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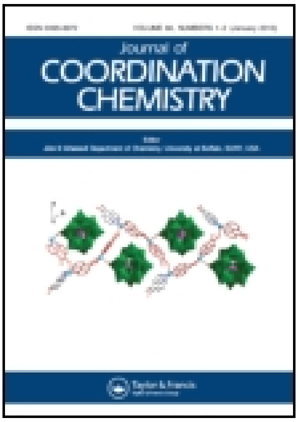

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Sonochemical synthesis of nano-structured lead(II) complex: precursor for the preparation of PbO nano-structures

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Sonochemical synthesis of nano-structured lead(II) complex: precursor for the preparation of PbO nano-structures

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Nano-structures of Pb(II) 2-D coordination polymers, $[Pb_2(\mu\text{-}2\text{-bpdbe})_2(NO_3)_4]_n$ (**1**) {2-bpdbe = 1,6-bis(2-pyridyl)-2,5-diaza-1,5-hexadiene}, were synthesized by the sonochemical method. The structure of **1** may be considered a coordination polymer of lead(II) formed by bridging 2-bpdbe ligands, making a 2-D array of $Pb(NO_3)_2$ and 2-bpdbe. The thermal stability of the material was studied by thermal gravimetric and differential thermal analyses. The new nano-structure coordination polymer was characterized by scanning electron microscopy, elemental analysis, and IR spectroscopy. The sizes of the nano-structures were approximately 50 nm. Nano-particles were obtained by thermolysis of **1** in oleic acid as a surfactant at 180°C and 200°C under air atmosphere and the size of the PbO particles were about 60 nm.

Keywords: Nano-particle; Sonochemical; Coordination polymer; Lead(II); Surfactant; PbO

1. Introduction

The design and synthesis of metal-coordination polymers attract interest for diverse topologies and potential applications in smart optoelectronic, magnetic, and microporous materials with specific structures, properties, and reactivities [1–18]. Nanometer-sized particles of metal-coordination polymers are attractive since unique properties are controlled by the large number of surface molecules, which experience a different environment than those in a bulk crystal. Controlling the growth of materials at the submicrometer scale is of central importance in the emerging field of nanotechnology [19–22]. Although considerable effort has been dedicated to the controlled synthesis of nano-scale particles of metals, oxides, sulfides, and ceramic materials, little attention has focused on nano-particles of supramolecular compounds, such as coordination polymers. Control of nano-sized building blocks, therefore, is vital for future successes of science and technology. To date most investigations on such compounds have been carried out in the solid state and studies of properties have been limited to investigations at the macroscopic scale. The potential use of coordination polymers as materials for nanotechnological applications has great promise since nanometer-scaled materials

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often exhibit the interesting size-dependent physical and chemical properties that cannot be observed in bulk analogs. Nano-sized coordination supramolecular materials are interesting candidates for applications in many fields, including catalysis, molecular adsorption, magnetism, nonlinear optics, luminescence, and molecular sensing.

In this article, we describe a simple synthetic sonochemical preparation of a nano lead(II) coordination polymer, $[Pb_2(\mu\text{-2-bpdbe})_2(NO_3)_4]_n$ (**1**) (2-bpdbe = 1,6-bis (2-pyridyl)-2,5-diaza-1,5-hexadiene), and the use of the compound to prepare PbO nano-particles. In recent years, many kinds of nanomaterials have been prepared by the sonochemical method [23–29]. There are different methods such as microwave-solvothermal synthesis [30, 31], hydrothermal route [32], and the surfactant-ligand co-assisting solvothermal method [33] used to synthesize nano- and micro-crystalline PbO.

2. Experimental

With the exception of the ligand 1,6-bis(2-pyridyl)-2,5-diaza-1,5-hexadiene (2-bpdbe), which was prepared according to the literature procedures [34, 35], all reagents and solvents for syntheses and analyses were commercially available from Merck and used as received. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer of Philips Company with monochromated Cu-Kα radiation ($\lambda = 1.54178$ Å). The samples were characterized with a scanning electron microscope (SEM) (Philips XL 30) with gold coating. IR spectra were recorded on a SHIMADZU-IR460 spectrometer in a KBr matrix. Crystallographic measurements of **1** were made at 100(2) K using a Bruker APEXII CCD area detector diffractometer equipped with a graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2. The molecular structure plots were prepared using ORTEPIII [36] and Mercury software [37].

2.1. *Preparation of $[Pb_2(\mu\text{-2-bpdbe})_2(NO_3)_4]_n$ (1)*

Compound **1** was prepared using the following method: 2-bpdbe (1 mmol, 0.238 g) and lead(II) nitrate (0.331 g, 1 mmol) were placed in the main arm of a branched tube. MeOH 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 2 days, colorless crystals were obtained, filtered, and air dried, m.p. = 255°C. Found (%): C, 29.48; H, 2.50; N, 14.75. Calculated for $C_{14}H_{14}N_6O_6Pb$ (%): C, 29.52; H, 2.46; N, 14.76. IR (selected bands; in cm^{-1}): 623(m), 777(s), 998(s), 1032(m), 1147(w), 1296(vs), 1378(vs), 1590(s), and 1659(s).

2.2. *Preparation of nano-sized $[Pb_2(\mu\text{-2-bpdbe})_2(NO_3)_4]_n$ (1) by the sonochemical method*

To prepare the nano-structure of **1**, we used an ultrasonic bath with different concentrations of metal and ligand solutions (0.05, 0.10, and 0.2 mol L^{-1}) with a power

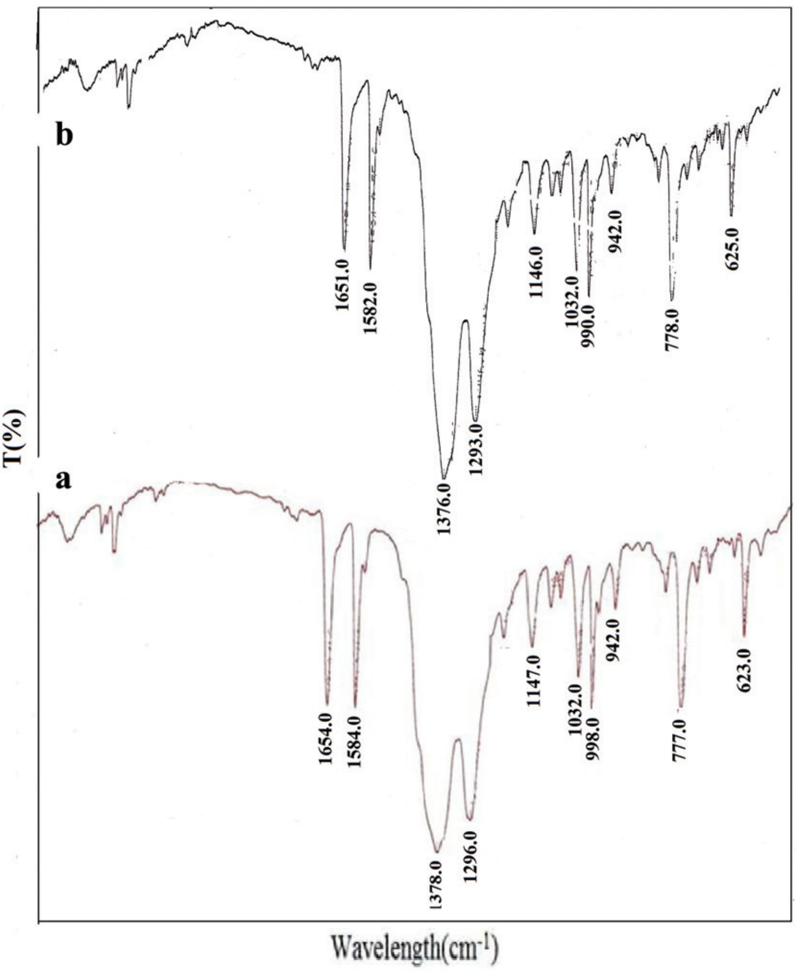

Figure 1. The IR spectra of (a) bulk materials as synthesized of compound $[Pb_2(\mu\text{-}2\text{-bpdbe})_2(NO_3)_4]_n$ (**1**) and (b) nano-sized compound $[Pb_2(\mu\text{-}2\text{-bpdbe})_2(NO_3)_4]_n$ (**1**) prepared by the sonochemical method.

of 60 W for 1 h. The precipitate from 0.1 mol L^{-1} concentration was filtered, subsequently washed with double distilled water, and then dried, m.p. = 255°C. Found (%): C, 29.48; H, 2.47; N, 14.75. Calculated for $C_{14}H_{14}N_6O_6Pb$ (%): C, 29.52; H, 2.46; N, 14.76. IR (selected bands; in cm^{-1}): 625(m), 781(s), 998(w), 1035(m), 1151(w), 1297(vs), 1376(vs), 1584(s), and 1655(s).

2.3. *Preparation of PbO nano-particles*

The precursor $[Pb_2(\mu\text{-}2\text{-bpdbe})_2(NO_3)_4]_n$ (**1**) (0.1 mmol) was suspended immediately in 1.58 ml oleic acid and formed light yellow solution. The solutions were degassed for 20 min and then heated to 180°C for 2 h. At the end of the reaction, a black precipitate formed. A small amount of toluene and a large excess of EtOH were added to the reaction solution and PbO nano-particles were separated by centrifugation. The solids

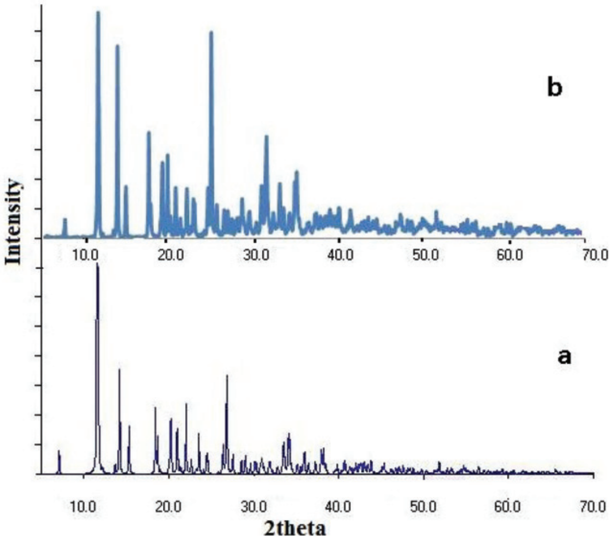

Figure 2. The XRD patterns of (a) calculated from single-crystal X-ray data of compound $[Pb_2(\mu\text{-2-bpdbe})_2(NO_3)_4]_n$ (**1**) and (b) nano-sized compound $[Pb_2(\mu\text{-2-bpdbe})_2(NO_3)_4]_n$ (**1**) prepared by the sonochemical method.

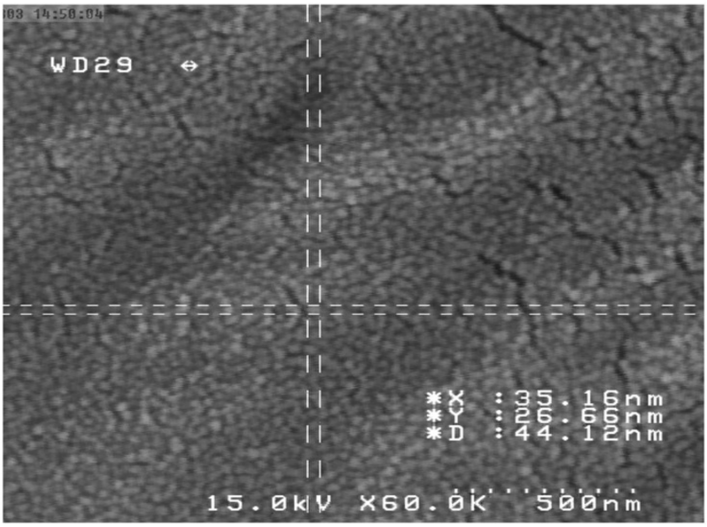

Figure 3. SEM photograph of compound **1** nano-powder produced by the sonochemical method.

were washed with EtOH and dried under air atmosphere. The process was repeated for **1** at 200°C for 2 h.

3. Results and discussion

Reaction of 1,6-bis(2-pyridyl)-2,5-diaza-1,5-hexadiene (2-bpdbe) and lead(II) nitrate lead to the formation of a new lead(II) complex $[Pb_2(\mu\text{-2-bpdbe})_2(NO_3)_4]_n$ (**1**).

Table 1. Crystal data and structure refinement for [Pb_2(μ-2-bpdbe)$_2$(NO_3)$_4$]$_n$ (**1**).

Identification code	**1**
Empirical formula	$C_{14}H_{14}N_6O_6Pb$
Formula weight	1139.00
Temperature (K)	293(2)
Wavelength (Å)	1.54187
Crystal system	Monoclinic
Space group	*P2(1)/c*
Unit cell dimensions (Å, °)	
a	8.91280(10)
b	24.9295(4)
c	8.9590(6)
α	90
β	115.848(8)
γ	90
Volume (Å^3), *Z*	1791.46(12), 2
Calculated density (Mg m^{-3})	2.112
Absorption coefficient (mm^{-1})	18.740
F(000)	1080
θ range for data collection (°)	6.56–68.17
Index ranges	$-10 \leq h \leq 6$; $-27 \leq k \leq 30$; $-10 \leq l \leq 10$
Reflections collected	3251
Independent reflections	2516
Absorption correction	Semi-empirical from equivalents
Refinement method	F^2 against all reflections
Data/restraints/parameters	3213/0/164
Goodness-of-fit on F^2	1.139
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0652$, $wR_2 = 0.1247$
R indices (all data)	$R_1 = 0.0789$, $wR_2 = 0.1556$

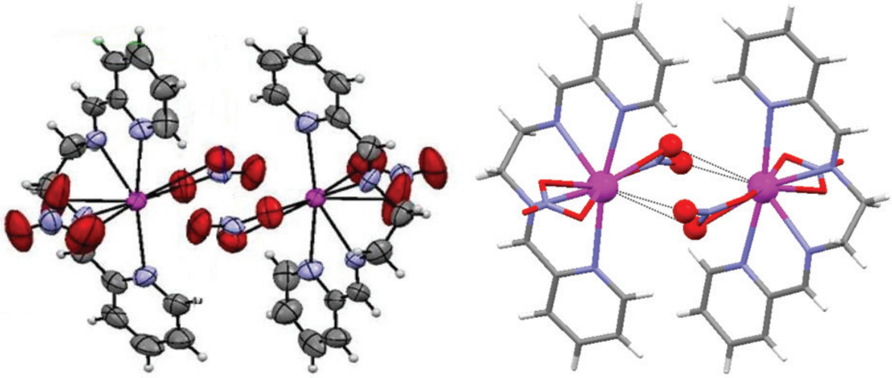

Figure 4. The ORTEP diagram and Pb···O secondary interactions of **1**. Atoms are represented by thermal ellipsoids ($p = 50\%$).

Nano-sized **1** was obtained by ultrasonic irradiation in a MeOH solution and single-crystalline material was obtained using a thermal gradient. The IR absorption bands with a variable intensity in the frequency range 1205–1585 cm^{-1} corresponded to vibrations of the pyridine rings, $\nu(NO_3)$ vibrations at 1380 cm^{-1}. The absence of any

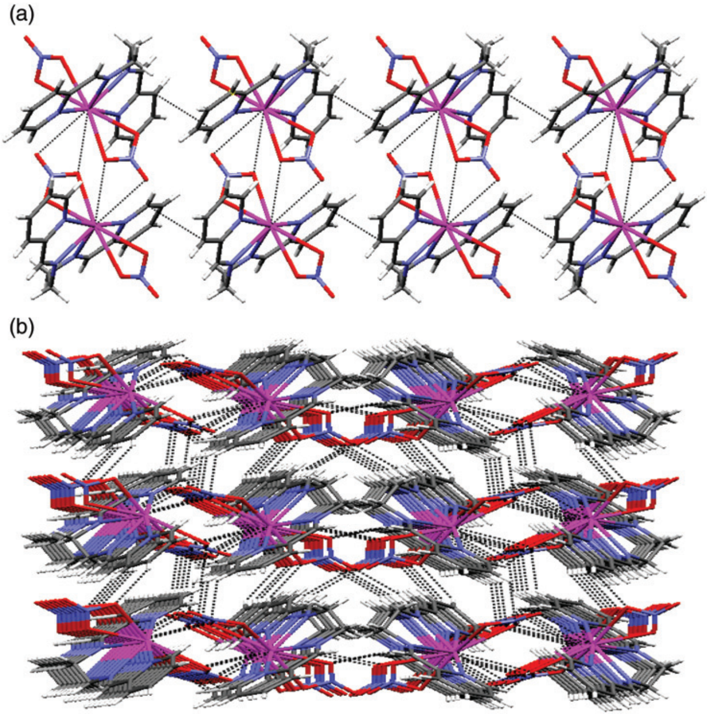

Figure 5. Showing: (a) 1-D double-chain and (b) 3-D supramolecular compound $[Pb_2(\mu\text{-}2\text{-}bpdbe)_2(NO_3)_4]_n$ (**1**) formed by π–π stacking and $O_{nitrate}\cdots HC_{py}$ and $C\cdots HC_{methylene}$ weak hydrogen-bonding, respectively.

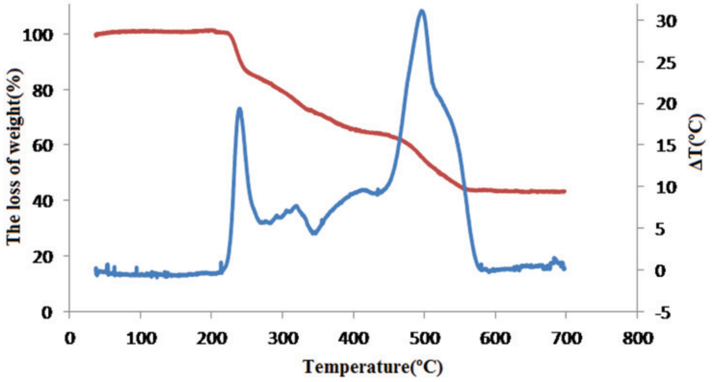

Figure 6. TGA and DTA diagrams of $[Pb_2(\mu\text{-}2\text{-}bpdbe)_2(NO_3)_4]_n$ (**1**).

bands at 3000–3400 revealed the absence of solvent in **1**. Elemental analysis and IR spectra of the nano-structure of **1** were comparable to the IR spectrum of the single-crystalline material (figure 1). Figure 2 shows the calculated XRD pattern from single-crystal X-ray data of **1** (figure 2a) in comparison with the XRD pattern of a typical sample of **1** prepared by the sonochemical process (figure 2b). Acceptable match, with slight difference in 2θ, were observed between the calculated and

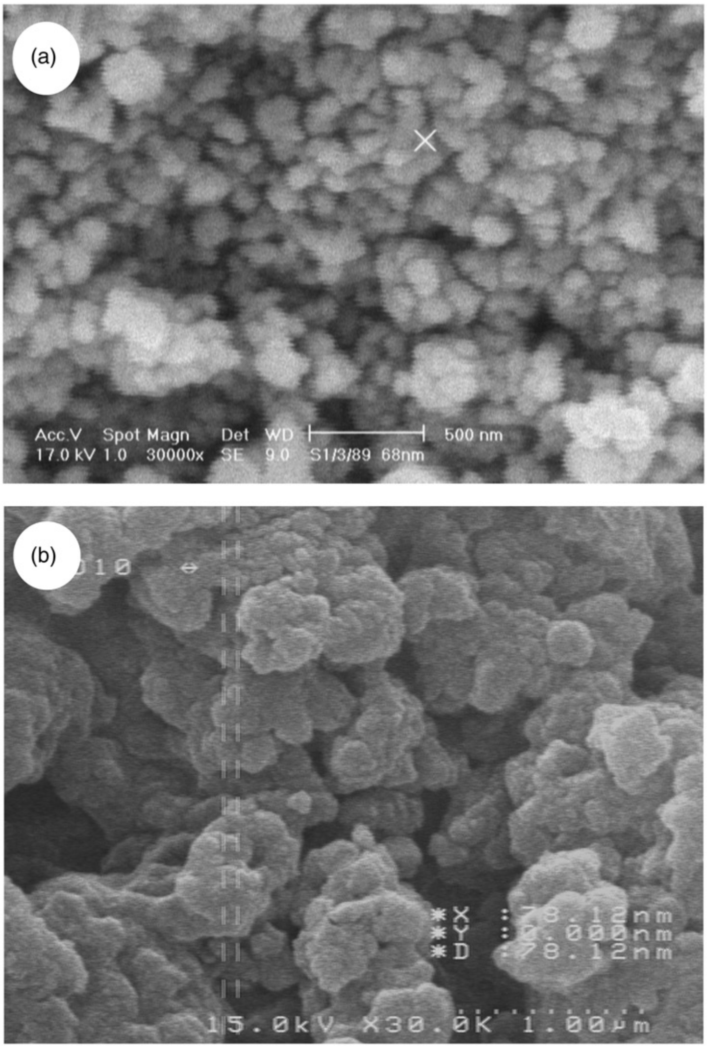

Figure 7. SEM photographs of PbO nano-particles produced by calcination of compound $[Pb_2(\mu\text{-}2\text{-}bpdbe)_2(NO_3)_4]_n$ (**1**) under two different temperatures using oleic acid as a surfactant, (a) 180°C and (b) 200°C.

experimental powder X-ray diffraction patterns but several reflections are shifted up to 2° in 2θ (figure 2). The observation indicates the compound obtained by the sonochemical process to match that obtained by single-crystal diffraction. The significant broadening of the peaks 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 (0.15418 nm), and θ and β the diffraction angle and full-width at half maximum of an observed peak, respectively. An SEM micrograph shows a broad distribution of the particle size, the average size of the particles is 40 nm, which is in agreement with that observed by scanning electron microscopy, as shown in figure 3.

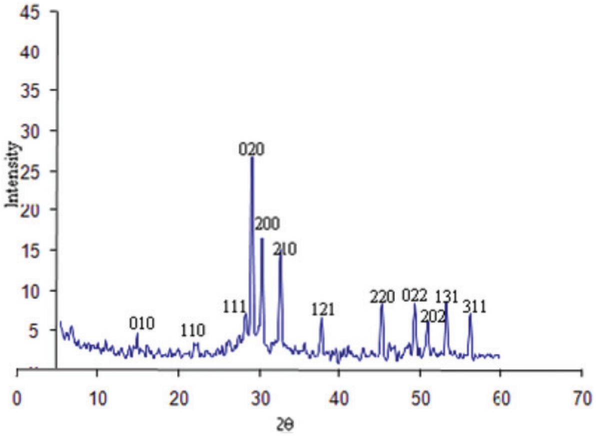

Figure 8. XRD pattern PbO prepared by thermolyses of compound $[Pb_2(\mu\text{-}2\text{-bpdbe})_2(NO_3)_4]_n$ (**1**).

Determination of the structure of **1** by X-ray crystallography (table 1 and figures 4 and 5) showed the Pb(II) ion to be coordinated by nitrate and 1,6-bis(2-pyridyl)-2, 5-diaza-1,5-hexadiene ligands. The structure consists of Pb(II) units coordinated by NO_3^- and 2-bpdbe ligands that form infinite layers as illustrated (figure 5). This is an eight-coordinate complex with a PbO_4N_4 chromophore. The structure is considered a coordination polymer of Pb(II) of linear chains that run parallel to the *c*-axis, with a building block of $[Pb_2(NO_3)_2]_n$ (**1**). The X–Pb–Y angles suggest a hole in the coordination sphere of the Pb(II) ion due to a stereo-chemically active lone pair. The Pb(II) ion, thus, has a hemidirected geometry as is observed for Pb(II) with high coordination numbers (9–10) [38]. The activity of the lone pair in the coordination sphere of Pb atoms in **1** is probably due to the presence of eight hard donor O and N atoms [39].

Compound **1** forms a 1-D double chain (figure 5a) by π-stacking interactions and a 3-D supramolecular structure by weak C–H hydrogen bonds of the methyl and pyridine hydrogen atoms toward the nitrate O atoms.

To examine the thermal stability of $[Pb_2(\mu\text{-}2\text{-bpdbe})_2(NO_3)_4]_n$ (**1**), thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 20°C and 700°C under argon flow (figure 6). Compound **1** is stable up to 250°C, at which decomposition begins. Mass loss calculations are consistent with the correct final decomposition product to be PbO. The DTA curve displays three distinct endothermic peaks at 260°C, 350°C, and 440°C as well as four exothermic peaks at 250°C, 320°C, 420°C, and 500°C (figure 6).

PbO nano-particles were synthesized from the decomposition of the precursor **1** in oleic acid in 180°C and 200°C (figure 7) under air atmosphere. The morphology and size of the as-prepared PbO samples were further investigated using SEM. Bulk powder of the precursor **1** produces regular shape of Pb(II) oxide nano-particles with the diameter about 68 nm at 180°C (figure 7a), but the prepared nano-size lead(II) oxide at 200°C does not produce regular shapes (figure 7b). The final product upon decomposing **1** is, based on XRD patterns (figure 8), orthorhombic PbO. The phase purity of the as-prepared orthorhombic PbO nano-particles is indicated by the diffraction peaks that index to orthorhombic PbO.

4. Conclusion

A new Pb(II) coordination polymer, $[Pb_2(\mu\text{-}2\text{-bpdbe})_2(NO_3)_4]_n$ (**1**), where 2-bpdbe = 1, 6-bis(2-pyridyl)-2,5-diaza-1,5-hexadiene, has been synthesized using a thermal gradient approach and by sonochemical irradiation. Compound **1** was structurally characterized by single-crystal X-ray diffraction. The crystal structure of **1** consists of a 2-D polymer and shows the coordination number in the Pb(II) ions is eight with active lone pair. Calcination under air produces nano-sized particles of PbO. Our study demonstrates that coordination polymers may be suitable precursors for the preparation of nano-scale materials without a need for special conditions, such as high temperature, long reaction times, and pressure controlling [40–45].

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-811858. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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References

[1] A.J. Cheethan. *Science*, **264**, 794 (1994).

[2] R.C. Finn, J. Zubieta. *Inorg. Chem.*, **40**, 2466 (2001).

[3] G. Alberti, U. Costantiono, J.L. Atwood, J.E.D. Davies, D.D. MacNicol, F. Vogtle (Eds). *Comprehensive Supramolecular Chemistry*, Vol. 7, Chap. 1, pp. 1–24, Elsevier Science, New York (1996).

[4] J.M. Thomas. *Chem. Commun.*, 675 (2001).

[5] A. Morsali, M.Y. Masoumi. *Coord. Chem. Rev.*, **253**, 1882 (2009).

[6] G.K.H. Shimizu, G.D. Enright, C.I. Ratcliffe, K.F. Preston, J.L. Reid, J.A. Ripmeester. *Chem. Commun.*, 1485 (1999).

[7] B. Moulton, M.J. Zawartko. *Chem. Rev.*, **101**, 1629 (2001).

[8] R. Kitaura, K. Fujimoto, S. Noro, M. Kondo, S. Kitagawa. *Angew. Chem., Int. Ed.*, **41**, 133 (2002).

[9] M. Oh, C.A. Mirkin. *Nature*, **438**, 651 (2005).

[10] A. Morsali, L.-G. Zhu. *Inorg. Chem. Commun.*, **7**, 1184 (2004).

[11] A. Morsali, A. Tadjarodi, R. Mohammadi, A.R. Mahjoub. *Z. Kristallogr. – NCS*, **216**, 379 (2001).

[12] A.Y. Robin, K.M. Fromm. *Coord. Chem. Rev.*, **250**, 2127 (2006).

[13] A. Morsali, R. Kempe. *Helv. Chim. Acta*, **88**, 2267 (2005).

[14] J. Zhou, Y.Z. Yuan, X. Liu, D.Q. Li, Z. Zhou, Z.-F. Chen, K.-B. Yu. *J. Coord. Chem.*, **59**, 1477 (2006).

[15] K.L. Zhang, F. Zhou, H.Y. Gao, Z.C. Pan, J.G. Lin, R. Lin. *J. Coord. Chem.*, **61**, 1494 (2008).

[16] Y.H. Zhao, H.B. Xu, K.Z. Shao, Y. Xing, Z.M. Su, J.F. Ma. *Cryst. Growth Des.*, **7**, 513 (2007).

[17] Y.H. Zhao, H.B. Xu, Y.M. Fu, K.Z. Shao, S.Y. Yang, Z.M. Su, X.R. Hao, D.X. Zhu, E.B. Wang. *Cryst. Growth Des.*, **8**, 3566 (2008).

[18] A. Morsali, A.R. Mahjoub, S.J. Darzi, M.J. Soltanian. *Z. Anorg. Allg. Chem.*, **629**, 2596 (2003).

[19] H.T. Shi, L.M. Qi, J.M. Ma, H.M. Cheng. *J. Am. Chem. Soc.*, **125**, 3450 (2003).
[20] H. Zhang, D.R. Yang, D.S. Li, X.Y. Ma, S.Z. Li, D.L. Que. *Cryst. Growth Des.*, **5**, 547 (2005).
[21] D.B. Kuang, A.W. Xu, Y.P. Fang, H.Q. Liu, C. Frommen, D. Fenske. *Adv. Mater.*, **15**, 1747 (2003).
[22] F. Kim, S. Connor, H. Song, T. Kuykendall, P.D. Yang. *Angew. Chem., Int. Ed.*, **43**, 3673 (2004).
[23] M. Martos, J. Morales, L. Sanchez, R. Ayouchi, D. Leinen, F. Martin, J.R. Ramos Barrado. *Electrochim. Acta*, **46**, 2939 (2001).
[24] M.V. Landau, L. Vradman, M. Herskowitz, Y. Koltypin. *J. Catal.*, **201**, 22 (2001).
[25] H. Wang, Y.N. Lu, J.J. Zhu, H.Y. Chen. *Inorg. Chem.*, **42**, 6404 (2003).
[26] J.H. Zhang, Z. Chen, Z.L. Wang, N.B. Ming. *J. Mater. Res.*, **18**, 1804 (2003).
[27] M.A. Alavi, A. Morsali. *Ultrason. Sonochem.*, **15**, 833 (2008).
[28] A. Askarinejad, A. Morsali. *Ultrason. Sonochem.*, **16**, 124 (2009).
[29] A. Askarinejad, A. Morsali. *Chem. Eng. J.*, **150**, 569 (2009).
[30] A.V. Murugan, R.S. Sonawane, B.B. Kale, S.K. Apte, A.V. Kulkarni. *Mater. Chem. Phys.*, **71**, 98 (2001).
[31] S.-H. Yu, J. Yang, Z.-H. Han, Y. Zhou, R.-Y. Yang, Y.-T. Qian, Y.-H. Zhang. *J. Mater. Chem.*, **9**, 1283 (1999).
[32] C. Li, X. Yang, B. Yang, Y. Yan, Y.T. Qian. *J. Cryst. Growth*, **291**, 45 (2006).
[33] J. Yang, J.H. Zeng, S.H. Yu, L. Yang, G.E. Zhou, Y.T. Qian. *Chem. Mater.*, **12**, 3259 (2000).
[34] Y.-B. Dong, M.D. Smith, R.C. Layland, H.-C. zur Loye. *Chem. Mater.*, **12**, 1156 (2000).
[35] E.C. Kesslen, W.B. Euler. *Tetrahedron Lett.*, **36**, 4725 (1995).
[36] L.J. Farrugia. *J. Appl. Cryst.*, **30**, 565 (1997).
[37] Mercury 1.4.1, Copyright Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (2001–2005).
[38] L. Shimoni-Livny, J.P. Glusker, C.W. Bock. *Inorg. Chem.*, **37**, 1853 (1998).
[39] R.L. Davidovich, V. Stavila, D.V. Marinin, E.I. Voit, K.H. Whitmire. *Coord. Chem. Rev.*, **253**, 1316 (2009).
[40] H. Sadeghzadeh, A. Morsali, V.T. Yilmaz, O. Buyukgungor. *Mater. Lett.*, **64**, 810 (2010).
[41] H. Sadeghzadeh, A. Morsali. *Polyhedron*, **29**, 925 (2010).
[42] M.J.S. Fard-Jahromi, A. Morsali. *Ultrason. Sonochem.*, **17**, 435 (2010).
[43] Z. Rashidi, A. Morsali. *J. Mol. Struct.*, **936**, 206 (2009).
[44] L. Hashemi, A. Morsali. *J. Inorg. Organomet. Polym. Mater.*, **20**, 856 (2010).
[45] A. Spokoyny, D. Kim, A. Sumrein, C.A. Mirkin. *Chem. Soc. Rev.*, **38**, 1218 (2009).