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Sonochemical Synthesis of a New Nano Lead(II) Coordination Polymer with 2,5-bis(2-pyridyl)-3,4-diaza-2,4-hexadiene ligand: A Precursor to Produce Pure Phase Nano-sized Lead(II) Oxide

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Abstract

A new nano-sized lead(II) coordination polymer, [Pb(2-bpdh)$(NO_3)_2]_n$(**1**); (2-bpdh = 2,5-bis(2-pyridyl)-3,4-diaza-2,4-hexadiene)}, was synthesized by a sonochemical method. The structure of **1** may be considered coordination polymer of lead(II) consist of metallocyclicchains formed by bridging NO_3^- and 2-bpdh ligands. The thermal stability of compound was studied by thermal gravimetric and differential thermal analyses. The new nano-structure coordination polymer was characterized by scanning electron microscopy, powder X-ray diffraction, elemental analyses and IR spectroscopy. The size of the samples was about 50 nm. Nano-particles of PbO were obtained by thermolysis of compound **1** in oleic acid as a surfactantat 180°C under air atmosphere and the size of this PbO particles were about 50 nm.

1. Introduction

During the past decade, chemists have been focused on new coordination polymers based on polydentate organic ligands due to their novel structural topologies and potential applications in sensing, catalysis, separations, or gas storage. Many attempts have been made to prepare variety of transition metal complexes using different spacers and their structures and properties have been determined [1-3]. On other hand the supramolecular architectures exhibit potential applications as molecular wires [4], electrical conductors [5], molecular magnets [6], in host-guest chemistry [7] and in catalysis [8]. The potential use of

coordination polymersas materials for nanotechnological applications would seem to be very extensive as nanometer-scaled materials often exhibit the new interesting size-dependent physical and chemical properties that cannot be observed in their bulk analogous. For this reason, nano-sized coordination supramolecular materials are interesting candidates for applications in many fields, including catalysis, molecular adsorption, magnetism, nonlinear optics, luminescence, and molecular sensing, but nano-scale particles of metal–organic coordination supramolecules have some times been investigated [9]. In this paper we describe a simple synthetic sonochemical preparation of a nano lead(II) coordination polymer, $[Pb(2\text{-bpdh})(NO_3)_2]_n$(1), (2-bpdh = 2,5-bis(2-pyridyl)-3,4-diaza-2,4-hexadiene), and the use of this new compound to prepare PbO nanoparticles. In recent years many kinds of nanomaterials have been prepared by sonochemical method [10-12]. There are different methods such as microwave-solvothermal synthesis [13], hydrothermal route [14] and surfactant-ligand co-assisting solvothermal method [15] 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) which was prepared according to the literature procedures [16,17], 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 Cuk_α 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 $[Pb(2\text{-bpdh})(NO_3)_2]_n$(1)

Compound **1** was prepared using the following method: 2-bpdh (1 mmol, 0.238 g), lead(II) nitrate (0.331 g, 1mmol) were placed in the main arm of a branched tube. Acetonitrile 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 2-3 days orange crystals obtained and then filtered off and air dried, m.p. = 225°C. IR (selected bands; in cm^{-1}): 571(m), 823(m), 1000(w), 1058(w), 1291(s), 1364(s), 1539(w) and 1599(s).

2.3. Synthesis of nano-sized $[Pb(2\text{-bpdh})(NO_3)_2]_n$(1)by sonochemical method

To prepare the nanostructure of compound **1** by sonochemical process, we used an ultrasonic bath was used with different concentrations of metal and ligand solutions (0.05, 0.10 and 0.15 M) and the power of 0.138 KW for 1 hour. To the prepared $Pb(NO_3)_2$ solution (20 ml), a proper volume of ligand (2-bpdh) solution in (acetonitrile: 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. = 225°C. IR (selected bands; in cm^{-1}): 572(w), 823(m), 1000(w), 1055(m), 1293(s), 1366(s), 1539(w) and 1592(s).

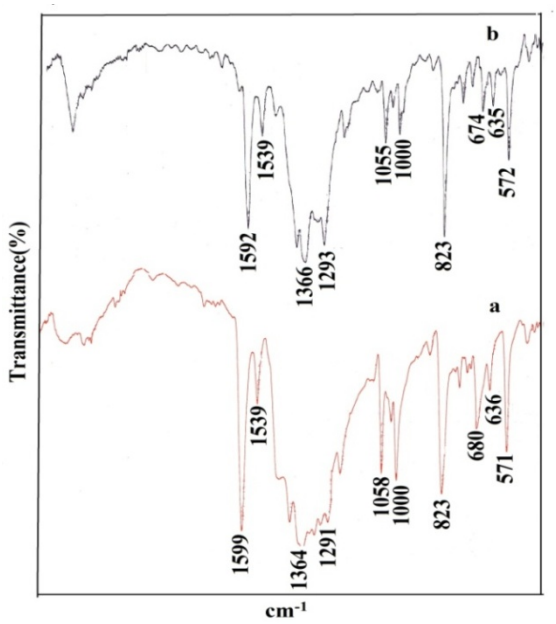

Fig. 1. The IR spectra of (**a**) bulk materials as synthesized of compound[Pb(2-bpdh)$(NO_3)_2]_n$(**1**) and (**b**) nano-sized compound [Pb(2-bpdh)$(NO_3)_2]_n$(**1**)prepared by sonochemical method.

2.3. Synthesis of PbO nanoparticles

The precursor [Pb(2-bpdh)$(NO_3)_2]_n$(1) (0.1 mmol) was dissolved immediately in 1.58 ml oleic acid and formed light yellow solution. These solutions were degassed for 20 min and then heated to 180°C for 2 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 PbO nanoparticles were separated by centrifugation. The solids were washed with EtOH and dried under air atmosphere.

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 [Pb(2-bpdh)$(NO_3)_2]_n$(**1**). Nano-sized compound **1** were obtained by ultrasonic irradiation in a water: acetonitrile (with 1:1 molar ratio) solutionand 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. $\nu(NO_3)$ vibrations are found at 1360-1370 cm^{-1}. IR spectra of the nanostructure of compound **1** show more similarity with the IR spectra of single crystalline material (Fig. 1). Fig. 2 shows the simulated XRD pattern from single crystal of compound **1** (Figure 2a)in comparison with the XRD pattern of a typical sample of compound **1** prepared by the sonochemical process (Fig. 2b). Acceptable match indicates 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 of nanometer dimensions.

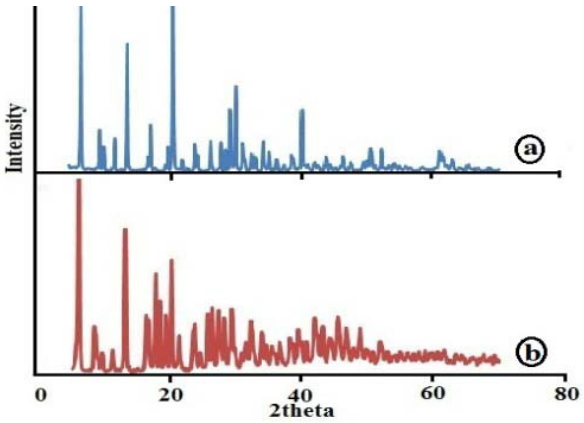

Fig. 2. The XRD patterns of (**a**) compound (**1**)prepared by thermal gradient method and (**b**) nano-sized compound (**1**) prepared by sonochemical method.

Calculations with Sherrer formula shows the average size of the particles is 55 nm, which is in agreement with that observed by scanning electron microscopy, as shown in Fig. 3.

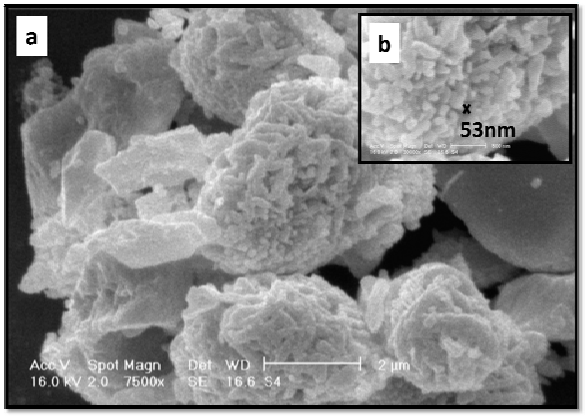

Fig. 3.SEM photographs of compound **1** nanoparticles produced by sonochemical method by 0.1 M concentration of initial reagents.

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 (Fig. 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 190 and 260 °C as well as two exothermic peaks at 300 and 470 °C (Figure 4).

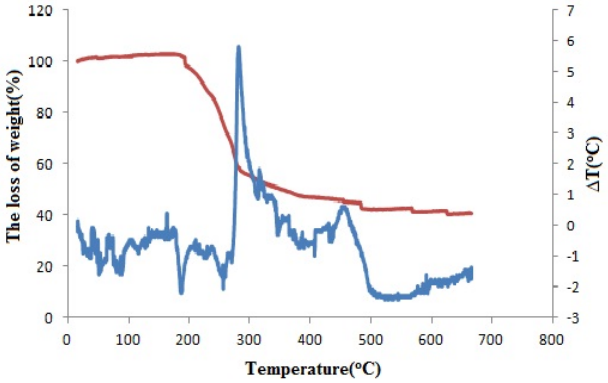

Fig. 4.TGA and DTA diagrams of $[Pb(2\text{-}bpdh)(NO_3)_2]_n$(**1**).

PbO nano-particles were synthesized from the decomposition of the precursor **1**in oleic acid in 180°C (Fig. 5) 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 50 nm (Fig. 5).

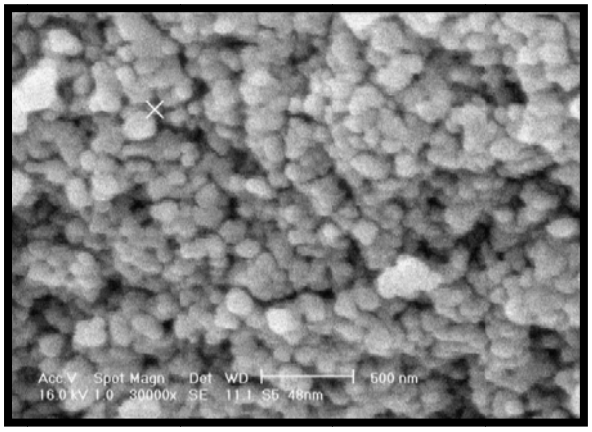

Fig. 5.SEM photographs of PbO nanoparticles produced by calcination of precursor **1**under using oleic acid as surfactant at 180°C.

The final product upon by decomposing the compound **1** is, based on their XRD patterns (Fig. 6), orthorhombic PbO. The phase purity of the as-prepared orthorhombic PbO nano-particles are completely obvious and all diffraction peaks are perfectly indexed to the orthorhombic PbO structure with the lattice parameters of a = 5.4903Å, c = 4.7520Å, 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. It was also tested the low temperatures, under 180°C, for thermolyses of compound **1,** but in temperatures under 180°C the size and morphology of nano-particles are not suitable. So The morphology and size of nanoparticles of Pb(II)O are depend on structure, additives and thermal conditions.

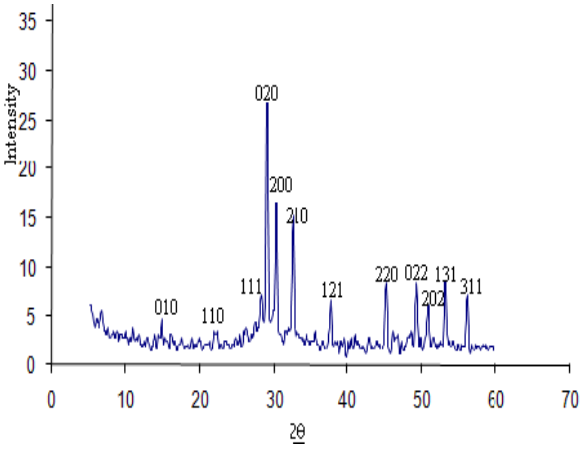

Fig. 6.XRD patterns of PbO prepared after thermolyses of compound $[Pb(2\text{-bpdh})(NO_3)_2]_n$(1).

4. Conclusion

A new Pb(II) coordination polymer, $[Pb(2\text{-bpdh})(NO_3)_2]_n$(1); 2-bpdh =2,5,bis(2-pyridyl)-3,4-diaza-2,4-hexadiene}, has been synthesized using a thermal gradient approach and by sonochemical irradiation. Calcination under air 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. This method of preparation may have some advantages such as: it take places with shorter reaction times, produces better yields and it also is likely to produce nano-sized particles of the coordination polymer but some disadvantage have been occurred for example the vowel pollution and possibility of solubility of product under ultra sound.

Acknowledgements

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