



Structural and X-ray powder diffraction studies of nano-structured lead(II) coordination polymer with η^2 Pb···C interactions

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ABSTRACT

A new nano-sized Pb(II) one-dimensional coordination polymer with η^2 Pb–C interactions, $[\text{Pb}_2(\mu_3\text{-ba})_2(\mu_2\text{-ba})_2]_n$ (**1**) [ba^- = benzylacetylacetonate] has been synthesized and characterized by SEM, X-ray powder diffraction, IR spectroscopy and elemental analyses. Single-crystal X-ray diffraction shows the coordination number of Pb(II) ions is seven and the lead atoms have hemidirected coordination sphere containing involving Pb···C interactions, $\text{C}_2\text{O}_7\text{Pb}$. PbO nanoparticles were obtained by calcinations of the nano-sized compound **1** at 600 °C.

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1. Introduction

β -dicarbonyl compounds include a class of important and extensively employed ligands [1,2]. They are very versatile and besides the usual bidentate behavior of monoanions, exhibit a great variety of coordination modes [2]. Equilibrium mixtures of the tautomeric keto and enol forms obtainable in β -diketones could be favored by replacement of the terminal groups by electron-withdrawing or electron-releasing substituents [3]. From structural study of Pb(II) complex of dibenzoylmethane (DBMH) ligand [4], it has been argued that polyhaptic-aromatic interactions play an important role in the solid state lattices. So it can be anticipated that this might be true for the Pb(II) complex of the benzylacetylacetonate (Hba). The Hba ligand contains both aliphatic and aromatic groups and because of its ability for forming of polyhaptic interactions may also be a good candidate for the investigation of the “stereo-chemical activity” of valence shell electron lone pairs in the lead(II) compounds.

Several different synthetic approaches have been offered for the preparation of coordination compounds [5,6]. 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. In this paper we describe a simple

synthetic sonochemical preparation of nano-structures of a new lead(II) coordination polymer with the benzylacetylacetonate (ba^-) and using of this new compound for preparation of PbO nanoparticles. PbO powders remain widely used because they are cheap and reliable materials for battery applications [7]. Sonochemistry is the research area in which molecules undergo a chemical reaction due to the application of powerful ultrasound radiation (20 KHz–10 MHz) [8]. Ultrasound induces chemical changes due to cavitations phenomena involving the formation, growth, and instantaneously implosive collapse of bubbles in liquid, which can generate local hot spots having a temperature of roughly 5000 °C, pressures of about 500 atm, and a lifetime of a few microseconds [9]. These extreme conditions can drive chemical reactions which have been developed to fabricate a variety of nano compounds [8]. In the recent years many kinds of nanomaterials have been prepared by this method [7].

2. Experimental

All reagents for the synthesis and analysis 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 the ultrasonic irradiation. Microanalyses were carried out using a Heraeus CHN–O– Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded using Perkin–Elmer 597 and Nicolet

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510P spectrophotometers. The structure has been solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXL [10]. Crystal data: $C_{40}H_{36}O_8Pb_2$, $M = 1059.09$, crystal system = orthorhombic, space group = $P2_12_12_1$, $a = 7.7515(12)$, $b = 20.604(3)$, $c = 22.149(3)$ Å, $V = 3537.5(9)$ Å³, D_c ($Z = 4$ f.u.) = 1.989 Mg/m³, $F(0\ 0\ 0)$ 2016. $R(wR) = 0.0183$ (0.0429) for 7964 reflections with $I > 2\sigma(I)$ and also the $R(wR) = 0.0205$ (0.0433) for all reflections, the Flack parameter is 0.00(7). The observed anisotropic thermal parameters, the calculated structure factors, and full lists of bond distances, bond angles and torsion angles are given in the Supplementary material. The molecular structure plot and simulated XRD powder pattern based on single-crystal data were prepared using MERCURY software [11]. X-ray powder diffraction (XRD) measurements were performed using a X'pert diffractometer of Philips company with mono chromatized Cu α radiation. The samples were characterized with a scanning electron microscope (SEM) (Philips XL 30) with gold coating.

To prepare the nano-structured $[Pb_2(\mu_3\text{-ba})_2(\mu_2\text{-ba})_2]_n$ (**1**), a 10 ml of 0.01 M solution of lead(II) acetate in MeOH was positioned in an ultrasonic bath. Into this solution 20 ml of a 0.02 M solution of the ligand ba^- was added dropwise in during 1 h. After the end of the titration the solution was remained in the bath for a selected aging time at a selected temperature. The temperature was varied between the room temperature, 40 and 70 °C. The obtained precipitates were filtered, subsequently washed with EtOH and then dried. d.p. = 200 °C, Yield: 0.450 g (85%). Anal. Calc. for $C_{40}H_{36}O_8Pb_2$: C, 45.32; H, 3.40; Pb, 39.09. Found: C, 45.80; H, 3.50; Pb, 39.40%. IR data (cm^{-1}): 3054(w), 2993(w), 1589(vs), 1558(s), 1519(vs), 1481(s), 1450(m), 1388(s), 1265(m), 1002(m), 765(m), 709(m). ¹H NMR: 2.10 (s, 6H), 5.90 (s, 2H), 7.3–7.8 (m, 10H). The different concentrations of lead(II) acetate and ligand ba^- solution (0.1 and 0.001 M) with same aging time, 1 h, were tested, however appropriate nano-size of compound **1** obtained under the mentioned conditions with same yield.

To isolate single crystals of $[Pb_2(\mu_3\text{-ba})_2(\mu_2\text{-ba})_2]_n$ (**1**), Hba (1 mmol, 0.162 g) and lead(II) acetate (0.189 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 immersed in an oil bath at 60 °C while the other arm was kept at ambient temperature. After 6 days, yellow crystals that deposited in the cooler arm were isolated, filtered off, washed with acetone and ether and air dried. d.p. = 205 °C.

Yield: 0.264 g (50%). Anal. Calc. for $C_{40}H_{36}O_8Pb_2$: C, 45.32; H, 3.40; Pb, 39.09. Found: C, 45.82; H, 3.56; Pb, 39.50%. IR data (cm^{-1}): 3054(w), 2993(w), 1589(vs), 1558(s), 1519(vs), 1481(s), 1450(m), 1388(s), 1265(m), 1002(m), 765(m), 709(m). ¹H NMR: 2.10 (s, 6H), 5.90 (s, 2H), 7.3–7.8 (m, 10H).

3. Results and discussion

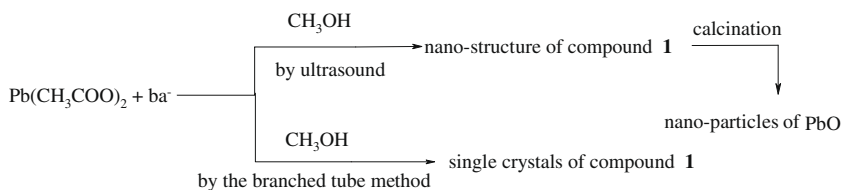
The reaction between “Hba” and lead(II) acetate using two different routes provided crystalline materials of the general formula $[Pb_2(\mu_3\text{-ba})_2(\mu_2\text{-ba})_2]_n$ (**1**). Scheme 1 gives an overview of the methods used for the synthesis of $[Pb_2(\mu_3\text{-ba})_2(\mu_2\text{-ba})_2]_n$ (**1**) using the two different routes. The elemental analysis and IR spectra of

the nano-wires and the single crystalline material are indistinguishable. The IR spectra of the nano-wires and the single crystalline materials show characteristic absorption bands for the ba^- ligand. The absorption bands with variable intensity in the frequency range 1400–1580 cm^{-1} correspond to ring vibrations of the ph moiety of the ba^- ligands, and vibrations of the carbonyl group are observed at 1388 and 1519 cm^{-1} [12].

Fig. 1a shows the simulated XRD pattern from single crystal X-ray data (see below) of compound **1** in comparison with the XRD pattern of a bulk materials as synthesized of compound **1** and nano-wires typical sample of **1** prepared by sonochemical process (Fig. 1b and c, respectively). Acceptable matches, with very slight differences in 2θ , were observed between the simulated (Fig. 1a) and experimental powder X-ray diffraction patterns of bulk and nano-structure (Fig. 1b and c, respectively). This indicates that the compound is a single crystalline phase and that this phase is identical to that obtained by single crystal diffraction. The significant broadening of the peaks of nano-structure (Fig. 1c) indicates that the particles are of nanometer dimensions. Estimated by the Sherrer formula, $D = 0.891\lambda/\beta\cos\theta$, where D is the average grain size, λ the X-ray wavelength (0.15405 nm), and θ and β the diffraction angle and full-width at half maximum of an observed peak, respectively, the average size of the particles is 65 nm, which is in agreement with that observed by scanning electron microscopy, as shown in Fig. 2.

Fig. 2a indicates the original morphology of the nano-wires with the diameter varying between 80 and 120 nm. The morphology of compound **1** prepared by the sonochemical method (Fig. 2a) is very interesting and it is composed of nano-wires with sizes of about 80–120 nm. The different concentrations of lead(II) acetate and ligand ba^- solution (0.1, 0.01 and 0.001 M) were tested, however appropriate nano-size of compound **1** obtained under concentration of 0.01 and 0.001 M. According to Fig. 2b, the particles obtained under concentration of 0.001 M have large sizes and the morphology of compound is formed from mixture of nano-plate and nano-wires. It is interesting the one-dimensional coordination polymer, $[Pb_2(\mu_3\text{-ba})_2(\mu_2\text{-ba})_2]_n$ (**1**), see below, produces nano-structure with one-dimensional morphology, showing coordination-induced formation upon morphology of nano-structure.

Single crystal X-ray analysis reveals that compound $[Pb_2(\mu_3\text{-ba})_2(\mu_2\text{-ba})_2]_n$ (**1**) crystallizes in a orthorhombic system with space group of $P2_12_12_1$. Determination of the structure of the compound **1** by X-ray crystallography showed (Fig. 3) there are two crystallographically independent lead(II) ions with seven coordinate, $Pb1O_7$ and $Pb2O_7$ (Fig. 3) units and also there is a relatively strength interaction between the Pb1 and Pb2 atoms. The crystal structure comprises a one-dimensional polymeric network bridged by ba^- anions. The separation between the two lead atoms in this complex is 3.750(4) Å, which is smaller to the sum of van der Waals radii of two Pb(II) [13–16]. There are four independent ba^- ligands in this compound. Two of the “ ba^- ” ligands act as both bidentate and bridging group from two sides (totally tetra-donors), where two oxygen atoms of the ba^- ligands coordinate to a lead(II) ion and also they bridge the two adjacent lead(II) ions. Two other ba^- ligands act as bidentate and bridging group from one side.



Scheme 1. Materials produced and synthetic methods.

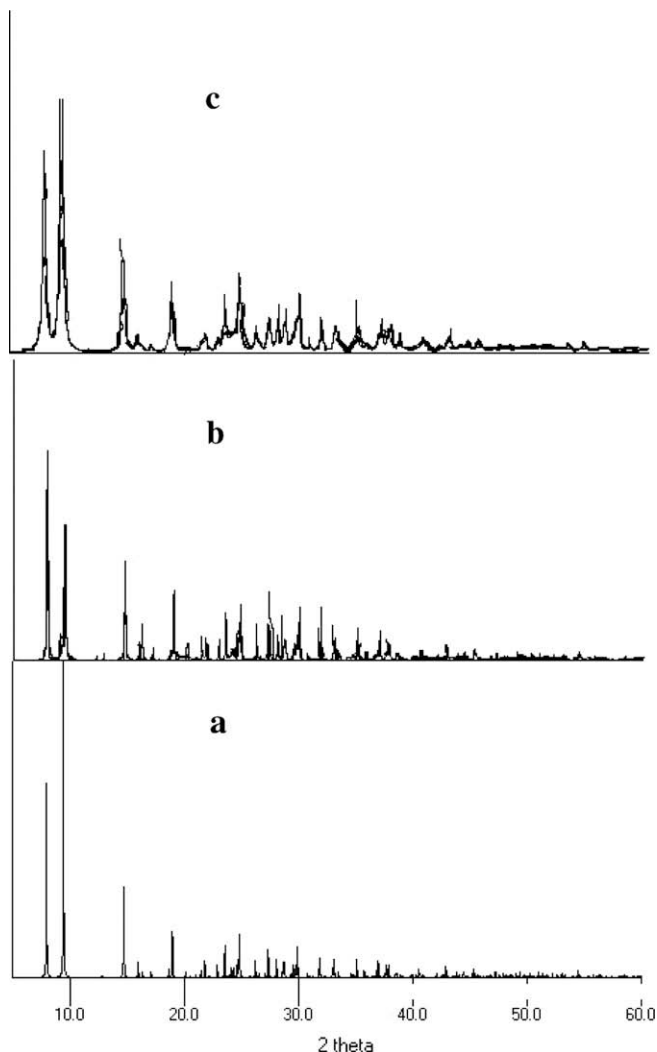


Fig. 1. The XRD patterns of (a) simulated from single crystal X-ray data of compound $[\text{Pb}_2(\mu_3\text{-ba})_2(\mu_2\text{-ba})_2]_n$. (1) (b) Bulk materials as synthesized of compound $[\text{Pb}_2(\mu_3\text{-ba})_2(\mu_2\text{-ba})_2]_n$. (1) and (c) nano-wires of compound $[\text{Pb}_2(\mu_3\text{-ba})_2(\mu_2\text{-ba})_2]_n$. (1).

The arrangement of ba^- ligands suggests a gap or hole in coordination geometry around the two lead(II) ions, $[\text{O}2\text{-Pb}1\text{-O}4$ and $\text{O}8\text{-Pb}2\text{-O}3$ angles are $132.76(2)$ and $129.01(8)^\circ$ in the Pb1 and Pb2 in compound **1**, respectively], occupied possibly by a “stereo-chemically active” lone pair of electrons on lead(II) ions [17]. Hence, the geometry with respect to Pb1 and Pb2 are hemidirected (Fig. 4a and b) [17,18].

A search was made generally for $\text{Pb}\cdots\text{C}$ approaches and it appears that Pb atoms in compound **1** may also be involved in an η^2 interaction with the phenyl groups far from the bridging-O donor atom. Thus, both Pb1 and Pb2 atoms are linked to two carbon atoms of phenyl groups, with distances $\text{Pb}1\cdots\text{C}35$, $\text{Pb}1\cdots\text{C}45$, $\text{Pb}2\cdots\text{C}15$ and $\text{Pb}2\cdots\text{C}25$ of $3.973(2)$, $3.585(2)$, $3.943(2)$, and $3.554(3)$ Å, respectively (Fig. 3a and b). Hence, the Pb^{II} coordination sphere is completed and rather than a PbO_7 coordination sphere, the complex can be considered to contain a dihapto interactions ($\text{C}_2\text{O}_7\text{Pb}$) center with an irregular nine coordination number but “holodirected” coordination sphere (Fig. 4c). The reported $\text{Pb}\cdots\text{C}$ separations range is $3.083\text{--}4.05$ Å in species $[\text{Pb}(\text{o-xylene})_2\text{-}(\text{Cl}_2\text{AlCl}_2)_2]$, $[\text{Pb}(\eta^6\text{-C}_6\text{H}_6)(\text{Cl}_2\text{AlCl}_2)_2]\cdot\text{C}_6\text{H}_6$ [19] $[\text{Pb}_2\{\text{SeC}_6\text{H}_2(\text{CF}_3)_3\}_4(\text{toluene})_2]$ [20] and $[\text{Pb}_2(\text{DBM})_4]$ [5]. Thus, $\text{Pb}\cdots\text{C}$ interactions in compound **1** appear to be yet another factor which can make varying contributions to the stability of complexes of this metal ion.

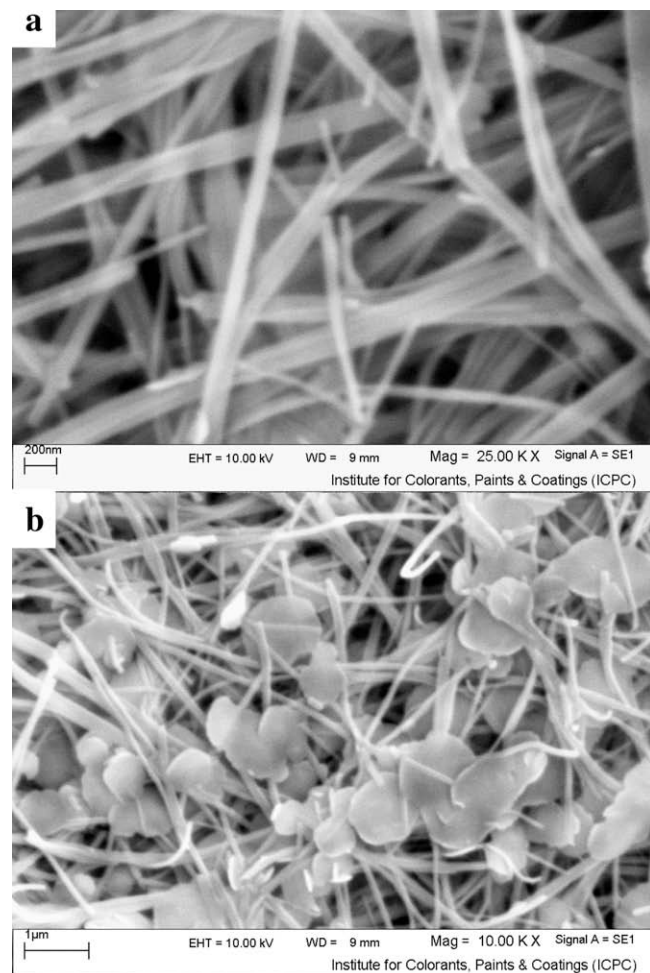


Fig. 2. SEM images of $[\text{Pb}_2(\mu_3\text{-ba})_2(\mu_2\text{-ba})_2]_n$. (1) nanostructures for various concentration of Pb^{2+} and ba^- ion (a) Pb^{2+} (0.01 M) and ba^- (0.02 M) (b) Pb^{2+} (0.001 M) and ba^- (0.002 M).

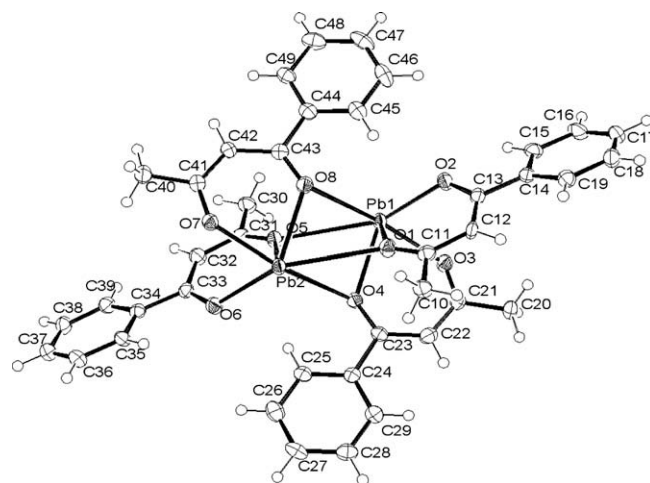


Fig. 3. X-Ray crystal structure (ORTEP representation) $[\text{Pb}_2(\mu_3\text{-ba})_2(\mu_2\text{-ba})_2]_n$. (1) Selected bond lengths (Å) and angles $[\text{Pb}_2(\mu_3\text{-ba})_2(\mu_2\text{-ba})_2]_n$: $\text{Pb}1\text{-O}3$ 2.331(2), $\text{Pb}1\text{-O}1$ 2.349(2), $\text{Pb}1\text{-O}2$ 2.378(2), $\text{Pb}1\text{-O}4$ 2.488(2), $\text{Pb}1\text{-O}5$ 3.049, $\text{Pb}1\text{-O}8$ 3.077, $\text{Pb}2\text{-O}7$ 2.317(2), $\text{Pb}2\text{-O}5$ 2.332(2), $\text{Pb}2\text{-O}6$ 2.378(2), $\text{Pb}2\text{-O}8$ 2.487(2), $\text{Pb}2\text{-O}3$ 2.800, $\text{Pb}2\text{-O}1$ 3.040, $\text{O}3\text{-Pb}1\text{-O}1$ 88.41(9), $\text{O}3\text{-Pb}1\text{-O}2$ 75.71(9), $\text{O}1\text{-Pb}1\text{-O}2$ 73.78(8), $\text{O}3\text{-Pb}1\text{-O}4$ 73.33(8), $\text{O}1\text{-Pb}1\text{-O}4$ 70.60(9), $\text{O}7\text{-Pb}2\text{-O}5$ 88.18(9), $\text{O}7\text{-Pb}2\text{-O}6$ 75.46(9), $\text{O}5\text{-Pb}2\text{-O}6$ 74.22(8), $\text{O}7\text{-Pb}2\text{-O}8$ 73.03(8), $\text{O}5\text{-Pb}2\text{-O}8$ 70.42(8), $\text{O}6\text{-Pb}2\text{-O}8$ 132.68(8).

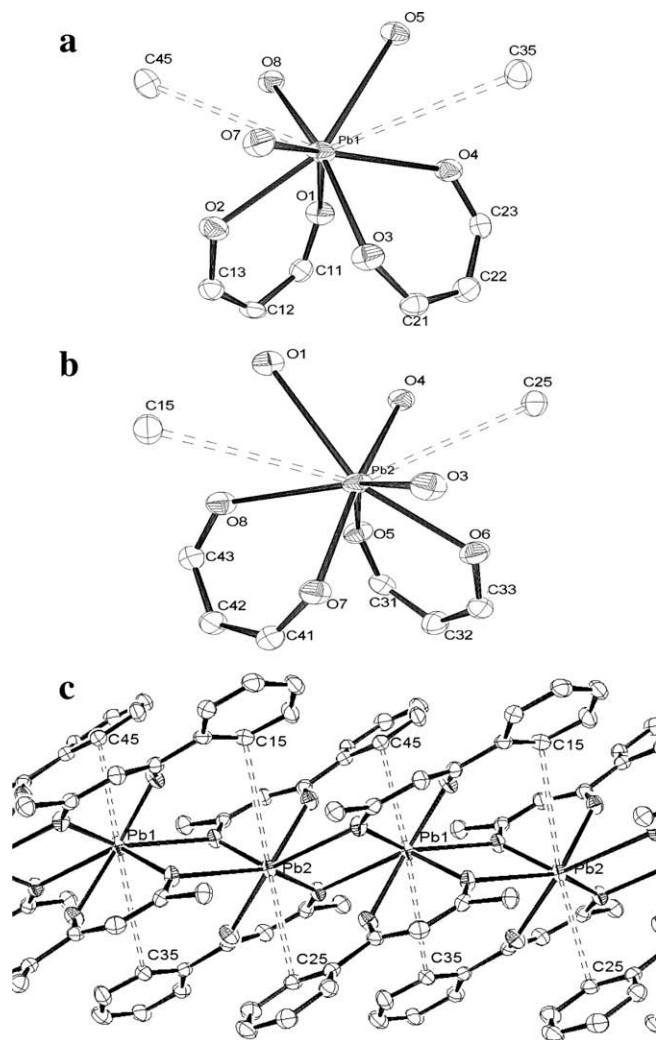


Fig. 4. Schematic representation of two different types of Pb^{II} environments along showing Pb···C interactions (a) for Pb(1), (b) for Pb(2) and (c) Showing of Pb···C interactions made visible for a fragment of the polymeric complex $[\text{Pb}_2(\mu_3\text{-ba})_2(\mu_2\text{-ba})_2]_n$ (**1**).

Nano-particles PbO have been generated by thermal decomposition of nano-sized compound **1**. The final product upon calcination of compound **1** is, based on their XRD patterns, PbO. The phase purity of the as-prepared tetragonal PbO nanoparticles are completely obvious and all diffraction peaks are perfectly indexed to the tetragonal PbO structure with the lattice parameters of $a = 3.9729 \text{ \AA}$, $b = 3.9729 \text{ \AA}$, $c = 5.0217 \text{ \AA}$, $Z = 2$ and $S.G = P4/nmm$ which are in JCPDS card file No. 05-0561. No characteristic peaks of impurities are detected in the XRD pattern.

Figs. 5 and 6 show SEM images of PbO nano-particles, produced by calcination of nano-sized compound **1** obtained under concentration of 0.01 and 0.001 M, respectively. The morphology and size of the particles are somewhat same in the two samples, under concentration of 0.01 and 0.001 M. However the precursor with morphology of nanowire gives spherical PbO nanoparticles and the morphology of the PbO particles is quite different from compound **1**. This point may be due to complete decomposition and breakup of the compound with change of morphology of nano-structure.

Also the bulk compound **1** was used as a precursor for preparation of PbO to compare the result with that from nano-size compound **1**. The SEM of PbO produced by calcination of bulk compound **1** showed that the produced PbO is not at nano-size. This point show that in this compound the size of precursor influ-

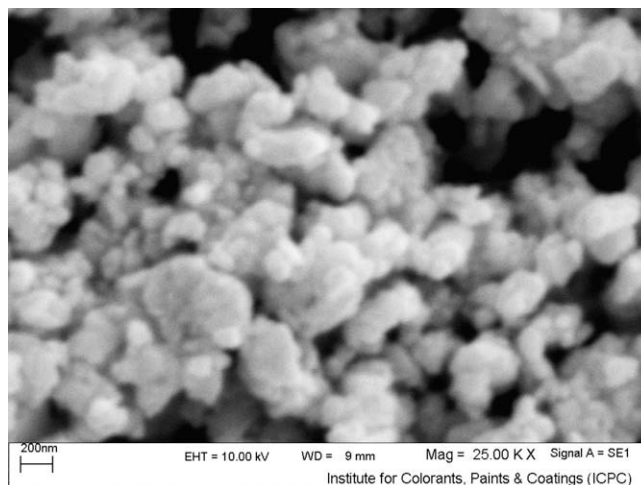


Fig. 5. SEM photograph of PbO nanoparticles (produced by calcination of nano-structured compound **1** with concentration of Pb⁺² (0.01 M) and ba⁻ (0.02 M)).

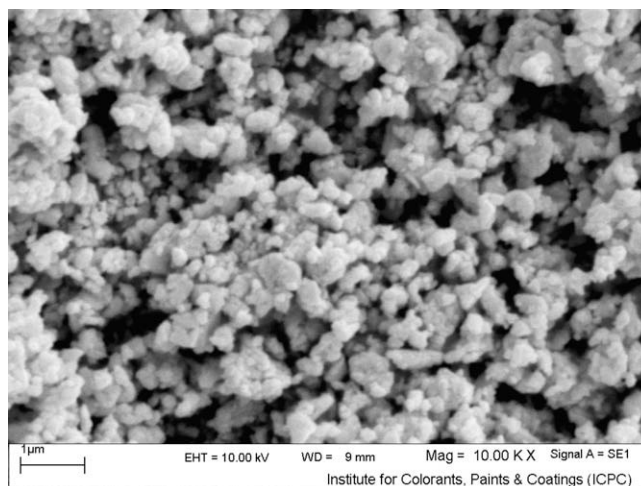


Fig. 6. SEM photograph of PbO nanoparticles (produced by calcinations of nano-structured compound **1** with concentration of Pb⁺² (0.001 M) and ba⁻ (0.002 M)).

ence upon the size PbO obtained by calcination of coordination polymer.

4. Conclusion

A new Pb(II) coordination polymer, $[\text{Pb}_2(\mu_3\text{-ba})_2(\mu_2\text{-ba})_2]_n$ (**1**), Hba = benzylacetylacetonone) has been synthesized using a thermal gradient approach and by a sonochemical method. Compound **1** was structurally characterized by single-crystal X-ray diffraction. The structure of **1** is interesting because (1) it represents a new, rarely observed one-dimensional framework with two independent holodirected lead(II) coordination spheres involving the Pb···C interactions, (2) comparison with the other reported oxygen donor ligands and $[\text{Pb}_2(\text{DBM})_4]$ compound [5] indicates the active lone pair on Pb^{II} in this complex may be covered by involvement in donor bonding and acts as both a Lewis acid and a Lewis base. This study demonstrates the coordination polymers may be suitable precursors for the preparation of nanoscale materials. To the best of our knowledge, this is the first report of synthesis of nano-particles of PbO from coordination polymers and it is very interesting that this paper is one of the few samples using sonica-

tion as an alternative synthetic procedure to form coordination polymers. This method for preparation of coordination polymers may be had some advantages such as: it takes place in shorter reaction times, produces better yields and also it may produce the coordination polymer at nano-size. On this perspective, further systematic studies of other coordination polymers with different metal ions are ongoing in our laboratory, which may offer new insights into metal–organic supramolecular assembly and nanochemistry.

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Appendix A. Supplementary material

CCDC 270210 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.07.016](https://doi.org/10.1016/j.jorganchem.2009.07.016).

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