Inorganica Chimica Acta 423 (2014) 101–105

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

# How the two factors of concentration and ultrasonic wave power affect on formation of kinetically or thermodynamically stable lead(II) complex nano-structures

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## ARTICLE INFO

*Article history:*
Received 9 June 2014
Received in revised form 23 July 2014
Accepted 4 August 2014
Available online 12 August 2014

*Keywords:*
Nano-plate
Supramolecular polymer
Lead(II)
Sonochemical
Kinetically stable
Thermodynamically stable

## ABSTRACT

The reaction between quinoline-2-carboxylic acid (HQ) and lead(II) acetate trihydrate ($Pb(OAc)_2{\cdot}3H_2O$) results in formation of kinetically stable and thermodynamically stable $[Pb_2(Q)_2(OAc)_2]_n$ (**1**) and $[Pb(Q)_2]_n$ (**2**), respectively. Compound **1** (kinetically stable) was formed in aprotic solvent of acetonitrile and is stable in it. We evaluated the reaction between HQ and $Pb(OAc)_2{\cdot}3H_2O$ in two different ultrasonic baths and investigated the effect of initial reagents concentration on morphology and kind of resulting products. The resulting samples were characterized by scanning electron microscopy, X-ray powder diffraction, IR spectroscopy and elemental analyses. Although these reactions were performed in acetonitrile, only in two samples compound **1** was synthesized. Thus in other four samples, the resulting products were compound **2**. Indeed, ultrasonic waves with ultra-high energy could change the kinetically stable **1** to thermodynamically stable **2** in acetonitrile. With the highest 0.1 M concentration of initial precursors, only thermodynamically stable product (**2**) obtained in both of two ultrasonic baths. In lower concentrations of initial precursors (0.025 M and 0.05 M), the kind of resulting product attributed to the type of ultrasonic bath and its wave power and frequency.

## 1. Introduction

The utilization of intermolecular interactions which generate specific supramolecular motifs has greatly enhanced the systematic approach to both the understanding and the design of highly organized molecular arrays in solids. Considerable attentions have been paid to the supramolecular polymers composed of 1D chains, 2D sheets and 3D networks due to the potential applications in separation, catalysis, as conductors, sensors and storage devices [1–3]. Much interest has been focused on the supramolecular polymeric structures constructed by coordination bonds, hydrogen bonding and aromatic $\pi$-stacking interactions [4–6]. Several different synthetic approaches have been offered for the preparation of coordination compounds [7]. Some of them are (1) slow diffusion of the reactants into a polymeric matrix, (2) diffusion from the gas phase, (3) evaporation of the solvent at ambient or reduced temperatures, (4) precipitation or recrystallisation from a mixture of solvents, (5) temperature controlled cooling and (6) hydrothermal synthesis. Nanometer-sized structures of supramolecular polymers are fascinating to explore, since their unique properties are controlled by the large number of surface molecules, which experience an entirely different environment than those in a bulk crystal. Controlling the growth of materials at the sub micrometer scale is of central importance in the emerging field of nanotechnology [8–11]. Although considerable effort has been performed to the controlled synthesis of nano-scale structures of metals, oxides, sulfides and ceramic materials [12–18], little attention was focused to date on nano-structures of supramolecular compounds [19–22]. Sonochemistry deals with the chemistry that takes place upon application of high-energy ultrasound to a reaction mixture. Ultrasound is cyclic mechanical vibration with a frequency between 20 kHz, the upper limit of human hearing, and 10 MHz. Since the wavelength is much larger than molecular dimensions, no direct interaction between ultrasound and molecules can be responsible for chemical reactions, but when high-energy ultrasound interacts with liquids, cyclic alternating areas of compression (high

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http://dx.doi.org/10.1016/j.ica.2014.08.003
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pressure) and rarefaction (low pressure) are formed. In the low pressure region, the pressure drops below the vapor pressure of the solvent and/or the reactants and small bubbles, i.e. cavities, are formed. The bubbles grow (tens of micrometers) under the alternating pressure through the diffusion of solute vapor into the volume of the bubble. Thus, ultrasonic energy is accumulated. Once the bubbles reach their maximum size, they become unstable and collapse. This process of bubble formation, growth, and collapse is called cavitation and it leads to the rapid release of energy with heating and cooling rates of $>10^{10}$ K s$^{-1}$, temperatures of $\sim$5000 K and pressures of $\sim$1000 bar. Thus, these "hot spots" present rather unusual conditions of short duration of extremely high temperature and pressures inside the collapsing bubble as well as in its vicinity (ring of $\sim$200 nm). At a little larger distance, intense shear forces are observed [23]. In our previous work, we studied the effect of different ultrasonic equipments on formation different morphologies of lead(II) coordination polymer nano-structures [24], in this work we reports that how the two factors of concentration and ultrasonic wave strength affect on formation of kinetically or thermodynamically stable nano-structures of lead(II) supramolecular polymers from the same initial reagents.

## 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 from Merck Company. The molecular structure plots were prepared using Mercury [25]. Two ultrasonic baths of Tecna 6 (with the maximum power of 138 W at 35 kHz) and SONICA-2200 EP, (with the maximum power of 305 W at 40 kHz) were used for the ultrasonic irradiation. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer manufactured by Philips with monochromatized Cu k$\alpha$ radiation and simulated XRD powder patterns based on single crystal data were prepared using the Mercury software [25]. The samples were characterized with a scanning electron microscope with gold coating.

### 2.2. Synthesis of $[Pb_2(Q)_2(OAc)_2]_n$ (**1**) and preparation of its single crystals

Similar to our previous procedure [26], lead(II) acetate trihydrate (1 mmol, 0.379 g) and quinoline-2-carboxylic acid (1 mmol, 0.173 g) were loaded into one arm of a branch tube and both of the arms were filled slowly by acetonitrile. 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 four weeks, d.p. = 232 °C, Yield: 0.302 g (69% based on final product), *Anal.* Calc. for $C_{24}H_{18}N_2O_8Pb_2$: C, 32.87; H, 2.07; N, 3.19. Found: C, 32.77; H, 2.00, N, 3.17%.

### 2.3. Synthesis of $[Pb(Q)_2]_n$ (**2**) and preparation of its single crystals

Similar to our previous procedure [26], we performed the reaction of lead(II) acetate trihydrate (1 mmol, 0.379 g) and quinoline-2-carboxylic acid (1 mmol, 0.173 g) in a branch tube, which both of its arms were filled slowly by distilled water. 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 three weeks, d.p. = above 302 °C, Yield: 0.402 g (73% based on final product), *Anal.* Calc. for $C_{20}H_{12}N_2O_4Pb$: C, 43.55; H, 2.20; N, 5.08. Found: C, 43.46; H, 2.25, N, 5.00%.

### 2.4. Studies the reaction of lead(II) acetate trihydrate and quinoline-2-carboxylic acid in Tecna 6 and SONICA-2200 ultrasonic baths

To investigate the reaction of lead(II) acetate trihydrate and quinoline-2-carboxylic acid (HQ) by sonochemical processes, we used 0.025, 0.05 and 0.1 M concentrations of metal ion and ligand solutions for 1 h in two different ultrasonic baths. To the dispersed acetonitrile solution of $Pb(CH_3CO_2)_2{\cdot}3H_2O$ (5 mL), an acetonitrile solution of HQ ligand (5 mL) was added in a drop wise manner under the ultrasonic irradiation. The obtained precipitate was filtered, subsequently washed with acetonitrile and then dried. In Tecna 6 ultrasonic bath found; C, 32.91; H, 2.12; N, 3.15%, C, 43.47; H, 2.26; N, 5.18% and 43.59; H, 2.29; N, 5.00% for the products of 0.025, 0.05 and 0.1 M concentrations of initial reagents, respectively. These values which were found from 0.025, 0.05 and 0.1 M concentrations of initial reagents are near to those calculated from compounds **1**, **2** and **2**, respectively. For the reactions in SONICA-2200 ultrasonic bath, found; C, 43.55; H, 2.20; N, 5.08%, C, 32.87; H, 2.07; N, 3.19% and C, 43.55; H, 2.20; N, 5.08% for the products of 0.025, 0.05 and 0.1 M concentrations of initial reagents, respectively. These values which were found from 0.025, 0.05 and 0.1 M concentrations of initial reagents are near to those calculated from compounds **2**, **1** and **2**, respectively.

## 3. Results and discussion

As we have reported [26], the reaction between quinoline-2-carboxylic acid (HQ) and lead(II) acetate trihydrate in acetonitrile by branch tube method provided crystalline materials of the general formula $[Pb_2(Q)_2(OAc)_2]_n$ (**1**). Single crystal structure determination [26] showed that compound **1** is a dimmer which was refined in space group $P2_1/c$ (Fig. 1a) with one type of $Pb^{II}$–ion. Quinoline-2-carboxylate ($Q^-$) acts in two different coordination modes; chelating, where one oxygen atom of the carboxylate group and the N atom of $Q^-$ coordinate to a $Pb^{II}$ ion and bridging mode, where the coordinated oxygen atom of the carboxylate group to $Pb^{II}$ ion coordinates to another $Pb^{II}$ ion, finally connects to two $Pb^{II}$ ions (Table S1 and Fig. 1a). Each $Pb^{II}$ ion is coordinated with one $Q^-$ ligand and an acetate anion ($OAc^-$) with Pb–O bond distances of 2.433(6) and 2.581(8) Å in a chelating mode. Thus each $Pb^{II}$ ion has stereo active lone electron pair with hemidirected coordination sphere of **Pb**$O_4$N. The Pb atom in compound **1** is also involved in an long Pb···O interactions with the uncoordinated oxygen atom of $Q^-$ (3.095 Å) and one of the $OAc^-$ oxygen atom (3.251 Å) from adjacent basic building block in its vacant coordination sphere. Approximate bond-valence parameters are useful in deciding if there is a significant bonding interaction between pairs of atoms [27]. Bond-valence sum analysis of Pb–O, Pb–N bonds (Table S1) and long Pb···O interactions in **1**, showed that the $V_{Pb} = 2.02$, thus long Pb···O interactions can be considered as bonding interactions which make compound **1** as a 1D supramolecular polymer (Fig. 1b). When compound **1** was immersed in distilled water, it converted to $[Pb(Q)_2]_n$ (**2**). The proposed reaction for this conversion is:

$$[Pb_2(Q-2-c)_2(OAC)_2]_n(1)\xrightarrow[inH_2O]{Immersing}[Pb(Q-2-c)]_n(2)+Pb(OAc)_2$$

which adjusts with removal of $Pb(OAc)_2$ from **1**. This conversion approved by formation of $Pb(OAc)_2$ precipitate after evaporation of water from reaction mixture. Structural transformations of compound **1** to **2** occurred by slowly dissolution of the crystals in protic