

Sonochemical Synthesis of two New Nano-structured Lead(II) and Mercury(II) Coordination Polymers

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Abstract

Two new nano-sized lead(II) and mercury(II) coordination polymers, [Pb(2-bpdh)(NO₃)₂(H₂O)]_n(**1**); (2-bpdh = 2,5-bis(2-pyridyl)-3,4-diaza-2,4-hexadiene)} and [Hg(4-bpdb)(SCN)₂]_n (**2**); (4-bpdb= 1,4-bis(4-pyridyl)-3,4-diaza-1,3-butadiene) were synthesized by a sonochemical method. The structure of **1** may be considered coordination polymer of lead(II) and Single crystal X-ray analysis of compound **2** reveals that consists of one-dimensional zigzag chains formed by bridging SCN⁻ and 4-bpdb ligand. The new nano-structures of coordination polymers were characterized by scanning electron microscopy, powder X-ray diffraction, elemental analyses and IR spectroscopy. The size of the samples was about 70 nm and 60 nm for compound **1** and **2**, respectively.

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1. Introduction

Mercury and Lead is well known as a highly toxic element that accumulates in the environment and enters the food chain of a variety of animals [1].

The biochemical processes involved in transportation and storage of mercury include interactions with proteins like metallothioneins [2]. The coordination chemistry of mercury(II) and lead(II) with sulfur-donor and N-donor ligands is,

therefore, a topic of our current research. The fact that these two ions interact with many molecules through coordination with deprotonated thiol, imidazole, disulfide, thioether, amino, pyridyl or carboxylate groups are well known and a great deal of effort has been devoted to the characterization of these interactions in model molecules and in proteins [3]. In the field of coordination polymers efforts have been made during the last decades to simultaneously exploit the influence exerted by both the transition metal ions as well as the organic spacers [4-8]. 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 [9,10] and valences and the geometric needs of the metal ions used. In this paper we describe a simple synthetic sonochemical preparation of a nano lead(II) and mercury(II) coordination polymers, $[\text{Pb}(2\text{-bpdh})(\text{NO}_3)_2]_n$ (**1**), (2-bpdh = 2,5-bis(2-pyridyl)-3,4-diaza-2,4-hexadiene) and $[\text{Hg}(4\text{-bpdh})(\text{SCN})_2]_n$ (**2**); (4-bpdh = 1,4-bis(4-pyridyl)-3,4-diaza-1,3-butadiene). The use of new compound **1** to prepare PbO nanoparticles was studied too. In recent years many kinds of nanomaterials have been prepared by sonochemical method [11-13]. There are different methods such as microwave-solvothermal synthesis [14], hydrothermal route [15] and surfactant-ligand co-assisting solvothermal method [16] used to synthesize nano- and micro-crystalline PbO.

2 Experimental

2.1 Materials and characterization

With the exception of the ligand 2,5-bis(2-pyridyl)-3,4-diaza-2,4-hexadiene (2-bpdh) and 1,4-bis(4-pyridyl)-3,4-diaza-1,3-butadiene (4-bpdh) which were prepared according to the literature procedures [17,18], 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 $\text{CuK}\alpha$ radiation. The samples were characterized with a scanning electron microscope (SEM) (Philips XL 30) with gold coating. IR spectra were recorded on a SHIMADZU-IR460 spectrometer in a KBr matrix.

2.2. Synthesis of $[\text{Pb}(2\text{-bpdh})(\text{NO}_3)_2(\text{H}_2\text{O})]_n$ (**1**)

Compound **1** was prepared using the following method: 2-bpdh (1 mmol, 0.238 g), lead(II) nitrate (0.331 g, 1 mmol) were placed in the main arm of a branched tube. Methanol was carefully added to fill both arms. The tube was sealed and the ligand-containing arm immersed in an oil bath at 60°C while the other arm was kept at ambient temperature. After 5 days light orange crystals obtained and then filtered off and air dried, m.p. = 235°C . IR (selected bands; in cm^{-1}): 570 (w), 822(m), 1000(w), 1057(w), 1300 (s), 1600(m) and 3400 (m).

2.3. Synthesis of nano-sized $[\text{Pb}(2\text{-bpdh})(\text{NO}_3)_2(\text{H}_2\text{O})]_n$ (**1**) by sonochemical method

To prepare the nanostructure of compound **1** by sonochemical process, we used an ultrasonic bath was used with 0.05M concentration of metal and ligand solution and the power of 0.138 KW for 1 hour. To the prepared $\text{Pb}(\text{NO}_3)_2$ solution (20 ml), a proper volume of ligand (2-bpdh) solution in (methanol: water with 1:1 molar ratio) (20 ml) was added in drop wise manner under the ultrasonic irradiation. The obtained precipitates were filtered, subsequently washed with double distilled water and then dried. m.p. = 230°C . IR (selected bands; in cm^{-1}): 570 (w), 820(m),

1001(w), 1058(w), 1321 (s), 1601(m) and 3415 (m).

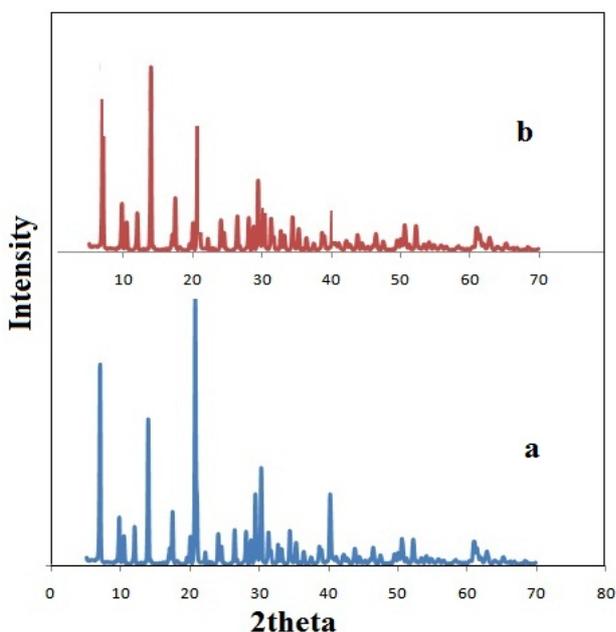


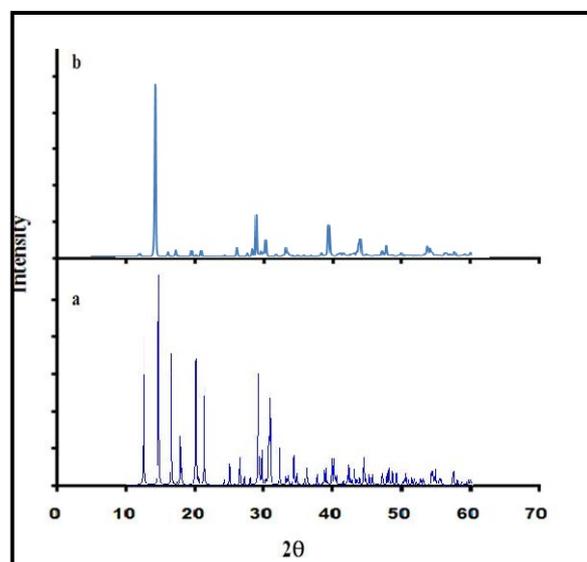
Fig. 1. The XRD patterns of (a) compound (1) prepared by thermal gradient method and (b) nano-sized compound (1) prepared by sonochemical method.

2.4. Synthesis of $[\text{Hg}(4\text{-bpdh})(\text{SCN})_2]_n(2)$

Compound 2 was prepared using the following method: 4-bpdh (1 mmol, 0.210 g), mercury(II) nitrate (0.324 g, 1mmol) and mercury(II) thiocyanate (0.336 g, 1 mmol) were placed in the main arm of a branched tube. Methanol was carefully added to fill both arms. The tube was sealed and the ligand-containing arm immersed in an oil bath at 60°C while the other arm was kept at ambient temperature. After 3 days light orange crystals obtained and then filtered off and air dried. IR (selected bands; in cm^{-1}): 516 (w), 815(m), 987(w), 1062(w), 1415 (m), 1603(s), 2110 (s) and 3437 (w).

2.5. Synthesis of nano-sized $[\text{Hg}(4\text{-bpdh})(\text{SCN})_2]_n(2)$ by sonochemical method

To prepare the nanostructure of compound 2 by sonochemical process, we used an ultrasonic bath was used with 0.025M concentration of metal and ligand solution and the power of 0.138 KW for 1 hour. To the prepared $\text{Hg}(\text{NO}_3)_2$ solution (20 ml), a proper volume of ligand (2-bpdh) and mercury(II) thiocyanate solution in methanol (20 ml) 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 (selected bands; in cm^{-1}): 517 (w), 820(m), 985(w), 1058(w), 1415 (m), 1602(s), 2113 (s) and 3439 (w).

Fig. 2. The XRD patterns of (a) compound (2) prepared by thermal gradient method and (b) nano-sized compound (2) prepared by sonochemical method.

3. Results and discussion

2,5-bis(2-pyridyl)-3,4-diaza-2,4-hexadiene (2-bpdh) and lead(II) nitrate leads to the formation of a new lead(II) coordination polymer $[\text{Pb}(2-$

bpdh)(NO₃)₂(H₂O)]_n(**1**). Nano-sized compound **1** were obtained by ultrasonic irradiation in a water: methanol (with 1:1 molar ratio) solution and single crystalline material was obtained using a thermal gradient method (branched tube). The IR absorption bands with a variable intensity in the frequency range 1205-1585 cm⁻¹ correspond to vibrations of the pyridine rings. ν(NO₃) vibrations are found at 1360-1370 cm⁻¹ and broad peak at 3400cm⁻¹ shows the presence of H₂O molecules. IR spectra of the nanostructure of compound **1** show more similarity with the IR spectra of single crystalline material. 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). Acceptable match indicates that the compound obtained by the sonochemical process is identical to that obtained by single crystal diffraction.

Calculations with Sherrer formula shows the average size of the particles is 70 nm, which is in agreement with that observed by scanning electron microscopy, as shown in Fig. 3.

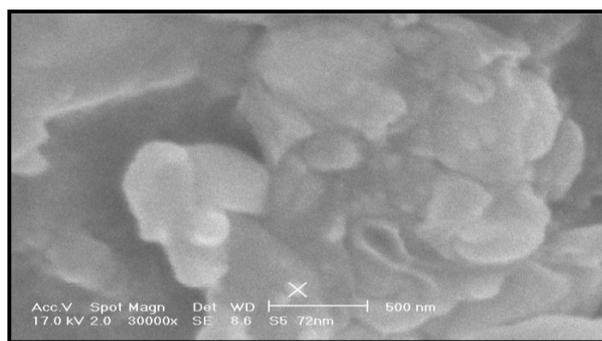


Fig. 3. SEM photographs of compound **1** nanoparticles produced by sonochemical method by 0.05 M concentration of initial reagents.

To examine the thermal stability of the compound (**1**), thermal gravimetric (TG) and

differential thermal analyses (DTA) were carried out between 20 and 700 °C under argon flow (Figure 4). Compound **1** is stable up to 200 °C, at which decomposition starts. Mass loss calculations show that the correct final decomposition product can be PbO. The DTA curve displays two distinct endothermic peaks at 90 and 270 °C as well as two exothermic peaks at 300 and 470 °C (Figure 4).

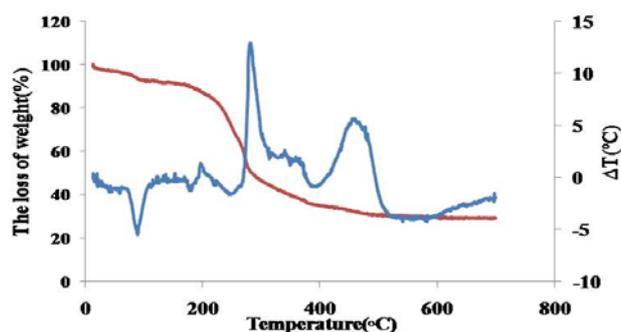


Fig. 4. TGA and DTA diagrams of [Pb(2-bpdh)(NO₃)₂(H₂O)]_n(**1**)

1,4-bis(4-pyridyl)-3,4-diaza-1,3-butadiene (4-bpdb), mercury(II) nitrate and mercury(II) thiocyanate leads to the formation of a new mercury(II) coordination polymer [Hg(4-bpdb)(SCN)₂]_n(**2**). Single crystal X-ray analysis reveals that compound **2** (Figure 5) consists of one-dimensional zigzag chains and the coordination environment of the Hg atoms is a distorted tetrahedron [19]. The nitrogen atoms of N-donor bifunctional ligands are linked to two different mercury atoms and the thiocyanate atoms are coordinated to mercury via S atoms but are not bridged to two mercury atoms. Consequently, structures **2** can be seen as grown from 1D structures to hybrid two-dimensional networks by the weak C-H...N H-bonding interactions, as shown in Fig. 5.

Nano-sized compound **2** were obtained by ultrasonic irradiation in methanol solution and single

crystalline material was obtained using a thermal gradient method (branched tube).

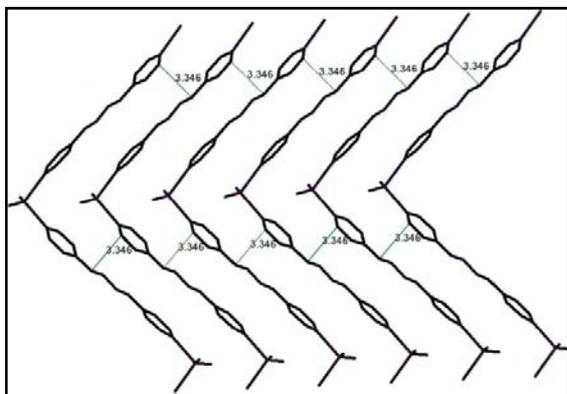


Fig. 5. Depiction of the weak stacking interaction in compound 2.

IR spectra of the nanostructure of compound 2 show more similarity with the IR spectra of single crystalline material. Figure 2 shows the simulated XRD pattern from single crystal of compound 2 (Figure 2a) in comparison with the XRD pattern of a typical sample of compound 2 prepared by the sonochemical process (Figure 2b). Acceptable match indicates that the compound obtained by the sonochemical process is identical to that obtained by single crystal diffraction. Calculations with Sherrer formula shows the average size of the particles is 60 nm, which is in agreement with that observed by scanning electron microscopy, as shown in Fig. 6.

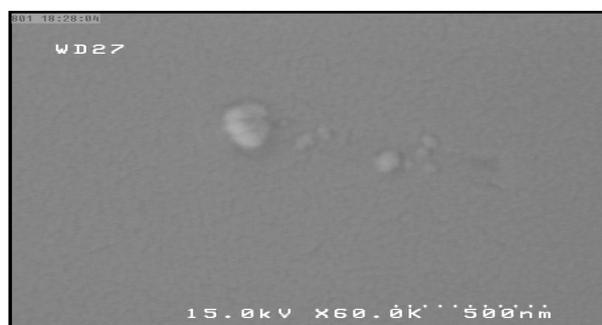


Fig. 6. SEM photographs of compound 2 nanoparticles produced by sonochemical method by 0.025 M concentration of initial reagents.

PbOnano-particles were synthesized from the decomposition of the precursor 1 in oleic acid in 200°C (Figures 7) under air atmosphere. The morphology and size of the as-prepared PbO samples were further investigated using Scanning Electron Microscopy (SEM). Bulk powder of the precursor 1 produces regular shape of lead(II) oxide nano-particles with the diameter about 40 nm (Figure 7).

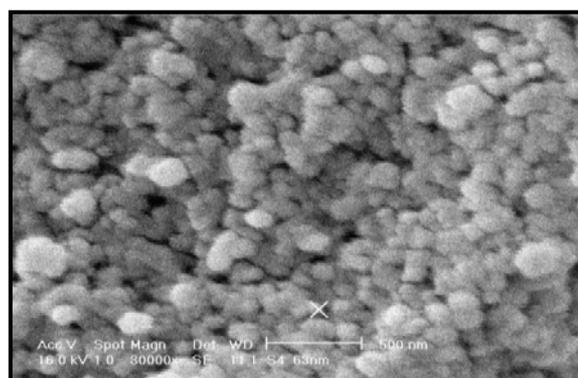


Fig. 7. SEM photographs of PbO nanoparticles produced by calcination of precursor 1 under using oleic acid as surfactant at 200°C.

The final product upon by decomposing the compound 1 is, based on their XRD patterns (Figure 8), orthorhombic PbO. The phase purity of the as-prepared orthorhombic PbOnano-particles are completely obvious and all diffraction peaks are perfectly indexed to the orthorhombic PbO structure with the lattice parameters of $a = 5.4903 \text{ \AA}$, $c = 4.7520 \text{ \AA}$, $Z = 4$ and S.G = Pcam which are in JCPDS card file No. 38-1477. No characteristic peaks of impurities are detected in the XRD pattern.

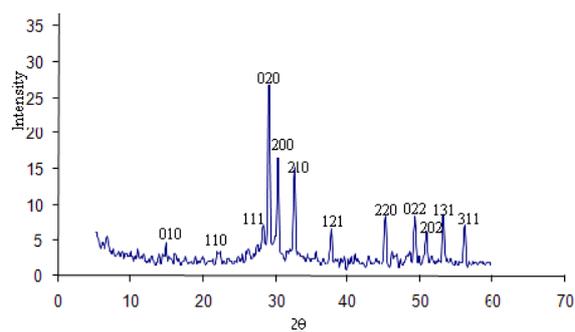


Fig. 8. XRD patterns of PbO prepared after thermolyses of compound $[\text{Pb}(2\text{-bpdh})(\text{NO}_3)_2(\text{H}_2\text{O})]_n(1)$

4. Conclusion

Two new Pb(II) and Hg(II) coordination polymers, $[\text{Pb}(2\text{-bpdh})(\text{NO}_3)_2(\text{H}_2\text{O})]_n(1)$; 2-bpdh = 2,5-bis(2-pyridyl)-3,4-diaza-2,4-hexadiene}, and $[\text{Hg}(4\text{-bpdh})(\text{SCN})_2]_n(2)$; (4-bpdh = 1,4-bis(4-pyridyl)-3,4-diaza-1,3-butadiene) have been synthesized using a thermal gradient approach and by sonochemical irradiation. Calcination under air of compound **1** produces nano-sized particles of PbO. This study demonstrates the coordination polymers may be suitable precursors for the preparation of nanoscale materials and it does not need special conditions like high temperature, long times and pressure controlling.

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