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A Novel Fishbone-Like Lead(II) Supramolecular Polymer: Synthesis, Characterization, and Application for Producing Nano Metal Oxide

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Abstract: The nanorods of $[Pb(L)Br_2]_n$ (1) (L = 1,2-bis (pyridin-3-ylmethylene)hydrazine) underwent ultrasound irradiation and were synthesized as a novel three-dimensional fishbone-like Pb(II)– organic coordination supramolecular compound. The morphology and nanostructure of the synthesized compound were determined through SEM, FTIR, elemental analyses, and XRD. Compound 1 was structurally characterized by single-crystal X-ray diffraction and revealed six-coordinated Pb (II) ions bonded to two N atoms from two L ligands and four bromine anions, forming a one-dimensional fishbone-like coordination polymer, which extended into a 3D supramolecular structure through weak intermolecular interactions. The bulk thermal stability of compound 1 was examined using thermogravimetric analysis (TGA). Moreover, PbO nanoparticles with sizes of 40–80 nm were obtained through the thermolysis of 1 at 180 °C using oleic acid as a surfactant.

Keywords: nanorods; Pb(II); ultrasonic irradiation; nano metal oxide; crystal structure

1. Introduction

Coordination compounds or metal–organic hybrid materials have remarkably attracted huge attention during the past twenty years. Inorganic–organic hybrid supramolecular materials include the self-assembly of an organic ligand with proper metal ions and functional groups with special directionality and functionality [1–5]. Structural blocks are created based on coordinating interactions and other poor non-covalent inter-molecular forces, including hydrogen bonds and pi stacking, which have key roles in their stability. The attraction to these compounds comes from the effects of basic structural chemistry, and their probable applications in areas including luminescence, catalysis, nonlinear optics, magnetism and molecular sensing and adsorption, which do not exist for mononuclear compounds [6–8]. Lowering the size of nano-scaled coordination supramolecular compounds increases the surface area. Preparing any types of nano-scaled coordination supramolecular compounds is therefore the main path toward the technological application of these novel materials [9].

Pb(II) frameworks have attracted interest because of their large ion radius, variable coordination number, and possible occurrence of a stereochemically active lone pair of 6s² outer electrons with a novel network of topologies and interesting properties [10–12]. According to the hard–soft acid–base theory, the intermediate coordination ability of Pb(II) means that it can flexibly coordinate small nitrogen or oxygen atoms as well as large sulfur atoms [13]. Investigation of the stereo-chemical activity of valence shell lone electron pairs in the polymeric and supramolecular compounds may be more interesting. The



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). spontaneous aggregation of several bridging ligands causes the gap to disappear, and the coordination of Pb (II) assumes a less common holodirected arrangement [14].

The present study introduces an eco-friendly and simple nanocrystal synthesis of a three-dimensional coordination supramolecular compound via ultrasonic irradiation. Organic synthesis was performed, and nanomaterials prepared using sonochemical techniques [15]. Further studies are still required for clarifying the application of the Ultrasound technique (*UST*) to constructing coordination supramolecular compounds. The present study investigated the fast synthesis of $[Pb(L)Br_2]_n$ (1) [L = 1,2-bis (pyridin-3-ylmethylene)hydrazine] as the nanocrystals of a one-dimensional fishbone-like Pb(II) coordination polymer. According to the findings obtained, Ultrasound technique (*UST*) synthesis is an efficient, low cost, simple and eco-friendly method for coordination supramolecular nanocompounds compared to conventional synthetic methods such as the solvent diffusion method and solvothermal and hydrothermal approaches [16].

Ultrasound technique (*UST*) leads to high-energy chemistry by processing acoustic cavitation, including bubbles, expansion, and their implosive collapse within a liquid intermediate [17]. UST results in alternative compressive and expansive acoustic waves to make and oscillate bubbles by irradiating liquids. Bubble can invade and consequently collapse fast, i.e., with cooling and heating rates of over 10^{10} Ks⁻¹. The huge energy concentration obtained over the collapse leads to a pressure of about one thousand bar and a local temperature of approximately 5000 K. The energy distribution to the surroundings during collapse and after bounce causes the hot spot gas temperature to swiftly reach the temperature of the surrounding area [18,19]. Ultrasonic irradiation can therefore be used to assist various chemical reactions progress at room temperature, and even certain reactions formerly difficult to actualize using conventional approaches [20–23]. The present study employed oleic acid as a surfactant and performed thermolysis of **1** at 180 °C to synthesize and structurally characterize a novel nano lead(II) metal–organic supramolecular compound with 1,2-bis (pyridine-3-ylmethylene)hydrazine ligand (Scheme 1) and simply synthesize PbO nanoparticles.



Scheme 1. 1,2-bis (pyridine-3-ylmethylene)hydrazine ligand.

2. Experiments

2.1. Measurements and Materials

Chemicals were obtained from Sigma-Aldrich (Seoul, South Korea) and used as received without further purification. Elemental analyses of the samples were carried out using a Vario Microanalyzer. FTIR was carried out by employing Bruker Vector 22 and KBr disks at 4000–400 cm⁻¹. Thermogravimetric analysis (TGA) was conducted under argon flow at 20–600 degrees Celsius and a heating rate of 3 °C/min using LABSYS evo (SETARAM).

X-ray powder diffraction (XRD) measurements were carried out using an X'pert diffractometer (Panalytical) with monochromatized Cu-K α radiation. In addition, XRD patterns were simulated in Mercury to acquire single-crystal information [24]. The morphology of the nanostructured compound was determined by scanning electron microscopy (SEM) (S-4200, Hitachi, Japan) and TEM (JEM-2200FS, JEOL). A 40 kHz Sonicator_3000 multiwave ultrasonic generator made by Misonix Inc. in the UST equipped with a titanium

oscillator (horn) and a converter/transducer 12.5 mm in diameter was utilized to perform ultrasound. The minimum power output of the generator was 600 W for one hour at ambient temperature. The chemical composition and status of the product were evaluated by X-ray photoelectron spectroscopy (XPS) (K-ALPHA, UK).

2.2. Preparation of 1,2-bis (pyridine-3-ylmethylene)hydrazine (L)

A mixture of 5 mmol (0.45 mL, 0.45 g) of hydrazine hydrate (35 wt.% in water) and a solution of 10 mmol (1.07 g) of nicotinaldehyde in 100 mL of methanol was refluxed for one day. Afterwards, the obtained yellow solids were filtered and then rinsed in methanol and dried in a vacuum (yield: 65%, 0.98 g), m.p. 140 °C, FTIR (KBr) = ν_{max} (698, 706, 817, 863, 1021, 1089, 1185, 1225, 1304, 1417, 1482, 1586, 1625, 2929) cm⁻¹. H NMR (CDCl₃, ppm): 8.66 (s, 2H), 8.70 (d, 2H), 8.97 (s, 2H), 7.41 (d, 2H), 8.22 (d, 2H).

2.3. Preparation of Nanostructure and Single Crystal $[Pb(L)Br_2]_n$ (1)

A total of 30 mL of a 0.1 M solution of PbBr₂ was added to 30 mL of a 0.1 M solution of the (*L*) ligand, and sonication performed with a high-density 40 kHz, 600 W UST probe to make the nanostructured [Pb(L)Br₂]_n (**1**). The obtained precipitate was filtered and rinsed in water and then dried in the air at the decomposition point: 330 °C. According to the analyses, C: 25.0%, H: 2.0% and N: 10.0% and C: 24.9%, H: 1.5% and N: 9.7% were obtained for C₁₂H₁₀Br₂N₄Pb. The selected FTIR bands (cm⁻¹) were as follows: 635*s*, 750*s*, 864*m*, 1045*m*, 1418*s*, 1482*m*, 1590*s*, 1620*s*, 3020*w*.

An appropriate single crystal of $[Pb(L)Br_2]_n$ (1) determining the X-ray structure was made and isolated by inserting 1 mmol of *L* into an arm of a tube with branches and 1 mmol of PbBr₂ to the other arm [25]. Having filled both the arms with methanol and sealing the tube, the arm containing the ligand was submerged in a 60 °C oil bath. Yellow crystals (decomposition point of 333 °C) were precipitated for 9 days on the other arm that was placed at room temperature. Afterwards, the crystals were filtered, rinsed in water, and dried in air with a yield of 70% (0.402 g). The results obtained were as follows: H: 2.0%, C: 25.5% and N: 10.0%. Moreover, C: 24.9%, H: 1.5% and N: 9.7% were obtained for C₁₂H₁₀Br₂N₄Pb. The selected FTIR bands (cm⁻¹) were as follows: 634s, 750s, 864*m*, 1045*m*, 1418s, 1482*m*, 1590s, 1620s, 3024*w*.

2.4. Preparation of Nanoparticles of Pb(II) Oxide

After dissolving 0.1 mmol of $[Pb(L)Br_2]_n$ (1) in 10 mL of oleic acid, the light-yellow solution obtained was degassed for forty-five minutes (with stirring and slow heating) and then heated for one hour at 180 °C, ultimately yielding a black precipitate. After adding a great amount of ethanol and a little toluene to the solution, lead(II) oxide nanoparticles were centrifuged and thereby isolated. The final solid was rinsed in ethanol and dried at room temperature (yield: 43%, 0.01 g).

2.5. X-ray Crystallography

A $0.65 \times 0.15 \times 0.09 \text{ mm}^3$ yellow compound crystal was placed over glass fiber using epoxy adhesives. An X-ray diffractometer (50 kV, 30 mA) with graphite monochromated Mo K_{α} radiation ($\lambda = 0.71073 \text{ Å}$) was used over $2\theta = 4.56-50.08^{\circ}$ to collect data. No significant data were missing from the data collected. The data were processed in the crystal structure analysis module of the Bruker AXS [26]. The modules of AXS utilized included SADABS (Bruker) for absorption correction, SHELXS-97 (Sheldrick) and XPREP (Bruker) for structure solution, SHELXTL (Sheldrick) for molecular graphics and publication materials, SHELXL-97 (Sheldrick) for structure refinement, APEX2 (Bruker) for data collection, and SAINT (Bruker) for cell refinement and data reduction. Furthermore, the method proposed by Waber and Cromer was used to obtain scattering factors for neutral atoms [27]. The crystal was of the monoclinic space group $P2_1/c$ given the systematic deficiency, E statistic, and effective structure refining. Furthermore, the structure was solved by utilizing direct techniques. For the data obtained from the compound, full-matrix least squares refinement was performed by minimizing the function of $\sum w (F_c^2 - F_0^2)^2$. Moreover, nonhydrogen atoms were anisotropically refined. The location of the hydrogen atoms was geometrically determined with 0.98Å (CH₃) and C–H = 0.95 (aromatic) and refined with Uiso(H) = -1.2 UeqC as riding atoms. Tables 1 and 2 present the crystallographic data, the bond lengths, and the angles.

Table 1. Crystal data and structure refinement for $[Pb(L)Br_2]_n$ (1).

Empirical Formula	$C_{12}H_{10}Br_2N_4Pb$	
Formula weight	555.23	
Temperature/K	293(2)	
Crystal system	monoclinic	
Space group	$P2_1/c$	
a/Å	4.005(7)	
b/Å	9.169(13)	
c/Å	34.27(4)	
$\alpha/^{\circ}$	90.00	
β/°	92.08(4)	
$\gamma/^{\circ}$	90.00	
Volume/Å ³	1258(3)	
Z	4	
$\rho_{calc} mg/mm^3$	2.922	
μ/mm^{-1}	19.751	
F(000)	1000.0	
Crystal size/mm ³	0.65 imes 0.15 imes 0.09	
2Θ range for data collection	4.76 to 50.08°	
Index ranges	$-4 \le h \le 3$, $-10 \le k \le 10$, $-37 \le l \le 40$	
Reflections collected	6637	
Independent reflections	1789[R(int) = 0.0834]	
Data/restraints/parameters	1789/0/160	
Goodness-of-fit on F ²	1.101	
Final R indexes $[I > = 2\sigma (I)]$	$R_1 = 0.1166$, $wR_2 = 0.2949$	
Final R indexes (all data)	$R_1 = 0.1255, wR_2 = 0.3013$	
Largest diff. peak/hole/e Å ^{-3} 5.58/ -3.65		

Table 2. Selected bond lengths (Å) and angles (°) for [Pb(L)Br₂]_n (1).

Pb1—N2	2.67 (2)	Pb1—Br1	2.992 (4)	
Pb1—N2 ⁱ	2.67 (2)	Pb1—Br1 ⁱⁱⁱ	2.975 (4)	
Pb1—Br1 ⁱⁱ	2.975 (4)	Pb1—Br1 ⁱ	2.992 (4)	
N2—Pb1—N2 ⁱ	180.000 (12)	N2—Pb1—Br1 ⁱⁱ	91.2 (6)	
N2—Pb1—Br1	84.4 (5)	Br1 ⁱⁱⁱ —Pb1—Br1 ⁱ	84.32 (13)	
N2 ⁱ —Pb1—Br1	95.6 (5)	Br1 ⁱⁱ —Pb1—Br1 ⁱ	95.68 (13)	
N2 ⁱ —Pb1—Br1 ⁱⁱⁱ	91.2 (6)	Br1 ⁱⁱⁱ —Pb1—Br1	95.68 (13)	
N2—Pb1—Br1 ⁱⁱⁱ	88.8 (6)	Br1 ⁱⁱ —Pb1—Br1	84.32 (13)	
N2—Pb1—Br1 ⁱ	95.6 (5)	Br1 ⁱ —Pb1—Br1	180.00 (9)	
N2 ⁱ —Pb1—Br1 ⁱ	84.4 (5)	Br1 ⁱⁱⁱ —Pb1—Br1 ⁱⁱ	180.00 (9)	
N2 ⁱ —Pb1—Br1 ⁱⁱ	88.8 (6)			

Symmetry code(s): (i) -x + 2, -y + 1, -z + 1; (ii) -x + 1, -y + 1, -z + 1; (iii) x + 1, y, z.

3. Results and Discussion

 $[Pb(L)Br_2]_n$ (1) was obtained as a novel one-dimensional fishbone coordination polymer from the reaction of lead(II) bromide with 1,2-bis (pyridine-3-ylmethylene)hydrazine (L). The nanostructure of the compound was determined in an aqueous solution through UST irradiation. The suitable single crystals of compound I for X-ray crystallography were obtained using the heat gradient of an aqueous solution based on the branched-tube method [28].

According to Figure 1, the bulk material developed using the branched-tube approach could not be differentiated from the nanostructured material obtained using the sonochemical approach in terms of FTIR spectrum and the results of elemental analysis. The FTIR spectrum of the single crystal materials and nanostructured material showed the representative absorption bands of the "L" ligand. Furthermore, the aromatic C–H absorption of hydrogen atoms caused a relatively weak band at approximately 3021 cm⁻¹. The aromatic ring vibration of the "L" ligand was also observed at frequencies of 1418–1590 cm⁻¹.



Figure 1. FT-IR spectrum of crystal and nano structure of 1.

Tables 1 and 2 show the results of single-crystal XRD for the structure of compound I. According to the single-crystal XRD in Figure 2, the structure of $[Pb(L)Br_2]_n$ crystallized in a monoclinic system with the space group of $P2_1/c$ resembled that of solid 1D fishbone metal–organic coordination polymers. Figure 2a shows the structure of the asymmetrical unit of **1** and an atom numbering arrangement selected. A Pb atom is coordinated by two N atoms of the *L* ligand with the same Pb–N distance of 2.670 Å and four bridged bromine anions with a Pb–Br distance of 2.992 (2.972, 2.992 and 2.972 Å). Figure 2b shows a coordination number of six for lead(II) atom in two modes with a PbN₂Br₄ donor set. The adjusted Pb…·Pb distances belonging to the chain were 4.001 Å. This order demonstrates a symmetry in the coordination geometry surrounding metal ions in a holodirected fashion. Given the labile interactions, the architecture of one-dimensional chains was allowed to interact with neighboring chains, and the structure was also allowed to be extended into three-dimensional supramolecular metal-organic coordination polymers, as shown in Figure 2d.



Figure 2. (a) Molecular structure of asymmetrical unit (1). (b) Coordination sphere of Pb(II) in **1.** (c) Fragment of the coordination polymer showing the 1D fish bone metal–organic coordination polymer. (d) From 1D architecture to supramolecular 3D coordination polymer via labile interactions (such as aromatic and π – π interaction, H-bonding).

Figure 3a shows the XRD pattern of compound 1 simulated from the single-crystal X-ray data, and Figure 3b shows the experimental XRD pattern of compound 1 prepared by using the sonochemical process. Except for slight changes in 2 θ , the experimental data were consistent with the simulated XRD patterns, suggesting that the compound obtained as a nano-structure using the sonochemical method was the same as that derived through single-crystal XRD. The major peak enlargmenet showed the nano-dimension of the particles. According to D = $0.891\lambda/\beta\cos\theta$ as the Scherrer equation, the mean size of the grain was estimated at 39 nm, with D representing the mean grain size, $\lambda = 0.15405$ nm as the X-ray wavelength, and θ and β as the diffraction and full-width angles, respectively, at 50% of a peak.



Figure 3. X-ray Powder Diffraction Pattern (XRPD) of compound **1** (**a**) computed from single-crystal X-ray data and (**b**) from the nanorods.

The crystalline substance was provided with $[Pb(L)Br_2]_n$ (1) through the reaction of 1,2-bis (pyridin-3-ylmethylene)hydrazine (L) with lead(II) bromide. In addition, the size and morphology of compound I prepared by the UST technique were analyzed with SEM. Figure 4 shows the SEM of compound I acquired by using a 600 W ultrasonic generator at a $[Pb^{2+}] = [L^-] = 0.1$ M concentration of primary reagents. Figure 4 also shows the nanorod morphology with a diameter of 45–140 nm for compound I. Further assessments are required for clarifying the formation of these structures. Packing the system at molecular levels, however, morphologically affects the nanostructured compound, suggesting coordination-encouraged creation over the morphology of the nanostructure [29–32].



Figure 4. SEM photographs of $[Pb(L)Br_2]_n$ (1) nanorods.

Figure 5 shows the results of the TGA of the single crystals and nanostructures performed at 25–600 °C in argon to investigate the thermal stability of compound 1. For single crystals of $[Pb(L)Br_2]_n$, after removing water molecules from the coordinated molecules and moisture at 80–110 °C, compound 1 was stable at up to 160 °C. Decomposition at 160–425 °C resulted in a mass loss of about 47.8%. In the case of nanostructured $[Pb(L)Br_2]_n$, the decomposition started at a lower temperature, around 145 °C, with the similar weight loss. This may be attributed to different crystallographic surfaces of both samples exposed to a thermal gradient [33]. The thermal stability of $[Pb(L)Br_2]_n$ is much lower than our previous reports on lead (II) coordination polymer, which may be attributable to differences in the structures of ligands coordinated to lead [34,35]. XPS findings showed that the solid residue at about 600 °C was PbO.



Figure 5. TGA plot of [Pb(L)Br₂]_n (1) in single crystal shape and nanostructured mode.

The final products of the decomposition of compound 1 based on their XRD arrangements as per Figure 6a matched the standard design of tetragonal PbO with S.G = P4/nmm, a = 3.947 Å, Z = 2, c = 4.988 Å and JCPDS (Joint Committee on Powder Diffraction Standards) card file No: 85-0711. Figure 6b displays the XPS results of nano PbO. The two asymmetric peaks at 142.28 eV and 137.48 eV were attributed to the transitions of $4f_{5/2}$ and $4f_{7/2}$ from Pb²⁺ ions in PbO, respectively, indicating that Pb²⁺ in the product was the same as PbO in shape. The O1 s spectrum showed a peak at 531.1 eV, which was estimated at 530.9 eV of O1 s in PbO in the literature. Figure 7 shows the SEM and TEM results of the residue obtained from the thermolysis of 1 at 180 °C by employing oleic acid as a surfactant, suggesting the regular shape of Pb(II) oxide nanoparticles. The significant broadening of the peaks indicates that the particles have nanometer dimensions. The average grain size D was estimated as 58 nm using the Scherrer formula, $D = 0.891\lambda/\beta cos\theta$, where λ is the X-ray wavelength (0.15405 nm) and θ and β are the diffraction angle and full-width at half maximum of an observed peak, respectively [36].



Figure 6. (a) XRD pattern and (b) XPS spectra of PbO nanoparticles prepared by thermolysis of compound **1**.



Figure 7. (a) SEM and (b) TEM images of PbO nano-structures produced by the thermolysis of nano-structures of compound **1**.

4. Conclusions

In this study, a sonochemical method was used to synthesize nano-structures of a new 1D fishbone coordination polymer of divalent lead with 1,2-bis (pyridin-3-ylmethylene)hydrazine (L). Single-crystal XRD was performed to structurally determine compound 1. A three-dimensional supramolecular compound included in the crystal structure of compound I demonstrated a coordination number of six in lead (II) ions. The complex takes the form of a 1D metal–organic system in solid state. As a result of several labile interactions with neighboring chains, the 1D chain extended into a 3D supramolecular coordination polymer. The sonochemically made compound 1 had nanorod morphology with diameter of 38–43 nm. Moreover, the calcination of compound I through the thermolysis of 1 at 180 °C by using oleic acid as a surfactant yielded a uniform PbO nanoparticle.

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