

RESEARCH PAPER

Synthesis and Crystal Structure of $[\text{Pb}(\text{gly})_2]_n$; New lead(II) Coordination Polymer with Glycine Ligand

Zarnoosh shokhchashm¹, Azar Hakimifar², Lida Hashemi², Ali Morsali^{2,*}, Michal Dusek³, Amir Reza Abbasi⁴, Mohammad Esmail Ebrahimzadeh⁵, Fateme Babaei⁵, Mojtaba Khanpour Matikolaie⁵

¹ Department of Chemistry, Payame Noor University, Abhar, Zanjan, Iran

² Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, Tehran, Iran

³ Institute of physics ASCR Cukrovarnicka 10 162 00 Prague Czech Republic

⁴ Faculty of Chemistry, Razi University, Kermanshah, Iran

⁵ Mazandaran Gas Company, Mazandaran, Iran

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ABSTRACT

$[\text{Pb}(\text{gly})_2]_n$ (**1**) (gly is the abbreviation of Glycine) have been synthesized and characterized by elemental analyses, IR, ¹H NMR and ¹³C NMR spectroscopy. The single crystal structure of **1** show the complex is 2D coordination polymer with octahedral environment that is formed into 3D supramolecule through hydrogen bond. Structural determination of compound **1** reveals the Pb(II) ion is four coordinated, bonded to a nitrogen, oxygen and two carbon atoms from the Glycine ligand. PbO nanoparticles were synthesized by calcinations of compound **1** at 500, 550 and 600 °C under air atmosphere. The PbO nanostructure was characterized by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). The thermal stability of compound **1** was studied by thermal gravimetric (TG) and differential thermal analyses (DTA).

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INTRODUCTION

Coordination polymers are a new Stage of crystalline porous polymers that are formed by copolymerization of multi dentate ligands with transition metal ions or metal ion clusters[1]. They have zeolite-like properties, such as high surface, microporosity, well-defined structures and the ability to Accord pore size on Å scale. Three dimensional coordination polymers are porous materials and attractive materials because of their capability to space various guests (in gas or liquid phase) in high concentrations and homogeneously. The Incarcerate effect in such materials leads to strange properties such as high gas storage and separation, catalysis, controlled

release or delivery of drug molecules etc [2-6]. The assembly of coordination polymers is affected by a combination of some factors, including the metal ion, organic ligand and auxiliary ligand, metal-to-ligand ratio, solvent and the reaction temperature[7-12]. The organic ligands are key to get some intriguing topologies and functional materials. The diffusion reaction is a Sensational method for the construction of coordination polymers with intriguing motifs [13-15]. We know that size, structure and shape have significant influence on properties of inorganic/organic materials, for Example optics, electric, optoelectronics, gas-sensor, and magnetic properties [16-20]. Micro/nano-energetic materials

* Corresponding Author Email: morsali_a@modares.ac.ir

with distinct structures and extremely small feature sizes also exhibit structure- and size-dependent properties, for Example thermal decomposition, sensitivity and operational performance [21, 22]. Controllable preparation of micro/nano-energetic materials with different morphologies and sizes is more importance for achieving desirable properties. It is more difficult for the synthesis of micro/nano-energetic materials than that of inorganic nano- structures because most of energetic compounds feature vander Waals or other weak intermolecular interactions among molecules, and they are dangerous explosives[23, 24].

To proceed, we describe the preparation of lead(II) coordination polymer, $[\text{Pb}(\text{gly})_2]_n$ (1) from reaction between lead(II) nitrate and mixtures of Glycine and sodium hydroxide in methanol and conversion into nanostructured PbO by thermolyses at 500, 550 and 600 °C in air without any surfactant or capping molecules. PbO is a polar inorganic crystalline material with many applications. PbO is very fascinating because of its numerous phases, such as Pb_2O , Pb_2O_3 , and Pb_3O_4 .

MATERIALS AND METHODS

Starting reagents for the synthesis were purchased and used without further purification from commercial suppliers (Sigma–Aldrich, Merck and others). IR spectra were recorded as nujol mulls using SHIMADZU 8900 and SEM Hitachi S4160 spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. Melting points were measured on an Electrothermal (BI 9300) apparatus.¹H NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz..

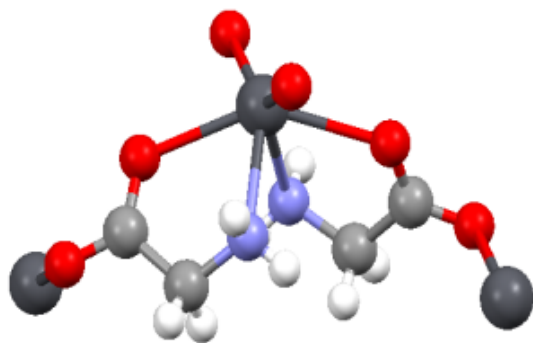


Fig. 1. The coordination environment of the compound $[\text{Pb}(\text{gly})_2]_n$ (1).

Synthesis of $[\text{Pb}(\text{gly})_2]_n$ (1) as a single crystal

Glycine (0.075g, 1mmol) and $\text{Pb}(\text{NO}_3)_2$ (0.331g, 1mmol) and Sodium hydroxide (0.04 g, 1mmol) were placed in one Bottom of a branched tube. Methanol was carefully added to fill tube, the tube sealed and the Bottom of branched tube immersed in a bath at 60 °C while the branched was at ambient temperature. After a week, crystals had deposited in the cooler arm which was filtered off, washed with Methanol, and air dried. Yield: 65 %, m.p. 218 °C is melting point.

IR (cm^{-1}) selected bonds: 499m, 578m, 676 m, 717 m, 812 w, 888 m, 945 m, 1069s, 1167 w, 1327w, 1378 m, 1436 w, 1560 s, 2006 w, 2059w, 2166 w, 2267 w, 2329 w, 2359 w, 2456 w, 2493 w, 2926 m, 3152 m, 3227 s.

¹H-NMR (DMSO, δ): 2.091(s, CH_2), 3.334(s, H_2O), 3.331(s, NH_2). ¹³CNMR (DMSO, δ):30.666(s, CH_2).

Synthesis of PbO nanoparticles

Calcinations of the single crystals of compound 1 at 500, 550 and 600°C in a furnace and static atmosphere of air for 4h yields mixture of PbO orthorhombic and PbO tetagonal nanoparticles.

RESULTS AND DISCUSSION

Reaction between lead(II) nitrate and mixtures of Glycine and sodium hydroxide in methanol

Table 1. Crystal data and refinement details of $[\text{Pb}(\text{gly})_2]_n$ (1).

Identification code	1
Empirical formula	$\text{C}_4\text{H}_8\text{N}_2\text{O}_4\text{Pb}$
Formula weight	355.324
Temperature	120(2)
Wavelength	0.71073
Space group	C2/c
unit cell dimensions	a=9.7165(6)Å $\alpha=90^\circ$ b=5.9658(4)Å $\beta=101.336(5)^\circ$ c =12.9875(6)Å $\gamma=90^\circ$
Volume	738.16 Å ³
Z	4
Density (calculated)	3.197 g cm ⁻³
Absorption coefficient	22.824 mm ⁻¹
Theta range for data collection	0.015 to 0.046
Index ranges	-12 ≤ h ≤ 12 -7 ≤ k ≤ 7 -16 ≤ l ≤ 16
Reflections collected	14393
Independent reflections	5181
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0186$ $wR_2 = 0.0234$
Largest diff. Peak, hole	0.687 and 0.617 e Å ⁻³

provided the crystalline material $[\text{Pb}(\text{gly})_2]_n$ (**1**). The structure of compound **1** was characterized by single-crystal X-ray techniques (Table 1). Determination of the structure of the **1** by X-ray crystallography showed each lead atom is chelated by nitrogen, oxygen and carbon atoms of "gly" ligands, therefore the coordination number in this complex is six (Fig. 1). Ortep diagram of compound **1** has been shown in Fig. 2.

The finest features on the construction of its 3D supramolecular architecture in **1** is that the hydrogen bonding serves to connect these 2D supramolecular sheets to 3D supramolecular Structure, as shown in Fig. 3. In the title compound, the Glycine molecules contribute to the formation of intermolecular hydrogen bonds involving lead atoms.

For compound **1** as single crystal IR (cm^{-1}) selected bands: the 578.70 (m), 1069.39 (s), 1167.05(w), 1378.48 . The IR spectrum of this compound show absorption bands resulting from Pb-O in the 578.70 cm^{-1} , single band CO in the 1069.39 and 1167.05 cm^{-1} , single band CH in the 1377.26 cm^{-1} , double band CO(in the COOH) in the 1559.16 cm^{-1} , single band CO(in the COOH) in the 1610 cm^{-1} , strain band in the 2925 cm^{-1} , NH_2 in the 3150 and 3272 cm^{-1} and strain band in the 3459 cm^{-1} shows the existence of Methanol molecule (Fig. 4).

The ^{13}C NMR spectrum of the DMSO and CH_2 solution of **1** display a distinct absorption band at 30.666 ppm and 80 ppm respectively. The ^1H NMR spectrum of the DMSO solution of **1** displays a distinct absorption band at 2.507 ppm. Spectrum of the H_2O

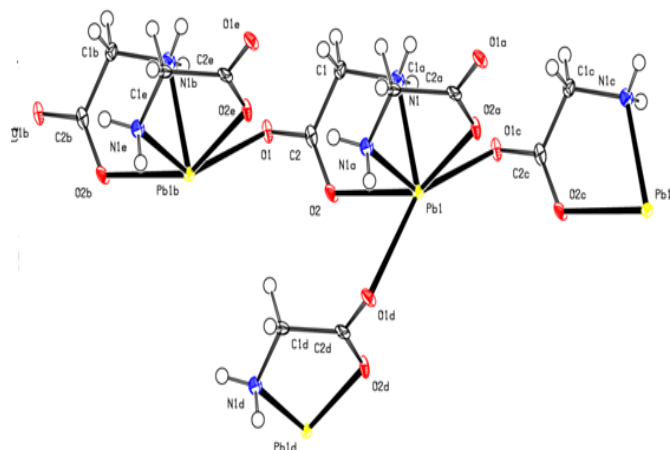


Fig. 2. Ortep diagram of $[\text{Pb}(\text{gly})_2]_n$ (**1**).

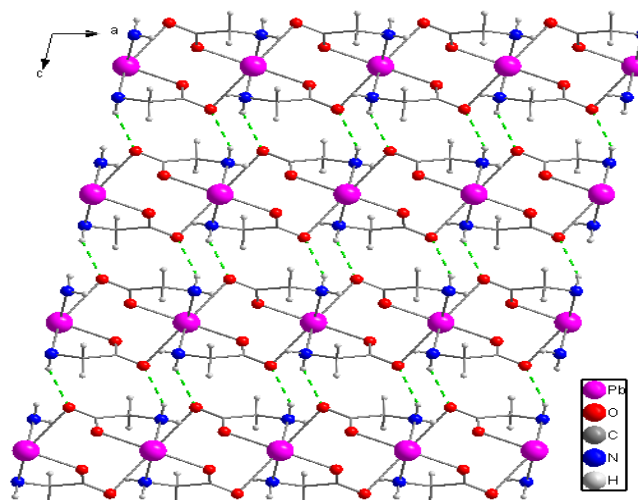


Fig. 3. A supramolecular Structure of $[\text{Pb}(\text{gly})_2]_n$ (**1**), viewed along b direction.

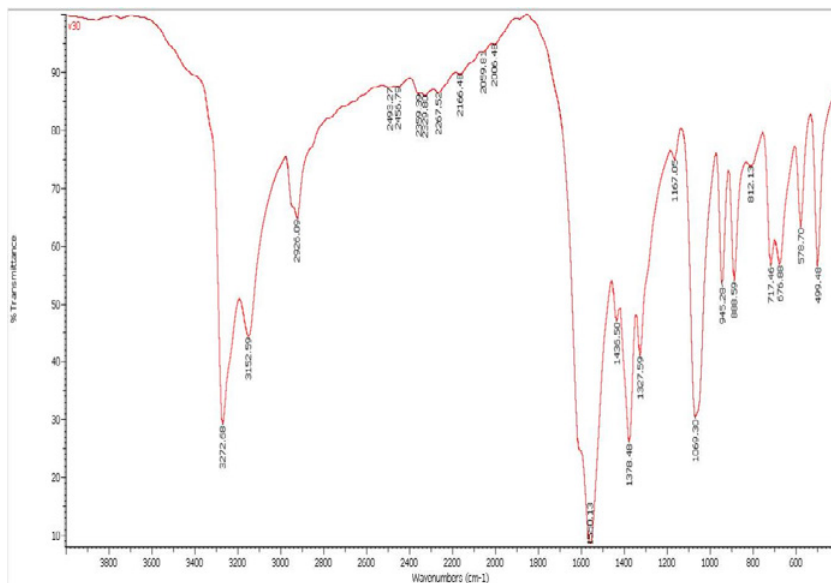


Fig. 4. IR spectra of the compound $[Pb(gly)_2]_n$ (1).

solution of **1** display at 3.334 ppm, 3.311 ppm and 2.091 ppm is show respectively distinct absorption band of NH_2 and CH_2 . To Study the thermal stability of the single crystals of compound $[Pb(gly)_2]_n$ (**1**), thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 50 and 700°C under argon flow (Fig. 5). The compound **1** destruction 100 until 200°C. Decomposition of compound **1** occurs between 100 and 200°C and between 200°C and 480°C with a mass loss of 52.5%. The DTA curve displays one distinct endothermic effect at 180°C for the single crystals of compound **1**.

Morphology and particle sizes of the nanostructures depend on the the calcinations method at different temperature and investigated by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). SEM image obtained from calcination of compound **1** at 500°C (Fig. 6), 550°C (Fig. 7) and 600°C (Fig. 8) shows the nanoparticle of lead(II) oxide (at 550°C nanorod and nanoparticle have been obtained).

For further demonstration, the EDAX of nanoparticle in 550°C has been shown in Fig. 9. The spectrum shows the presence of Pb as the only element component.

To investigate the composition and phase information of the final products, X-ray diffraction (XRD) was carried out in Fig. 10 that shows the XRD pattern of the residue obtained from calcination of compound **1** at 600 °C. The spectrum shows the presence of pb as the only element component.

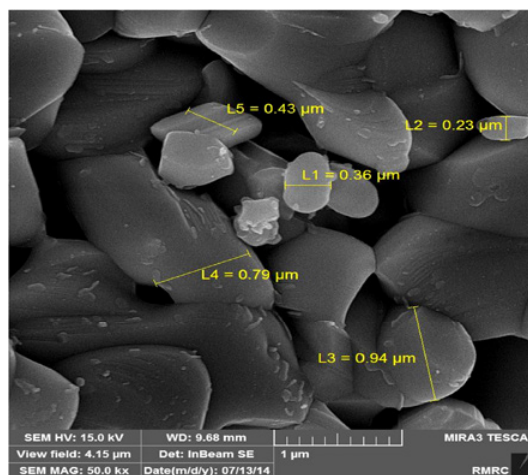


Fig. 6. The SEM image of PbO nanostructure produced by calcination of **1** at 500°C.

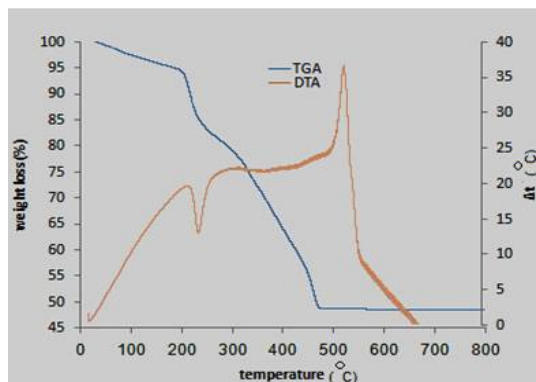


Fig. 5. Thermal behavior of compound $[Pb(gly)_2]_n$ 1.

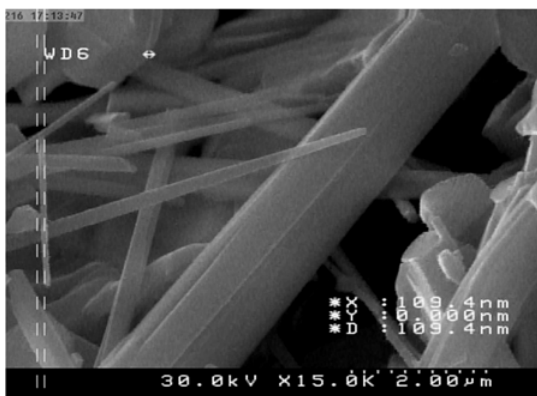


Fig. 7. SEM images of PbO nanostructure prepared by calcination of 1 at 550°C.

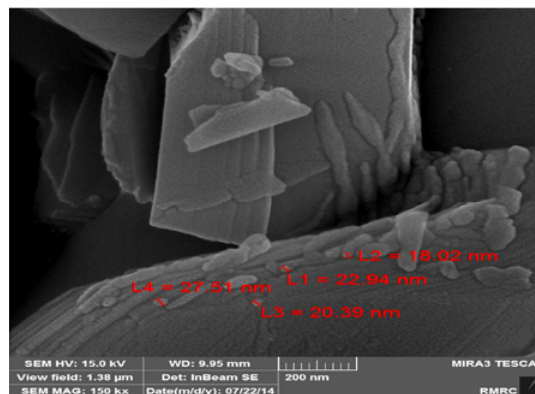


Fig. 8. SEM images of PbO nanostructure prepared by calcination of 1 at 600°C.

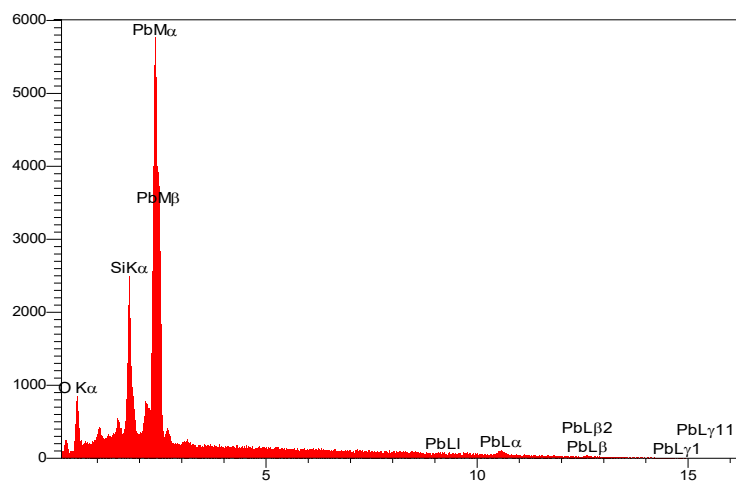


Fig. 9. EDX pattern of PbO nanostructure prepared by calcination of compound 1 at 550°C.

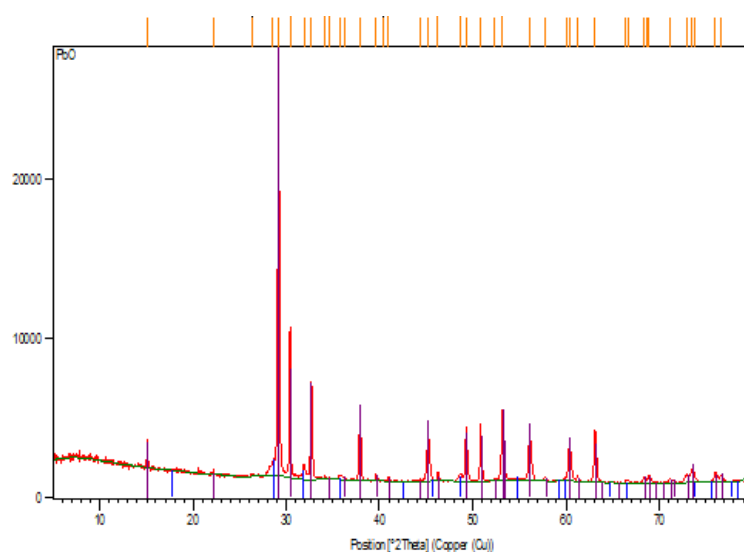


Fig. 10. XRD pattern of orthorhombic and tetragonal PbO nanostructure prepared by calcination of compound 1 at 600 °C

CONCLUSION

A new Pb(II) coordination polymer, $\{[Pb(gly)_2]_n\}$ (**1**) (gly is the abbreviation of Glycine)}, has been synthesized using branched tube method. Compound **1** was structurally characterized by single crystal X-ray diffraction, IR spectroscopy and Thermal gravimetric (TG) and differential thermal analysis (DTA). The crystal structure of compound **1** consists of a 3D supramolecular compound and shows the coordination number in the Pb(II) ions is six. Calcination of the compound **1** at 500, 550 and 600°C under air atmosphere yields mixture of orthorhombic and tetragonal PbO nanoparticles and nanorods.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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