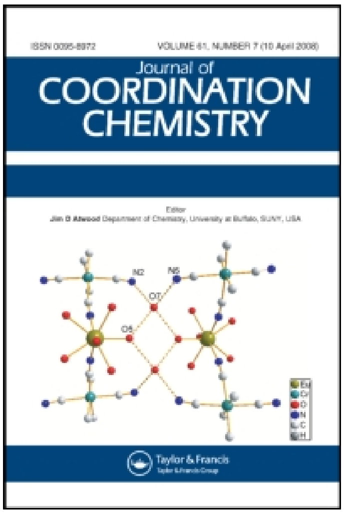

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Sonochemical synthesis and structural characterization of a nano-structure Pb(II) benzentricarboxylate coordination polymer: new precursor to pure phase nanoparticles of Pb(II) oxide

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Sonochemical synthesis and structural characterization of a nano-structure Pb(II) benzentricarboxylate coordination polymer: new precursor to pure phase nanoparticles of Pb(II) oxide

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Microcrystals of a new Pb(II) coordination polymer, $[Pb_2(1,3,5\text{-}HBTC)_2(H_2O)_4]\cdot H_2O$ (**1**) (1,3,5-H_3BTC = 1,3,5-benzentricarboxylic acid), was synthesized by a sonochemical method. The structure was characterized by scanning electron microscopy, X-ray powder diffraction, elemental analyses, and IR spectroscopy. Thermal stability was studied by thermal gravimetric and differential thermal analyses. After the calcination of nanosized **1** at 400°C, pure phase nanosized Pb(II) oxide has been produced.

Keywords: Nanoparticle; Coordination polymer; Pb(II); PbO

1. Introduction

Metal coordination polymers have been widely studied as an important interface between synthetic chemistry and materials science. Specific structures, properties, and reactivities of coordination polymers were not found in mononuclear compounds [1–3] and led to a wide range of potential applications [4–8].

Several different synthetic approaches have been offered for the preparation of coordination compounds [9]: (1) slow diffusion of reactants into a polymeric matrix, (2) diffusion from the gas phase, (3) evaporation of the solvent at ambient or reduced temperatures, (4) precipitation or recrystallization from a mixture of solvents, (5) temperature-controlled cooling, and (6) hydrothermal synthesis. In this article, we describe a simple sonochemical preparation of a Pb(II) coordination polymer with 1,3,5-benzentricarboxylic acid (1,3,5-H_3BTC), $[Pb_2(1,3,5\text{-}HBTC)_2(H_2O)_4]\cdot H_2O$ (**1**), and the use of this new compound for the preparation of PbO nanoparticles. In sonochemistry, molecules undergo a chemical reaction due to the application of powerful ultrasound radiation (20 KHz–10 MHz) [10]. Ultrasound induces chemical changes because of cavitation phenomena involving the formation, growth, and instantaneously implosive collapse of bubbles in liquid, which can generate local hot

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spots having a temperature of roughly 5000°C, pressures of about 500 atm, and a lifetime of a few microseconds [11]. These extreme conditions can drive chemical reactions to a variety of nano compounds [10]. In recent years many nanomaterials have been prepared by this method [12].

There are different methods such as microwave–solvothermal synthesis [13, 14], hydrothermal route [15, 16], and surfactant–ligand co-assisting solvothermal method [17] used to synthesize nano- and micro-crystalline PbO.

2. Experimental

All reagents and solvents were commercially available and used as received. A multiwave ultrasonic generator (Sonicator_3000; Misonix Inc., Farmingdale, NY, USA) was used. 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. The thermal behavior was measured with a PL-STA 1500 apparatus with a temperature ramp of $20^{\circ}\mathrm{C\,min^{-1}}$. 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 Mercury [18]. Crystallographic measurements were made using a Bruker APEX area-detector diffractometer. The intensity data were collected using graphite monochromated Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. Structure solution and refinement were done using the SHELXTL program package [19]. The samples were characterized with a scanning electron microscope (SEM) (Philips XL 30) with gold coating.

To prepare the microcrystals of $[Pb_2(1,3,5\text{-}HBTC)_2(H_2O)_4]\cdot H_2O$ (**1**), a 15 mL of a 0.01 M solution of Pb(II) nitrate in water was positioned in a high-density ultrasonic probe and 15 mL of a 0.01 M 1,3,5-H_3BTC in water was added dropwise to that solution. After addition, the solution remained in the bath for a selected aging time at a selected temperature. The obtained precipitates were filtered, washed with EtOH, and then dried. The same reaction was repeated in EtOH to find the best morphology. The obtained precipitates were filtered off and then dried in air.

Product: m.p. >300°C, yield: 0.155 g (67%). Found (%): C, 23.31; H, 1.75; O, 29.22. Calcd for $C_{18}H_{18}O_{17}Pb_2$ (%): C, 23.53; H, 1.95; O, 29.51. IR bands: 507w, 714s, 1257s, 1368s, 1522s, 1599m, 1687m, and 3335m.

To isolate single crystals of $[Pb_2(1,3,5\text{-}HBTC)_2(H_2O)_4]\cdot H_2O$ (**1**), 1,3,5-H_3BTC (1 mmol, 0.210 g) and Pb(II) nitrate (0.137 g, 0.5 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 was immersed in an oil bath at 60°C, while the other arm was kept at ambient temperature. After 6 days, colorless crystals that deposited in the cooler arm were isolated, filtered off, washed with acetone and ether, and air dried.

Product: m.p. >300°C, yield: 0.103 g (45%). Found (%): C, 23.45; H, 1.70; O, 29.20. Calcd for $C_{18}H_{18}O_{17}Pb_2$ (%): C, 23.53; H, 1.95; O, 29.51. IR bands: 506w, 715s, 1257s, 1364s, 1522s, 1597m, 1688m, and 3334m.

For the preparation of bulk materials of **1,** single crystals prepared by the branched tube were ground up.

3. Results and discussion

Reaction between "1,3,5-H_3BTC" and Pb(II) nitrate using two different routes provided crystalline materials of the general formula, $[Pb_2(1,3,5\text{-}HBTC)_2(H_2O)_4] \cdot H_2O$ (**1**). Single crystalline material was obtained using a heat gradient applied to a solution of the reagents (the "branched tube method"), and micro-crystals were prepared by the ultrasonication of the aqueous solution. Elemental analyses and IR spectra of the nanosized and single crystalline material are indistinguishable with characteristic absorption bands for $HBTC^{2-}$ and water. Absorption bands with variable intensity in the frequency range 1400–1580 cm^{-1} correspond to ring vibrations of the phenyl of $HBTC^{2-}$, and vibrations of the carboxylate groups are observed at 1364 and 1522 cm^{-1} [20]. Peaks at 3334 and 1522 cm^{-1} are due to the stretching and bending of H_2O ligand.

The simulated XRD pattern from single crystal X-ray data of **1** is compared with the XRD pattern of microcrystalline **1** prepared by the sonochemical process. Acceptable matches, with very slight differences in 2θ, were observed between the simulated and experimental XRD patterns of micro-structure (Supplementary material). This indicates that the compound is a single crystalline phase, identical to that obtained by single crystal diffraction. The significant broadening of the peaks of microcrystals indicates that the crystals are of micrometer dimensions. For further investigation we used ethanol as solvent in the sonochemical process, but sizes of **1** were not in nanoscales. The SEM (Supplementary material) of **1** prepared by the sonochemical methods show that they are composed of crystals with sizes of about 1.2 μm.

Single crystal XRD analysis of **1** (figures 1 and 2; tables 1 and 2) produced by the branched tube method reveals that Pb(II) is coordinated by 1,3,5-$HBTC^{2-}$ and two waters; the complex in the solid state (figure 2) is a 3-D polymeric network. The coordination number of Pb(II) is nine (figure 1) with each "1,3,5-$HBTC^{2-}$" anion hepta-dentate, connecting four Pb^{+2} ions. One carboxylate group is both bidentate and bridging (totally tetradentate) in a μ-2,4 mode. Two oxygens of one carboxylate (marked *) coordinate to a Pb(II) and also bridge two adjacent Pb(II) ions. The other carboxylate group of 1,3,5-$HBTC^{2-}$ (marked #) is only bidentate (marked *). The –COOH is monodentate and one –OH is not coordinated to Pb(II).

In **1**, the lone pair on lead is "inactive" in the solid state and the arrangement of oxygens does not suggest any gap or hole in coordination geometry [21]. Hence, the geometry with respect to Pb-1 is holodirected. The inactive lone pair for Pb-1 with coordination number nine and *hard* donor atoms is common [21].

There is a lack of solvent bound to Pb(II) [21] and water is rarely coordinated. $[Pb_2(1,3,5\text{-}HBTC)_2(H_2O)_4] \cdot H_2O$ contains five water molecules, one disordered and not coordinated.

The uncoordinated oxygens of 1,3,5-$HBTC^{2-}$ and uncoordinated water in **1** form O–H ··· O hydrogen bonds (figure 3 and table 3).

To examine the thermal stability of the microcrystals and single crystalline samples of **1**, thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were

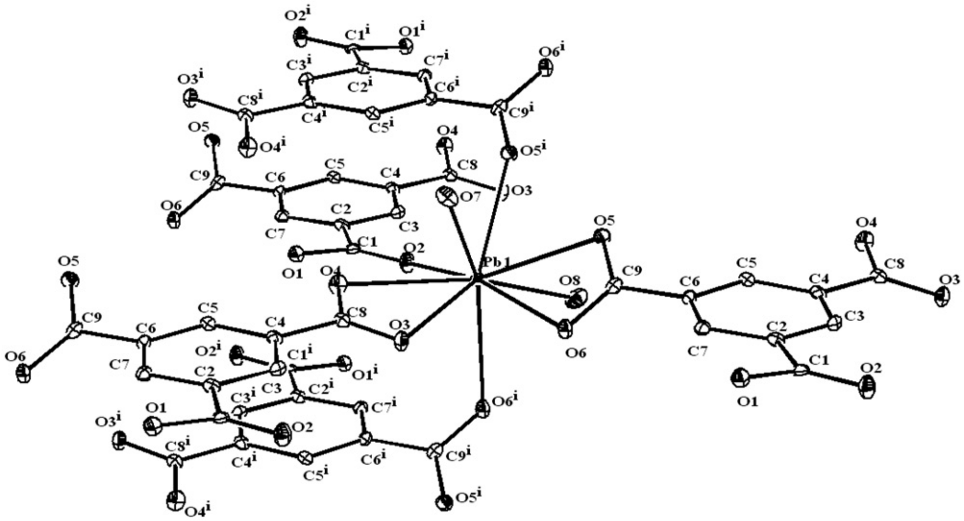

Figure 1. X-ray crystal structure (ORTEP representation) of $[Pb_2(1,3,5\text{-}HBTC)_2(H_2O)_4]\cdot H_2O$ (**1**) showing coordination environment around Pb(II). Ellipsoids 50% probability. Hydrogen atoms are omitted for clarity.

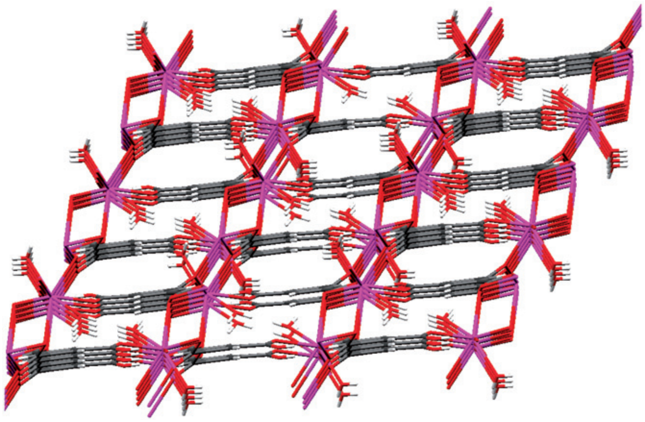

Figure 2. A fragment of the 3-D framework in **1**.

carried out between 25°C and 700°C under nitrogen flow (Supplementary material). Single crystals of **1** are stable to 90°C temperature at which the water molecules begin to be removed with a mass loss *ca* 9.80%. The solid residue formed at 170°C is water-free $[Pb(1,3,5\text{-}HBTC)]_n$, that is stable to 400°C. Decomposition of the "1,3,5-HBTC^{2-}" takes place between 400°C and 450°C with an exothermic effect at 460°C. The TGA curve of the micro-crystals material has the same general appearance as its single crystalline counterpart. Micro-crystals of **1** are slightly less stable and start to gradually decompose at *ca* 70°C.

Nanoparticles PbO have been generated by the thermal decomposition of microcrystals of **1**. The final product upon calcination is, based on their XRD patterns (figure 4), orthorhombic PbO. The phase purity of the as-prepared orthorhombic PbO

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

Identification code	**1**
Empirical formula	$C_{18}H_{18}O_{17}Pb_2$
Formula weight	920.72
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	7.3696(12)
b	8.1418(13)
c	10.1221(16)
β	105.046(2)
Volume (Å^3), Z	550.05(15), 1
Calculated density (mg m^{-3})	2.780
Absorption coefficient (mm^{-1})	15.375
$F(000)$	426
Crystal size (mm^3)	0.11 × 0.10 × 0.08
θ range for data collection (°)	2.67–31.20
Index ranges	$-9 \le h \le 9$; $-10 \le k \le 10$; $-13 \le l \le 13$
Reflections collected	5736
Independent reflections	2719 [R(int) $=0.0228$]
Absorption correction	Multi-scan
Max. and min. transmission	0.292 and 0.241
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2719/13/194
Goodness-of-fit on F^2	1.040
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0202$ and $wR_2 = 0.0435$
R indices (all data)	$R_1 = 0.0225$ and $wR_2 = 0.0447$
Largest difference peak and hole (e Å^{-3})	1.322 and −1.316

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

Pb1–O3	2.596(3)
Pb1–O4	2.693(3)
Pb1–O5	2.641(3)
Pb1–O6^{i}	2.621(3)
Pb1–O6	2.732(3)
Pb1–O1	3.095(14)
O3–Pb1–O6^{i}	71.77(8)
O7–Pb1–O6^{i}	81.77(9)
O3–Pb1–O5	115.54(9)
O7–Pb1–O5	76.08(9)
O6^{i} –Pb1–O5	49.99(8)
O3–Pb1–O4	49.38(8)
O7–Pb1–O4	73.51(9)
O6^{i}–Pb1–O4	120.75(8)

$^{i}-x, -y, -z$.

nanoparticles are completely obvious and all diffraction peaks are perfectly indexed to the orthorhombic PbO structure with the lattice parameters of $a = 5.8931$ Å, $b = 5.4904$ Å, $c = 4.7528$ Å, $Z = 4$ and space group = *Pbcm* which are in JCPDS card file No. 77-1971. No characteristic peaks of impurities are detected in the XRD pattern. SEM images of PbO nanoparticles produced by the calcination of **1** are provided in Figure 5.

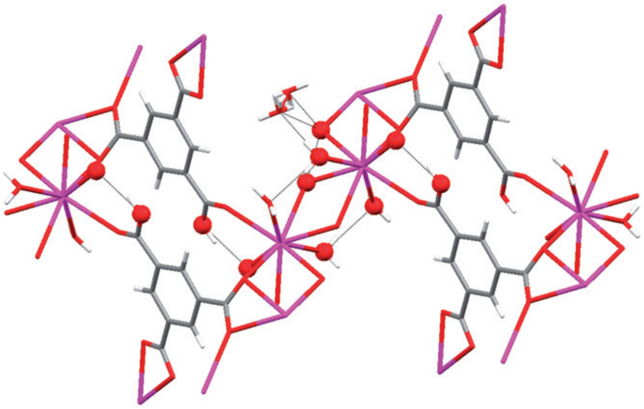

Figure 3. Hydrogen bonding in **1**.

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

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O1–H1···O4 [$-1+x$, $-1+y$, $-1+z$]	0.84	1.77	2.591(4)	165
O7–H7···O9	0.82	1.84	2.652(8)	171
O7–H7···O8 [$-1+x$, $-1+y$, $-1+z$]	0.813(19)	1.95(2)	2.760(4)	171
O8–H8···O3 [$1-x$, $1-y$, $1-z$]	0.825(19)	2.05(3)	2.818(4)	154

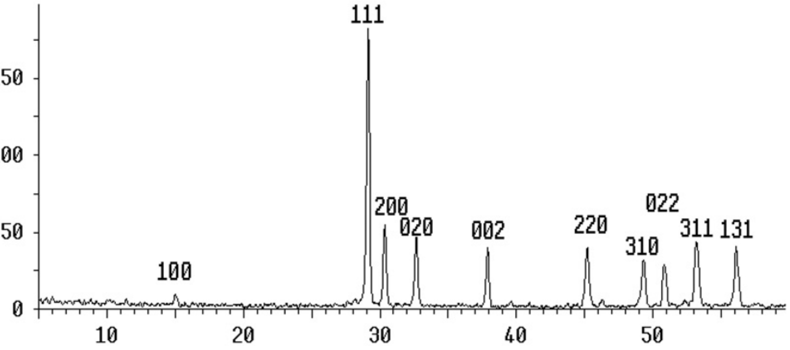

Figure 4. XRD pattern of PbO nanoparticles prepared by the calcination of microcrystals of **1**.

4. Conclusion

A Pb(II) coordination polymer, $[Pb_2(1,3,5\text{-}HBTC)_2(H_2O)_4]\cdot H_2O$ (**1**) (1,3,5-H_3BTC = 1,3,5-benzentricarboxylic acid), has been synthesized using a thermal gradient approach and by a sonochemical method. Many Pb(II) coordination polymers have been synthesized with different coordination numbers. For example, the single-crystal structure of $[Pb_2(phen)_4(hfa)_2(\mu\text{-}NO_3)_2]$ [22] shows that the complex has a dimeric unit as a result of nitrate bridging with the coordination number of eight, or two new 2-D coordination polymers, $[Pb_2(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}2\text{-sb})_2(DMF)]_n$ and $\{[Pb_2(\mu\text{-}4,4'\text{-bipy})(\mu\text{-}2\text{-sb})_2(H_2O)_2]\cdot H_2O\}_n$ [23], have seven- and eight-coordinate

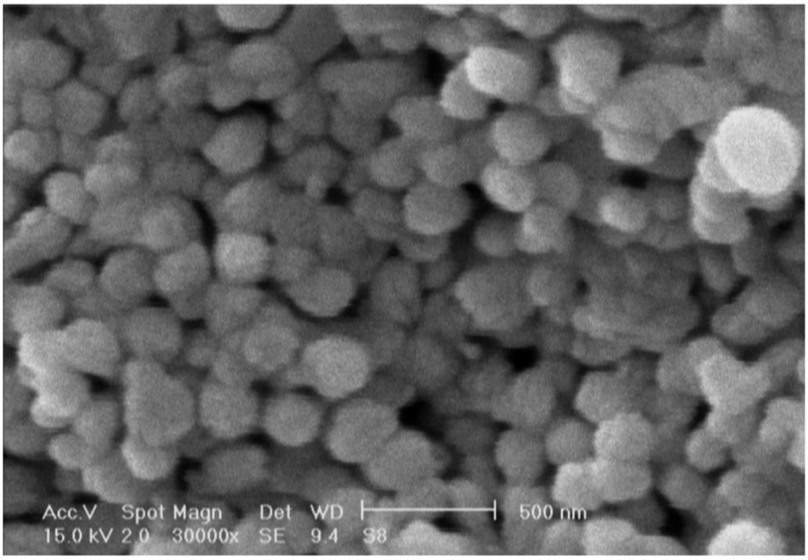

Figure 5. SEM photographs of PbO nanoparticles (produced by calcinations of microcrystals of $[Pb_2(1,3,5\text{-HBTC})_2(H_2O)_4]\cdot H_2O$ (**1**)).

holodirected geometries. Some Pb(II) coordination polymers with 2-D structures were reported, for instance, in the Pb(II) complexes of *o*-phthalate [24], $[Pb(pht)(H_2O)]_n$, can be observed. However, $[Pb(\mu\text{-4-pyc})(\mu\text{-Br})]_n$ [25] shows a 3-D structure with coordination number nine and holodirected geometry. Reduction of the crystal size of the coordination polymers to a few dozen micrometers result in lower thermal stability compared to the single crystalline samples. Calcination of **1** produces PbO nanoparticles. There have been few reports of nanoparticles of pure phase PbO from coordination polymers. This article is one of the few samples using sonication as an alternative synthetic procedure to form coordination polymers [26–30]. This method for the preparation of coordination polymers has advantages such as shorter reaction times, better yields, and nanosize coordination polymer.

Supplementary material

Crystallographic data for the structures reported in this article has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-722465. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44–1223/336033; Email: deposit@ccdc.cam.ac.uk].

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