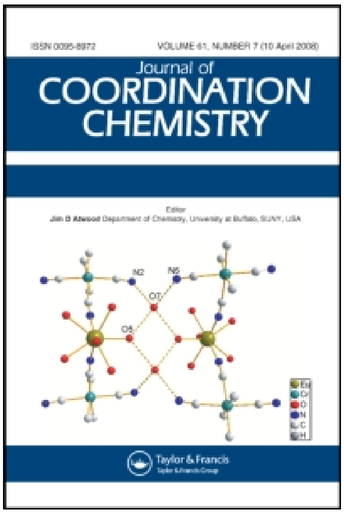

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Sonochemical syntheses and characterization of a new nano-sized 2-D lead(II) coordination polymer as precursor for preparation of PbBr(OH) nano-structure

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Nano-particles of a new 2-D Pb(II) coordination polymer, $[Pb(4\text{-pyc})(Br)(H_2O)]_n$ (**1**) (4-Hpyc = 4-pyridinecarboxylic acid), were synthesized by a sonochemical method. Crystal structure of **1** was determined by X-ray crystallography. The nano-particles were characterized by scanning electron microscopy, X-ray powder diffraction, IR spectroscopy, and elemental analyses. PbBr(OH) nano-structure was obtained by the calcination of nano-particles of **1** at 400°C.

Keywords: Nano-structure; Coordination polymer; Lead(II); Crystal structure

1. Introduction

Chemical and physical properties of solid materials strongly depend on both the size and the shape of the microscopic particles they are made from. This is especially true for materials with morphological features smaller than a micron in at least one dimension, which are commonly called nanomaterials. In these materials the ratio of surface area to volume is vastly increased when compared to compounds with larger grain sizes and quantum mechanical effects such as the ‘‘quantum size effect’’, which begin to play a significant role. These effects play only a minor role when going from macro to micro dimensions, but become increasingly important when reaching the nanometer size [1–9].

Coordination polymers exhibit potential applications as molecular wires [10], electrical conductors [11], molecular magnets [12], in host–guest chemistry [13], and in catalysis [14]. In contrast to inorganic materials, specific syntheses of nano-structured supramolecular compounds are surprisingly sparse. Equally the use of organometallic

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supramolecular compounds as precursors for the preparation of inorganic nanomaterials has not yet been investigated thoroughly.

Powerful ultrasound radiation used in this method creates microscopic bubbles in the solvent *via* cavitation. These bubbles collapse instantaneously, generating local hot spots with temperatures up to 5000°C and pressures of about 500 atm, within a few microseconds [15]. These extreme conditions provide an environment in which a large number of crystallization nuclei are formed, leading to the formation of many nano-sized particles, rather than just a few larger particles [15]. This method has been widely used to fabricate nano-sized particles of a variety of compounds [15, 16], and in recent years many such materials have been prepared using this method [16]. Moreover, lead compounds have important optical and electrical applications [17].

In this article we describe a simple sonochemical preparation of nano-sized particles of a new lead(II) coordination polymer, $[Pb(4\text{-pyc})(Br)(H_2O)]_n$ (4-Hpyc = 4-pyridinecarboxylic acid), and its use for the preparation of nano-structured PbBr(OH). Sonochemistry is one method that can be used to control the growth of particles.

2. Experimental

All reagents and solvents for syntheses and analyses were commercially available and used as received. A multiwave ultrasonic generator (Sonicator_3000; Misonix Inc., Farmingdale, NY, USA), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 600 W, was used for ultrasonic irradiation. IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer manufactured by Philips with monochromated Cu-Kα radiation and simulated XRD powder patterns based on single crystal data were prepared using the program Mercury [18]. The crystallite sizes of selected samples were estimated using the Sherrer formula. The samples were gold coated for characterizion with a scanning electron microscope. The crystal data collection was performed at 296 K on a Stoe-IPDS-2 diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS97 and refined on F^2 by full-matrix least-squares using SHELXL97. All hydrogens were easily found from the difference Fourier map and refined isotropically. Details of crystal data, data collection, structure solution, and refinement are given in table 1. The observed anisotropic thermal parameters and full lists of bond distances, angles, and torsion angles are given in Supplementary material.

To prepare nano-particles of **1**, 30 mL of a 0.1 mol L^{-1} solution of lead(II) acetate (3 mmol, 1.137 g), 4-Hpyc (3 mmol, 0.369 g), and sodium bromide (3 mmol, 0.306 g) in H_2O were positioned in a high-density ultrasonic probe, operating at 20 KHz with a maximum power output of 600 W. The obtained precipitates were filtered off, washed with water, and then dried in air. m.p. > 300°C. Found (%): C, 16.98; H, 1.50; N, 3.24. Calcd for $C_6H_6BrNO_3Pb$ (%): C, 16.94; H, 1.32; N, 3.29. IR bands: 692(m), 765(m), 852(w), 1392(vs), 1523(s), 1569(m), 1636(m), 3300(w).

Table 1. Crystal data and structure refinement for **1**.

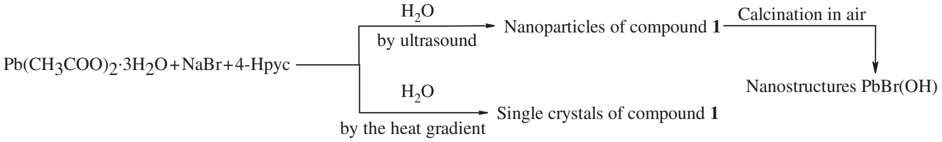
Empirical formula	$C_6H_6BrNO_3Pb$
Formula weight	425.20
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions (Å)	
a	6.0675(3)
b	6.9454(3)
c	19.8525(8)
Volume (Å^3), Z	836.61(6), 4
Calculated density (Mg m^{-3})	3.376
Absorption coefficient	24.905
F(000)	752
θ range for data collection (°)	2.05–26.5
Index ranges	$-7 \le h \le 7$, $-8 \le k \le 8$, $-24 \le l \le 23$
Reflections collected	6378
Independent reflections	1725 (R(int) = 0.0858)
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1738/3/117
Goodness-of-fit on F^2	1.231
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0493$ and $wR_2 = 0.1141$
R indices (all data)	$R_1 = 0.0490$ and $wR_2 = 0.1140$
Largest difference peak and hole (e Å^{-3})	2.163 and −2.453

To isolate single crystals of **1**, 4-Hpyc (1 mmol, 0.123 g), lead(II) acetate (1 mmol, 0.379 g), and sodium bromide (1 mmol, 0.102 g) were placed in the main arm of a branched tube [19]. Water 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 3–5 days, colorless crystals deposited in the cooler arm were isolated. The single crystals were filtered off, washed with acetone and ether, and air dried. Yield: 0.174 g, 40%, m.p. > 300°C. Found (%): C, 17.01; H, 1.53; N, 3.26. Calcd for $C_6H_6BrNO_3Pb$ (%): C, 16.94; H, 1.32; N, 3.29. IR bands: 692(m), 765(m), 850(w), 1391(vs), 1524(s), 1569(m), 1634(m), 3300(w).

3. Results and discussion

3.1. *Synthesis and characterization*

Sonochemistry is an elegant approach for the synthesis of nano-materials [15–17]. In this method molecules form nano-sized particles by the application of powerful ultrasound radiation (20 KHz–10 MHz) [16], mostly by instantaneous formation of a plethora of crystallization nuclei1 [5–17]. Reaction between 4-pyridinecarboxylic acid (4-Hpyc) with a mixture of lead(II) acetate and sodium bromide led to the formation of the new lead(II) 3-D coordination polymer $[Pb(4\text{-pyc})(Br)(H_2O)]_n$. Nano-particles of **1** were obtained by ultrasonic irradiation in water and single crystalline material was obtained using a heat gradient applied to a solution of the reagents (the ‘‘branched tube method’’). Scheme 1 gives an overview of the methods used for the synthesis of **1** using the two different routes.



Scheme 1. Synthetic methods for **1**.

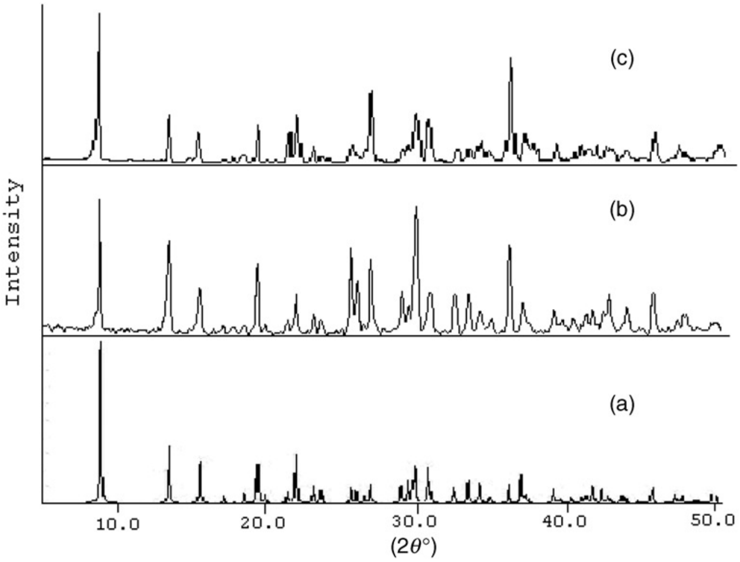


Figure 1. The XRD patterns of (a) simulated from single-crystal X-ray data of **1**; (b) nano-particles of **1** produced by sonochemical method; (c) bulk materials of **1** as synthesized by heat gradiant.

The elemental analysis and IR spectra of the nano-particles and of single crystals are indistinguishable. The relatively weak IR absorptions around 3025–3035 cm^{-1} are due to C–H modes involving aromatic ring hydrogens. Absorptions with variable intensity at 1391–1569 cm^{-1} correspond to the vibrations of the pyridine rings. The broad band at 3300 shows the existence of water in **1** [20].

Figure 1 shows the XRD pattern of **1** simulated from its single-crystal X-ray data (see below), the XRD pattern of **1** prepared by the sonochemical process, and typical **1** prepared by the branched tube method. Acceptable matches were observed between the simulated and experimental powder XRD patterns, indicating that the compounds obtained by sonochemical process have crystalline phases, almost identical to that obtained by the branched tube method.

The morphology of **1** prepared by the sonochemical method (figure 2) is composed of particles with sizes of about 30 nm. The mechanism of formation of this network structure needs to be further investigated; however, it may be a result of the crystal structure of the compound which is a 3-D network (see below), that is, the packing of the structure on a molecular level might have influenced the morphology of the nanostructure of the compound.

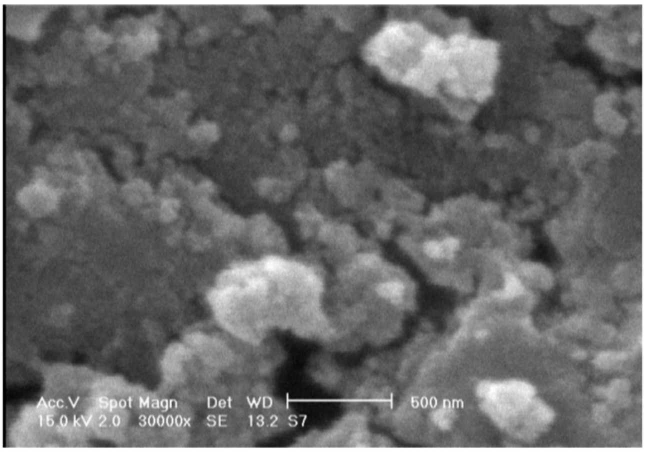


Figure 2. SEM photographs of **1** nanoparticles.

Table 2. Bond lengths (Å) and angles (°) for **1**.

Pb1–Br1	3.127(4)
Pb1–Br1$^{\mathrm{i}}$	3.132(4)
Pb1–O1	2.695(19)
Pb1–O2	2.58(2)
Pb1–O3	2.362(12)
Pb1–Br1–Pb1	151.58(7)
O3–Pb1–O2	82.4(6)
O3–Pb1–O1	81.6(5)
O2–Pb1–O1	49.7(7)
O3–Pb1–Br1	77.2(5)
O2–Pb1–Br1	119.9(6)
O1–Pb1–Br1	71.6(6)
O3–Pb1–Br1$^{\mathrm{i}}$	77.6(5)
O2–Pb1–Br1$^{\mathrm{i}}$	69.1(5)
O1–Pb1–Br1$^{\mathrm{i}}$	117.2(6)

$^{\mathrm{i}}\ -x+1/2,\ -y,\ z+1/2$.

Different concentrations of metal and ligand solutions (0.01, 0.05, and 0.1 mol L^{-1}) were tested. Appropriate nano-sized particles of **1** were obtained only under the above mentioned conditions and the produced nano-particles were used for the thermal analyses.

3.2. *Description of crystal structure*

Single-crystal XRD analysis (tables 1 and 2) of **1** shows that each lead is coordinated by two oxygens and one nitrogen of 4-pyc$^-$, one oxygen of water, and two bromides (figures 2 and 3). The 4-pyc$^-$ act as bridging ligands *via* a bidentate chelating carboxylate and the N_{pyridyl}. The 2-D coordination polymer of **1** is interlinked by water hydrogens with oxygens of 4-pyc$^-$, $O–H_{\mathrm{water}} \cdots O_{\mathrm{carboxylate}}$ hydrogen bonds (table 3),

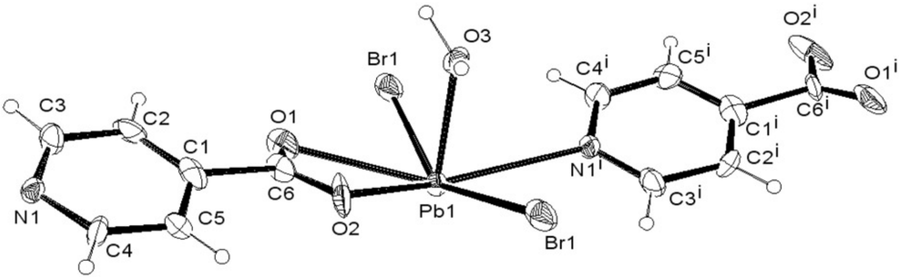


Figure 3. ORTEP diagram of **1** (i: $-x+1/2$, $-y$, $z+1/2$).

Table 3. Hydrogen bonds for **1** (Å and °).

D–H ··· A	*d*(D–H)	*d*(H ··· A)	*d*(D ··· A)	∠(DHA)
O3–H3A ··· O1[$1/2+x$, $1/2-y$, $1-z$]	0.9900	1.9800	2.74(3)	131.4(10)
O3–H3B ··· O2[$-1/2+x$, $1/2-y$, $1-z$]	1.0000	1.810	2.79(3)	163.6(10)

and secondary $Pb \cdots O_{carboxylate}$ interactions forming a 3-D supramolecule (figure 2). The $Pb \cdots Pb$ distance within [Pb(μ-4-pyc)(μ-Br)$_2$] moieties is 6.067(4) Å. The complex is a 2-D neutral metallopolymer bridged by Br^- and 4-pyc$^-$, forming an infinite framework as illustrated in figure 3 and "Supplementary material". There is one coordinated water and the structure of **1** may also be considered as a coordination polymer of lead(II) consisting of units with a building block of [Pb(H_2O)] with Br^- and 4-pyc$^-$ bridging two lead(II) ions. The X–Pb–Y angles suggest that there is a hole in the coordination sphere of the lead which has hemidirected geometry [21–23].

3.3. *Thermal analysis*

To examine the thermal stability of the nano-sized particles and single crystals of **1**, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 20 and 600°C under nitrogen (Supplementary material). Compound **1** is stable up to 150°C where it loses the coordinated waters with an endothermic effect at 152°C. The experimental mass loss of 4.30% is consistent with the calculated value of 4.23% for the elimination of one water molecule. After this **1** is stable, not decomposing till 342°C, at which temperature decomposition starts. Between this temperature and 600°C, decomposition of **1** occurs with a mass loss of 48.47% (Calcd 47.78%). Mass loss calculations show that the final decomposition product is PbO. Nano-sized **1** is less stable and starts to decompose at 330°C. Detectable decomposition of the nanoparticles of **1** thus starts at about 12°C earlier than that of its bulk counterparts, probably due to the much higher surface to volume ratio and more heat is needed to annihilate the lattices of the single crystals. The DTA curves displays two distinct endothermic effects at 154 and 324°C for the single crystals of **1** (Supplementary material) and two distinct exothermic effects at 399 and 485°C. The difference between the four maximum intensities in the DTA curves also indicate, in agreement with the TGA

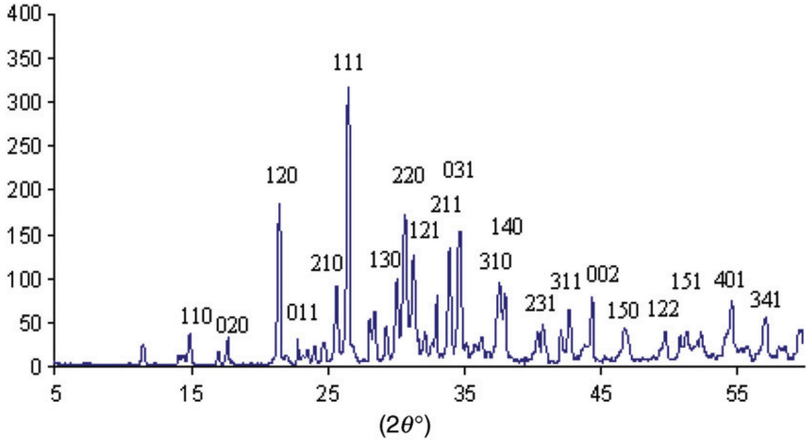


Figure 4. XRD pattern of PbBr(OH) prepared by calcinations of **1**.

results, lower stability of the nano-particles when compared with their single crystal counterparts.

Thermal decomposition of nano-sized **1** in air produced PbBr(OH) nano-structure (Supplementary material), as established by powder XRD patterns (figure 4). The obtained patterns match with the standard patterns of orthorhombic PbBr(OH) [24, 25]. This nano-structure shows a high degree of crystallinity with sharp and well-defined peaks in the XRD pattern. Orthorhombic PbBr(OH) nano-structure is the only crystalline phase present and all diffraction peaks were indexed with the PbBr(OH) lattices with the parameters of $a = 7.3850(8)$ Å, $b = 10.013(1)$ Å, $c = 4.0835(5)$ Å, $Z = 4$ in *Pnam* for PbBr(OH) (JCPDS card file No. 30-0697). No characteristic peaks of impurities are detected in the XRD pattern. The broadening of the peaks indicated that the structures are of nanometer scale.

4. Conclusion

A new Pb(II) coordination polymer, $[\mathrm{Pb(4\text{-}pyc)(Br)(H_2O)}]_n$ (4-Hpyc = 4-pyridinecarboxylic acid), has been synthesized using a thermal gradient approach and by sonochemical irradiation. Compound **1** was structurally characterized by single-crystal XRD. The crystal structure of **1** consists of a 3-D supramolecule and shows that the coordination number of $\mathrm{Pb^{II}}$ is six. Reduction of the particle size of the coordination polymers of **1** to a few dozen nanometers results in lower thermal stability when compared to the single crystalline samples. Calcination of nano-sized **1** under air produces nano-sized PbBr(OH). This study demonstrates that coordination polymers may be suitable precursors for the preparation of nanoscale materials and, depending on their packing, may produce different and interesting morphologies. We have synthesized different products by calcination, such as PbO, $\mathrm{PbI_2}$, PbS, $\mathrm{PbBr_2}$, and $\mathrm{Pb_2(SO_4)O}$, and it seems that the kind of precursors, the temperature, and the atmosphere are important factors in products obtained by calcination [26–30]. This is the first report of a synthesis of nano-sized structures of PbBr(OH). The precursor is one of the few samples prepared by sonication as an alternative synthetic procedure to form nano-sized structures of a coordination polymer.

Supplementary material

Crystallographic data for the structure reported in this article has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-739062.

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