3.8; N, 16.18%. Crystal data: $a=9.14(1)$, $b=10.272(8)$, $c=7.509(2)$ Å, $\alpha=103.72(4)$, $\beta=95.83(8)$, $\gamma=107.94(8)^\circ$.

Synthesis of $K_2Mn_2(SO_4)_3$, MnOS, Mn_3O_4 nanoparticle

The precursor $[\{Mn(NCS)_2(4,4'$ -bipy)(H_2O) $_2\}(4,4'$ -bipy)] $_n$ (0.1 mmol) was dissolved immediately in 10 mL water and formed light yellow solution. This solution was put into oven and then heated less than 400°C for 3 h. At the end of the reaction, a black precipitate was formed. A small amount of toluene and a large excess of EtOH were added to the reaction solution and $K_2Mn_2(SO_4)_3$, MnOS, Mn_3O_4 nanoparticles were separated by centrifugation. The solids were washed with EtOH and dried under air atmosphere. After the reaction, calcined mixture was identified by using ++XRD spectrum and scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

$MnSO_4 \cdot H_2O$ and 4,4' bipy and KSCN lead to the formation of a new manganese(II) coordination polymer $[\{Mn(NCS)_2(4,4'$ -

bipy)(H₂O)₂}(4,4'-bipy)]_n. Nano-sized compound 1 was obtained by ultrasonic irradiation in water. Figure 1 shows the simulated XRD pattern from single crystal of compound 1 (Figure 1a) in comparison with the XRD pattern of a typical sample of compound 1 prepared by the sonochemical process (Figure 1b). Matching Figure 1a and Figure 1b, indicated that the compound obtained by the sonochemical process is identical to that obtained by single crystal diffraction. The significant broadening of the peaks indicates that the particles are in nanometer dimension.

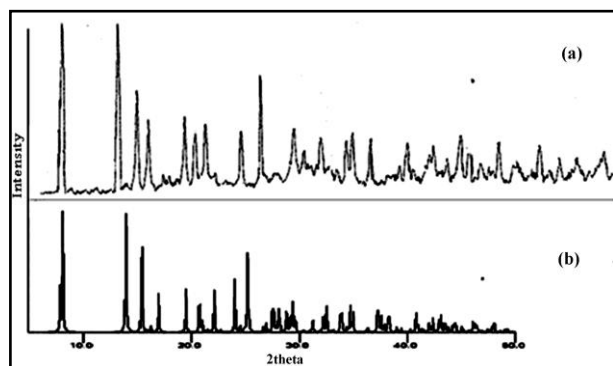


Fig. 1. XRD patterns: (a) simulated pattern based on single crystal data of compound 1, (b) Nano-particles of compound 1 prepared by sonochemical process.

The morphology and size of compound 1 prepared by the sonochemical method, was characterized by scanning electron microscopy (SEM). Measurement software shows that size of particles is about 55 nm (Figure 2).

The SEM image also shows the formation of mixture K₂Mn₂(SO₄)₃, MnOS and Mn₃O₄ nanoparticles (Figure 3). These experiments indicate that the nano-sized precursor produces smaller particles of mixture of K₂Mn₂(SO₄)₃, MnOS and Mn₃O₄. Figure 4 provides the XRD pattern of the residue obtained from calcination of compound 1. The obtained pattern matches with the standard pattern of K₂Mn₂(SO₄)₃ (JCPDS card number 20-0909) and MnSO (JCPDS card number 22-0439) and Mn₃O₄ (JCPDS card number 24-0734). As the calcination process was successful for the preparation of K₂Mn₂(SO₄)₃, MnOS and Mn₃O₄ nanoparticles, we used the nano-sized compound 1 prepared by the sonochemical process at a concentration of 1mM and 305W power of ultrasonic irradiation for the preparation mixture of K₂Mn₂(SO₄)₃, MnOS, Mn₃O₄ nanoparticles. The

XRD pattern shows that the residue is mixture of K₂Mn₂(SO₄)₃, MnOS and Mn₃O₄.

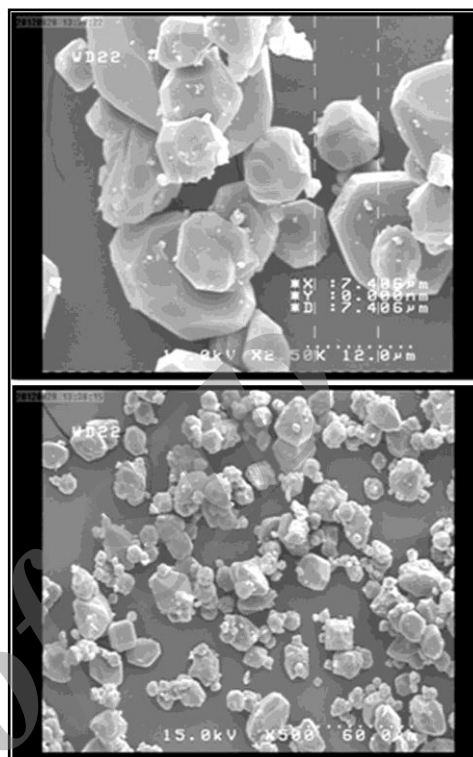


Fig. 2. SEM photographs of compound 1 nanoparticles produced by sonochemical method by 1mmol concentration of initial reagents

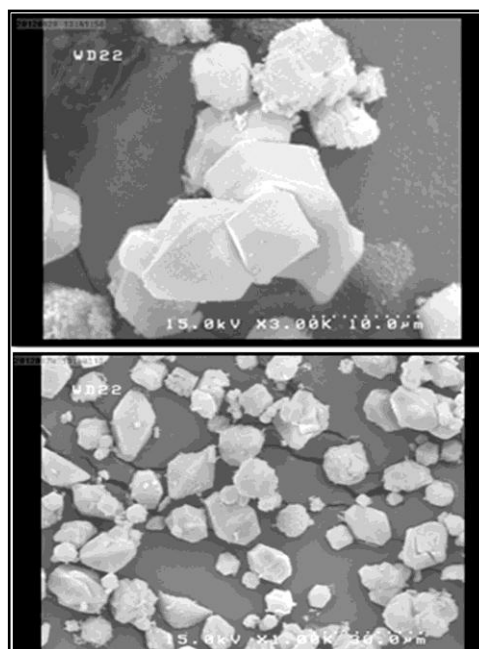


Fig.3: SEM photographs of K₂Mn₂(SO₄)₃, MnOS and Mn₃O₄ nanoparticles produced by calcination of precursor 1 at 180 °C

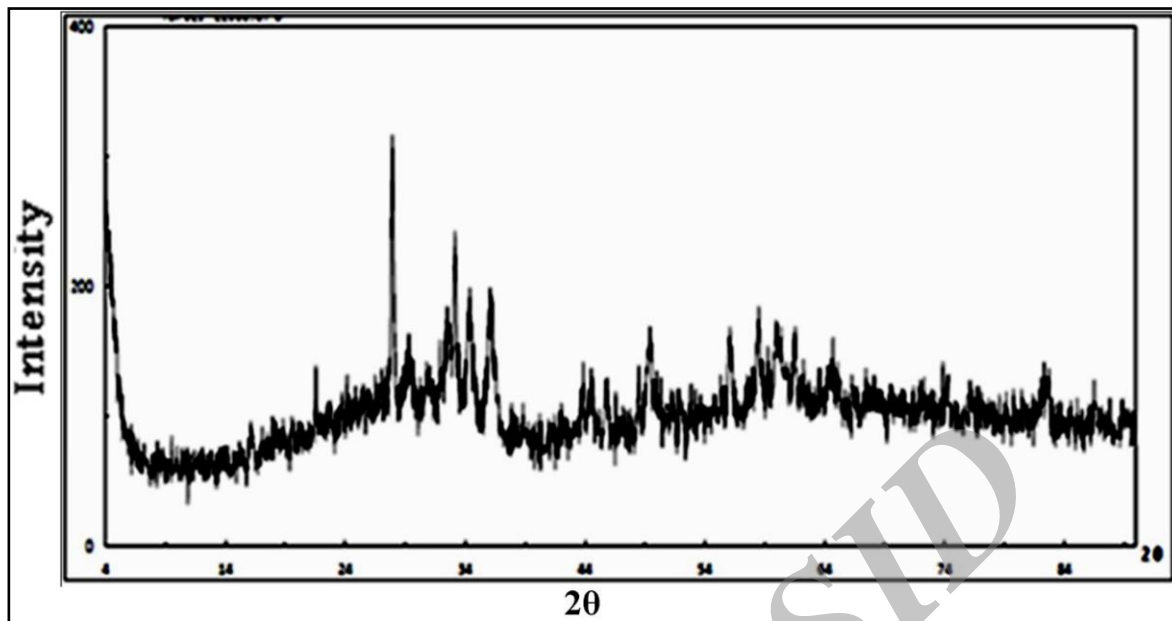


Fig. 4. XRD pattern of mixture $K_2Mn_2(SO_4)_3$, MnOS and Mn_3O_4 nanostructure prepared by calcination of compound 1.

CONCLUSIONS

A nano-sized Mn(II) coordination polymer, $[Mn(NCS)_2(L)(H_2O)_2(L)]_n$, (1) ($L^- = 4,4'$ -Bipyridine), was synthesized by sonochemical irradiation and compared with its crystalline structure. Compound 1 was characterized by X-ray powder diffraction (XRD). To prepare the nanostructure of compound 1, 1mmol of initial reagents, 0.1 M, were tested. Appropriate nano-sized particles of compound 1 were obtained at a concentration of 0.01 M. Particles size and morphology of the nanoparticle depend on the power of ultrasound irradiation used. Results show when the particles size decreases, the power of ultrasound irradiation increases. Calcinations of compound 1 produced mixture of $K_2Mn_2(SO_4)_3$, MnOS, Mn_3O_4 nanoparticles. Particles size and morphology of the mixture of $K_2Mn_2(SO_4)_3$, MnOS, Mn_3O_4 nanoparticles depend on the initial particles size of compound 1.

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Cite this article as: N. Mosallanejad: Sonochemical Synthesis and Characterization of a nano-sized manganese (II) coordination polymer, $[\{Mn(NCS)_2(4,4' -bipy)(H_2O)_2\}(4,4' -bipy)]_n$; with 4,4'-Bipyridine (4,4'-bipy) ligand.
Int. J. Nano Dimens. 5(3): 285-289, Summer 2014