Effect of two sonochemical procedures on achieving to different morphologies of lead(II) coordination polymer nano-structures

Kamran Akhbari, Ali Morsali, Pascal Retailleau

Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14115-4838, Tehran, Islamic Republic of Iran
Centre de Recherche de Gif, Institut de Chimie des Substances Naturelles, CNRS-UPR2301, 1 Avenue de la Terrasse, Bât 27, 91198 Gif sur Yvette cedex, France

ARTICLE INFO

Article history:
Received 3 February 2013
Received in revised form 13 March 2013
Accepted 29 March 2013
Available online 6 April 2013

Keywords:
Nano-structure
Coordination polymer
Lead(II)
Sonochemical
Solid-state
Structural transformation

ABSTRACT

Micro and nano-structures of a lead(II) coordination polymer, [Pb2(2-Me-8-Hq)2(MeOH)2]n (1), [2-Me-8-HqH = 2-methyl-8-hydroxyquinoline] were synthesized by two sonochemical methods. These new micro and nano-structures were characterized by scanning electron microscopy, X-ray powder diffraction, IR spectroscopy and elemental analyses. Compound 1 was structurally characterized by single-crystal X-ray diffraction and consists of primary dimeric unit of [Pb2(2-Me-8-Hq)2(MeOH)2]. Self assembly between the dimeric units of [Pb2(2-Me-8-Hq)2(MeOH)2] from Pb-O bonds results in formation of a one-dimensional lead(II) coordination polymer. The PbII-ion in compound 1 has PbO4N2 coordination sphere with a stereo-chemically 'active' electron lone pair on the metals. By a reversible solid-state structural transformation, we successfully prepared [Pb2(2-Me-8-Hq)2]n (2) by thermal desolvation of 1. Thermal stability of compound 1 was studied by thermo gravimetric and differential thermal analyses. In addition nano-structure of PbO was prepared from calculation process of compound 1 at 873 K.

1. Introduction

The design and construction of coordination polymers are of extensive interest in recent years [1]. Recently, CP (coordination polymer) nanocrystals, nanosized coordination polymers with finite repeating units, have aroused a growing interest due to their special properties that differ from conventional bulk CP [2–4]. NCPs (nano coordination polymers) are generally synthesized by exploiting the insolubility of the particles in a given solvent system. Wang et al. reported the first synthesis of non-cyanometallate NCPs in 2005 [5]. Several different synthetic approaches have been offered for the preparation of coordination compounds [6]. Some of them are slow diffusion of the reactants into a polymeric matrix, diffusion from the gas phase, evaporation of the solvent at ambient or reduced temperatures, precipitation or recrystallisation from a mixture of solvents, temperature controlled cooling, hydrothermal synthesis and sonochemical syntheses. Sonochemistry is the research area in which molecules undergo a reaction due to the application of powerful ultrasound radiation (20 kHz–10 MHz) [7]. Ultrasound induces chemical or physical changes during cations, a phenomenon involving the formation, growth, and instantaneously implosive collapse of bubbles in a liquid, which can generate local hot spots having temperatures of roughly 5000 °C, pressures of about 500 atm and a lifetime of a few microseconds [8]. These extreme conditions can drive chemical reactions, but they can also promote the formation of nano-sized particles, mostly by the instantaneous formation of a plethora of crystallization nuclei [8,9]. This has been widely used to fabricate nano-sized particles of a variety of compounds [7]. In recent years many kinds of nano-sized materials have been prepared by this method [10–15]. In this work, continuing to our previous works on sonochemical syntheses of coordination polymer nano-structures [16–21], we wish to report another coordination polymer from PbII ion, [Pb2(2-Me-8-Hq)2(MeOH)2]n (1), (2-Me-8-HqH: 2-methyl-8-hydroxyquinoline). Solid-state structural transformation is one of the hot topics in supramolecular chemistry which have received considerable interests in crystal engineering [22]. In a solid-state structural transformation, by thermal desolvation of coordinated MeOH molecules in 1, we successfully prepared [Pb2(2-Me-8-Hq)2]n (2) nano-belts and micro-structures with nano-structural surface.

2. Experimental

2.1. Materials and physical techniques

All reagents and solvents for the synthesis and analysis were commercially available and were used as received. Single crystal diffraction measurements were made at 293(2) K using an Enraf-Nonius kappacCD diffractometer. The intensity data were collected using graphite monochromated Mo–Kα radiation. The
structures were solved by direct methods and refined by full-matrix least-squares techniques on \( \text{F}^{2} \). The molecular structure plots were prepared using Mercury [23]. Structure solution and refinement were accomplished using SHELXL-97 program packages. An ultrasonic bath (Tecnac 6; 50–60 Hz and 0.138 kW) and a multi-wave ultrasonic generator (Sonicator_3000; Misonix, Inc., Farmingdale, NY, USA), equipped with a converter/transducer and titanium oscillator (horm), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 600 W, were used for the ultrasonic irradiation. Melting points were measured on an Electrothermal 1100 apparatus. X-ray powder diffraction (XRD) measurements were performed using a Xpert diffractometer (PANalytical, Almelo, The Netherlands), equipped with a Cu Kα 1.5079 Å, sealed tube at ambient temperature in the temperature range of 20° to 100° at a scan speed of 2°/min. The thermal behavior was measured with a PL-STA 1500 apparatus. Microanalyses were carried out using a Heraeus Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded in the range of 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) using a Shimadzu IRPrestige-21 spectrophotometer. Microanalyses were carried out using a Heraeus Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded in the range of 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) using a Shimadzu IRPrestige-21 spectrophotometer.

2.2. Synthesis of \([\text{Pb}_2(2\text{-Me-8-Hq})_2(\text{MeOH})_2]_n\) (1) and preparation of its single crystals

\( \text{Pb(NO}_3\text{)}_2 \) (2 mmol, 0.662 g) and 2-methyl-8-hydroxyquinoline \( (2 \text{ mmol, 0.318 g}) \) were loaded into one arm of a branch tube and both of the arms were filled slowly by methanol. The chemical-bearing arm was immersed in an oil bath kept at 60°C. Crystals were formed on the inside surface of the arm kept at ambient temperature after a few days, d.p. = 310°C. Yield: 0.616 g (67% based on final product), Anal. calc. for \( \text{C}_{22}\text{H}_{24}\text{N}_{4}\text{O}_{10}\text{Pb}_{2} \): C, 28.73; H, 2.71; N, 6.15%; C, 28.73; H, 2.71; N, 6.15%. In order to obtain de-solvated complex of \([\text{Pb}_2(2\text{-Me-8-Hq})_2(\text{MeOH})_2]_n\) (2), we placed the block crystals of compound 1 in electric furnace at 160°C for 5 h. The resulting sample lost its transparency and was not found suitable for single crystal X-ray crystallography. d.p. = 315°C. Anal. calc. for \([\text{Pb}_2(2\text{-Me-8-Hq})_2]_n\) (2) with the proposed molecular formula of \( \text{C}_{20}\text{H}_{16}\text{N}_{4}\text{O}_{8}\text{Pb}_{2} \): C, 28.07; H, 1.87; N, 6.52; O, 28.16; H, 1.95, N, 6.61%. It should be mentioned that this compound was crystallographically characterized by Ng et al., too [24].

2.3. Synthesis of \([\text{Pb}_2(2\text{-Me-8-Hq})_2(\text{MeOH})_2]_n\) (1) nano-structures in ultrasonic bath

To prepare the nano-structures of compound 1 by sonochemical process, we used ultrasonic bath with 0.05, 0.1 and 0.15 M concentrations of metal and ligand solutions and the power of 0.138 kW for 1 h. To the solution of 2-Me-8-HqH ligand in methanol (4 ml), a methanol solution of \( \text{Pb(NO}_3\text{)}_2 \) (4 ml) was added in a drop wise manner under the ultrasonic irradiation. The obtained precipitates were filtered, subsequently washed with methanol and then dried (Found: C, 28.81; H, 2.55; N, 6.12% and C, 28.73; H, 2.71; N, 6.15%). The produced materials from the reaction of 2-Me-8-HqH ligand with lead(II) nitrate by three different methods and fabrication of lead(II) oxide from compound 1 nano-structures.
for the products of 0.1 and 0.15 M concentrations of initial reagents, respectively). In the case of 0.05 M concentration of initial reagents, no precipitate was formed in ultrasonic bath. In order to obtain nano-structures of \( [\text{Pb}_2(2-\text{Me-8-Hq})_2]_n \) (2) by solid-state structural transformation, we placed powders of compound 1 in an electric furnace at 160 °C for 5 h. (C, 28.14; H, 1.75; N, 6.61% and C, 28.10; H, 1.70; N, 6.63% for the products of 0.1 and 0.15 M concentrations of initial reagents, respectively). Finally, PbO nano-structures were prepared by calcination process of compound 1 nano-structures at 873 K in a furnace and static atmosphere of air for 5 h.

2.4. Synthesis of \([\text{Pb}_2(2-\text{Me-8-Hq})_2(\text{MeOH})_2]_n \) (1) micro-structures by ultrasonic generator

To prepare the nano-structures of \([\text{Pb}_2(2-\text{Me-8-Hq})_2(\text{MeOH})_2]_n \) (1) by another sonochemical process, a high-density ultrasonic probe immersed directly into the solution of 2-Me-8-Hq ligand

![Fig. 1.](image1.png)

*Fig. 1.* Primary structural units of \([\text{Pb}_2(2-\text{Me-8-Hq})_2(\text{MeOH})_2]_n \) (1) Dimer. (Pb = violet, O = red, C = gray, N = blue and H = white). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

![Fig. 2.](image2.png)

*Fig. 2.* (a) Formation of 1D coordination polymer in \([\text{Pb}_2(2-\text{Me-8-Hq})_2(\text{MeOH})_2]_n \) (1) as a result of additional Pb-O bonds between adjacent dimmers. (b) Existence of hydrogen bonding network in \([\text{Pb}_2(2-\text{Me-8-Hq})_2(\text{MeOH})_2]_n \) (1) and (c) the role of hydrogen bonding network in \([\text{Pb}_2(2-\text{Me-8-Hq})_2(\text{MeOH})_2]_n \) (1) to expand 1D structure of it to 2D supramolecular polymer. (Pb = violet, O = red, C = gray, N = blue and H = white). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
(25 ml, 0.1 M) in methanol, then into this solution, a proper volume of Pb(NO₃)₂ in methanol solvent (25 ml, 0.1 M) was added in a drop wise manner. The solution was ultrasonically irradiated with the power of 9 W for 1 h. The obtained precipitates were filtered, subsequently washed with methanol and then dried (Found; C, 28.88; H, 2.57; N, 6.12%). In order to obtain nano-structures of [Pb₂(2-Me-8-Hq)₂]ₙ (2) by solid-state structural transformation, we placed powders of compound 1 nano-structures in electric furnace at 160 °C for 5 h. (C, 28.14; H, 1.81; N, 6.49%). Finally in order to obtain PbO nano-structures, fine powder of compound 1 nano-structures was calcined at 873 K in a furnace and static atmosphere of air for 5 h.

2.5. Synthesis of [Pb₂(2-Me-8-Hq)₂(MeOH)₂]ₙ (1) powders by reflux procedure

To evaluate the role of ultrasonic waves on morphology of 1 and have a comparison between their results, we perform another reaction without sonication. A solution of 2-Me-8-HqH ligand (10 ml, 0.1 M) in methanol was added to a proper volume of Pb(NO₃)₂ in methanol solvent (10 ml, 0.1 M) and was stirred for an hour. The obtained precipitates were filtered, subsequently washed with methanol and then dried (Found; C, 28.97; H, 2.53; N, 6.16%).

3. Results and discussion

The scheme 1 shows the reaction between lead(II) nitrate and 2-Me-8-HqH by three different methods.

The reaction between 2-methyl-8-hydroxyquinoline (2-Me-8-HqH) and Pb(NO₃)₂ provided crystalline materials of the general formula [Pb₂(2-Me-8-Hq)₂(MeOH)₂]ₙ (1). Determination of the structure of this compound by X-ray crystallography (Tables 1 and 2) showed the compound is a dimer (Fig. 1) with one type of Pb²⁺ ion, 2-methyl-8-hydroxyquinoline acts as bidentate chelating ligand with the form of deprotonated (2-Me-8-Hq⁻) ligand (Fig. 1). The oxygen atom of 2-Me-8-Hq⁻ also bridges to another Pb²⁺ ion and a dimer of 1 is formed. The Pb²⁺ ion in 1 is coordinated by one N and two O atoms of 2-Me-8-Hq⁻ ligand, one O atom of nitrate anion and one O atom from coordinated methanol molecule (Fig. 1). Two other O atoms of nitrate anions in 1 are chelated to Pb atom of adjacent dimer (with Pb(1)-O(3) and Pb(1)-O(4) bond distances of 3.382 and 3.385 Å, respectively), finally results in formation of one-dimensional coordination polymer along the crystallographic b axis (Fig. 2a). Thus we could consider PbO₆N₁ coordination sphere around Pb atoms in 1 (Figs. 1 and 2a and Table 2). In compound 1, the lone pair of Pb(II) is ‘active’ in the solid state. However, the arrangement of O-atoms suggests a gap or hole in coordination geometry around the Pb(II) coordination.
sphere (Fig. 1), a gap possibly occupied by a ‘stereo-active’ electron lone pair. Hence, the geometry of the nearest coordination environment of every Pb(II)-atoms is likely to be caused by the geometrical constraints of coordinated N and O atoms, and by the influence of a stereo-chemically ‘active’ electron lone pair. Our investigations also indicate that a hydrogen bonding network also exists in 1 which stabilizes its structure (Fig. 2b). This hydrogen bonding interaction formed between –OH hydrogen atom of coordinated methanol molecule and O atom nitrate anion from adjacent unit (Fig. 2b). This hydrogen bonding network expands 1D coordination polymer of 1 to a 2D supramolecular polymer (Fig. 2c).

Thermo gravimetric (TG) and differential thermal analyses (DTA) of compound 1 single crystals show that this compound is stable up to 70 °C in the static atmosphere of nitrogen (Fig. 3), at which temperature removal of coordinated methanol molecules with a mass loss of 6.31% (calcd 6.96%) starts up to 165 °C. After removal of coordinated solvent molecule, the desolvated compound which could be related to \( \text{[Pb}_2(2\text{-Me-8-Hq})_2\text{]n} \) (2), is stable up to 300 °C. As it is obvious from Fig. 3, removal of coordinated methanol molecules and pyrolyzes of compound 1 are accompanied with two endothermic peaks at 84 and 150 °C and one exothermic peak at 313 °C, respectively.

As approved by TG analyses, on heating at 160 °C, compound 1 change to compound 2. To further confirmation of the removal and reabsorbing of the coordinated methanol molecules by compound 1, IR spectra were recorded for a fully solvated sample and for the same sample after heating experiments (Fig. 4). The IR spectrum of 1 shows characteristic absorption bands for the 2-Me-8-Hq ligand and coordinated methanol molecules (Fig. 4a). The absorption bands with variable intensity in the frequency range 1350–1600 cm\(^{-1}\) correspond to ring vibrations of the aromatic rings in 2-Me-8-Hq ligand. In addition, the absorption band at the frequency of 1270 cm\(^{-1}\) corresponds to coordinated NO\(_3^-\) anion. The \(\nu_{\text{O-H}}\) vibration of the coordinated methanol molecule is observed as a weak broad band around 3100–3600 cm\(^{-1}\), no such band was observed for the sample after heating (Fig. 4b). This solid-state structural transformation is reversible and IR spectrum (Fig. 4c) of desolivated sample after solid–gas reaction of it with methanol vapors for 12 h shows no differences related to compound 1. Thus the desolivated sample (compound 2) is converted back to 1 by re-absorption of methanol and this transformation is flexible and dynamic.

In order to evaluate the role of sonochemical methods in syntheses of compound 1 nano-structures and the effect of two different ultrasonic generator equipments, we used Tecna ultrasonic

![Fig. 6. SEM images of (a) compound 1 nano-structures obtained from 0.1 M concentration of initial precursor in ultrasonic bath, (b) and (c) compound 2 prepared by thermal desolvation of compound 1 at 160 °C for 5 h.](image)

![Fig. 7. SEM images of (a) compound 1 nano-structures obtained from 0.15 M concentration of initial precursor in ultrasonic bath and (b) compound 1 obtained from 0.1 M concentration of initial precursors without sonication.](image)
bath and multiwave ultrasonic generator of Misonix to preparation of 1 in nano-scale. Fig. 5a shows the simulated XRD pattern from single crystal X-ray data of the compound 1 and Fig. 5b shows the XRD pattern of a typical samples of [Pb₂(2-Me-8-Hq)₂(-MeOH)]₂ (1) prepared in ultrasonic bath. Acceptable matches, with slight differences in 2θ, were observed between the simulated from single-crystal X-ray data pattern (Fig. 5a) and its from the experimental powder X-ray diffraction pattern for nano-structures of crystalline sample as obtained from the synthesis by sonochemical process (Fig. 5b). The result of XRD powder pattern indicates that the experimental data are in good agreement with the simulated XRD powder pattern based on single crystal data, hence this compound obtained as a mono-phase. Solid-state structural transformation (by thermal treatment of compound 1) results in a significant change of the powder pattern (Fig. 5c), which now does not match with the pattern of compound 1 (Fig. 5b). This new pattern attributed to formation of compound 2 with no coordinated methanol molecules. Fig. 5d indicates that this structural transformation is dynamic and solid–gas reaction of sonochemically synthesized sample with methanol vapors results in formation of compound 1, again. As was described for the bulk sample (Fig. 4), IR spectra of sonochemically synthesized samples with ultrasonic bath (Fig. S1) and Misonix ultrasonic generators (Fig. S2) approved these reversible transformations. The morphology and structure of the samples which was prepared by both sonochemical equipments were investigated by Scanning Electron Microscopy (SEM). Fig. 6a indicates the original morphology of compound 1 nano-structures prepared in ultrasonic bath, mixture of aggregated nano-particles and nano-belts is formed. Solid-state structural transformation of 1 to 2 by thermal treatment results in conversion of some aggregated nano-particles to nano-belts (Fig. 6b and c). As was mentioned previously, by 0.05 M concentration of initial reagents, compound 1 did not precipitate in ultrasonic bath. Fig. 7a shows the morphology of compound 1 prepared by 0.15 M concentration of initial reagents. A comparison between SEM images (Fig. 6a and 7a) shows that by concentration increase from 0.1 M to 0.15 M, tendency of compound 1 to agglomeration increased and cubic form of compound 1 micro-structure was formed. Fig. 8a and b indicate the original morphology and surface morphology of compound 1 micro-structures prepared by Misonix.

![SEM images of (a and b) compound 1 micro-structures obtained from 0.1 M concentration of initial precursor by ultrasonic generator, (c) compound 2 prepared by thermal desolvation of compound 1 at 160 °C for 5 h and (d and e) nano-structural surface of 2 as a result of removal of coordinated methanol molecules in 1.](image-url)
ultrasonic generator. In order to find the role of ultrasonic waves on formation compound \(1\) micro and nano-structures, we perform another reaction without sonication. Fig. 7b shows the morphology of this sample with 0.1 M concentration of initial reagents. Thus sonochemical synthesis of compound \(1\) nano-structures by Misonix ultrasonic generator was not successful and in comparison with non sonicated sample (Fig. 7b) this sample only has more regular morphology. In fact, comparison between Fig. 7a and 8a indicates that by performing ultrasonic waves in syntheses procedure of compound \(1\) with 0.1 M concentration of initial reagents, the tendency of micro-structures to agglomerate decreased and on the other hand the regularity of micro-structures increased. As a reversible solid-state structural transformation and by thermal treatment of both samples, we successfully prepared \([\text{Pb}_2(2\text{-Me-8-Hq})_2\text{MeOH}]_2\) (2). This solid-state structural transformation led to conversion of some aggregated nano-particles to nano-belts and formation of micro-structures with nano structural surface in 2, respectively. Probably removal of coordinated methanol molecules in micro-structures of \(1\), which were synthesized by ultrasonic generator, resulted in formation compound \(2\) with nano-structural surface. In addition the morphology and size of resulting PbO which was obtained from calcination of compound \(1\) fine powder at 600 °C, shows that in this case, size decrease of initial precursor has no influence on formation of nano lead(II) oxide from compound \(1\). This paper is one of the few examples highlighting samples using sonication as an alternative synthetic procedure to form coordination polymers. This method for preparing coordination polymers may offer some advantages such as: it takes places in shorter reaction times, produces better yields and also it may produce the polymers at nano-size. From this perspective, further systematic studies of other polymers with different metal ions are ongoing in our laboratory, which may offer new insights into metal–organic supramolecular assembly and nanochemistry.

4. Conclusions

One-dimensional lead(II) coordination polymer, \([\text{Pb}_2(2\text{-Me-8-Hq})_2\text{MeOH}]_2\) (1), has been synthesized by branch tube and by two sonochemical methods. Self assembly between the dimmeric units of \([\text{Pb}_2(2\text{-Me-8-Hq})_2\text{MeOH}]_2\) from Pb–O bonds results in formation of a this polymer. One Pb\(^{2+}\)–ion in this compound has PbO\(_6\)N\(_2\) coordination sphere with a stereo-chemically ‘active’ electron lone pair on the metal. Sonochemical syntheses of \(1\) in ultrasonic bath results in formation of aggregated nano-particles and nano-belts while syntheses of it by Misonix ultrasonic generator results in formation of compound \(1\) micro-structures. In ultrasonic bath, the tendency of compound \(1\) to agglomeration increased by increase in concentration of initial reactants and cubic form of compound \(1\) micro-structure was formed. Sonochemical synthesis of compound \(1\) nano-structures by Misonix ultrasonic generator was not appropriate and in comparison with non sonicated sample, the resulting product only has more regular morphology. By performing ultrasonic waves (with Misonix ultrasonic generator) in syntheses procedure of compound \(1\) with 0.1 M concentration of initial reagents, the reactivity of micro-structures to agglomerate decreased and on the other hand the regularity of micro-structures increased. This polymer is one of the few examples highlighting samples using sonication as an alternative synthetic procedure to form coordination polymers. This method for preparing coordination polymers may offer some advantages such as: it takes places in shorter reaction times, produces better yields and also it may produce the polymers at nano-size. From this perspective, further systematic studies of other polymers with different metal ions are ongoing in our laboratory, which may offer new insights into metal–organic supramolecular assembly and nanochemistry.

Acknowledgements

Supporting of this investigation by Tarbiat Modares University is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ultrasonch.2013.03.013.

References


h) K. Akhbari, A. Morsali, Halogen dipole moment effect of phenolic ring on formation of stair like polymers or polymers with tetranuclear cubic cage units; new precursors for preparation of TCI and TiO₂ nanostructures, CrystEngComm 14 (2012) 1618–1628.


