



Sonochemical synthesis of two new nano lead(II) coordination polymers: Evaluation of structural transformation via mechanochemical approach



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ABSTRACT

Two new lead(II) mixed-ligand coordination polymers, $[\text{Pb}(\text{PNO})(\text{SCN})]_n$ (**1**) and $[\text{Pb}(\text{PNO})(\text{N}_3)]_n$ (**2**), (HPNO = picolinic acid N-oxide) were synthesized by a sonochemical method and characterized by scanning electron microscopy, X-ray powder diffraction, IR spectroscopy and elemental analysis. Compounds **1** and **2** were structurally characterized by single crystal X-ray diffraction. The thermal behavior of **1** and **2** were studied by thermal gravimetric analysis. Structural transformations of compounds **1** and **2** were evaluated through anion-replacement processes by mechanochemical method. Moreover, the effect of sonication conditions including time, concentrations of initial reagents and power of irradiation were evaluated on size and morphology of compounds **1** and **2**.

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1. Introduction

Coordination polymers (CPs) are one of the most important classes of organic–inorganic hybrid materials which have been advanced in recent years [1,2]. They are employed in various applications such as ion exchange, catalysis, sensing, luminescence, nonlinear optics (NLO), magnetism, electrical conductivity, separation and storage [3–6]. Structural transformation research has considerably developed over the last decade. Since CPs possess reactive functional groups and flexible frameworks, they have been thoroughly investigated in structural transformation studies [7–9]. Green mechanochemical methods, such as grinding and milling are valuable approaches to achieve structural transformations [10–15]. Among all different synthetic routes [16], sonochemical method is one of the simplest strategies in order to preparation of CPs [17]. Ultrasonic irradiation is considered as a green energy source because of shorter reaction times and higher yields in comparison with thermal energy sources. Also, this method is more convenient, cost effective and easily controlled for synthesis of nano-scaled materials. Sonication conditions can influence chemical reactions. They can also promote the formation of nano-sized structures, mostly by the instantaneous formation of crystallization nuclei. In recent years, many kinds of CPs have been prepared by this method [18–21].

This article focuses on the simple synthetic sonochemical preparation of micro and nano structures of two new mixed-ligand lead(II) CPs, $[\text{Pb}(\text{PNO})(\text{SCN})]_n$ (**1**) and $[\text{Pb}(\text{PNO})(\text{N}_3)]_n$ (**2**), (HPNO = picolinic acid N-oxide) and investigation of irreversible mechanochemical solid-state transformations from 3-dimensional (3D) **2**, to 2-dimansional (2D) **1** via anion-replacements. Also, effect of ultrasonic irradiation time and power as well as concentration of initial reagents on shape and size of the particles are studied.

2. Experimental

2.1. Materials and physical techniques

All reagents and solvents for the synthesis and analysis were commercially available and used as received. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded using a Thermo Scientific Nicolet IR100 (Madison, WI) Fourier-transform infrared (FT-IR) spectrometer. Elemental analyses were carried out using a Heraeus CHNO-Rapid analyzer. Powder X-ray diffraction (PXRD) measurements were performed using a Philips X'pert diffractometer with monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The thermal behavior was measured on a PL-STA 1500 apparatus at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ to $800 \text{ }^\circ\text{C}$ in a static atmosphere of nitrogen. The nano-structures were characterized by field-emission scanning electron microscopy (FE-SEM) on a Hitachi S4160 instrument with a gold coating. The single-crystal X-ray data were collected on a STOE IPDS II image plate

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Table 1
Experimental details for synthesis of compounds **1** and **2** nano-structures.

Compound	Concentration [PNO]/[X]/[Pb (OAc) ₂] (M), X = SCN ⁻ , N ₃ ⁻	Time (min)	Power (W)	Morphology
1	[0.01]/[0.01]/[0.01]	30	12	Nano-rod
	[0.05]/[0.05]/[0.05]	30	12	Nano-rod
	[0.1]/[0.1]/[0.1]	30	12	Nano-rod
	[0.1]/[0.1]/[0.1]	10	12	Nano-rod
	[0.1]/[0.1]/[0.1]	60	12	Nano-rod
	[0.1]/[0.1]/[0.1]	30	24	Nano-rod
2	[0.01]/[0.01]/[0.01]	30	12	Nano-plate
	[0.05]/[0.05]/[0.05]	30	12	Nano-plate
	[0.1]/[0.1]/[0.1]	30	12	Nano-plate
	[0.1]/[0.1]/[0.1]	10	12	Nano-plate
	[0.1]/[0.1]/[0.1]	60	12	& Nano-rod
	[0.1]/[0.1]/[0.1]	30	24	Nano-plate

diffractometer at 296 K. Graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) and the ω -scan technique were used. The structure was solved by direct methods using SHELXS-97 [22] and refined through the full-matrix least-squares method using SHELXL-97 [23].

2.2. Synthesis of single crystal [Pb(PNO)(SCN)]_n (**1**)

Suitable single crystals of **1** for X-ray diffraction were obtained using the branched tube method: PNO (0.104 g, 0.75 mmol), potassium thiocyanate (0.074 g, 0.75 mmol) and lead(II) acetate trihydrate (0.284 g, 0.75 mmol) were placed in the arm to be heated. A mixture of methanol and water (ratio 1:3) was carefully added to fill both arms. The tube was sealed and the ligand-containing arm was placed in an oil bath at 60 °C, whereas the other was maintained at ambient temperature. After 5 days, light yellow deposited crystals in the cooler arm were filtered and washed with acetone, m.p. >300 °C (yield: 76%). C₇H₄N₂O₃PbS: calcd. C, 20.8; H, 0.99; N, 6.94%; found: C, 20.6; H, 0.96; N, 6.92%. FT-IR (KBr cm⁻¹): 671 cm⁻¹ (s, ν (Pb–O)), 765 cm⁻¹ (m, ν_{oop} (C–H)_{ring}), 859 cm⁻¹ (s, ν (C–C)), 1160 cm⁻¹ (m, ν (C–H)_{ring}), 1194 cm⁻¹ (vs ν (N–O)_{N-oxide}), 1349 cm⁻¹ (vs ν_{sym} (CO₂–Pb)), 1432 cm⁻¹ (m, ν (C=C)_{Ar}), 1629 cm⁻¹ (s, ν_{asym} (CO₂–Pb)), 2085 cm⁻¹ (vs ν (SCN)), 3095 cm⁻¹ (w, ν_{sym} (C–H)).

2.3. Synthesis of single crystal [Pb(PNO)(N₃)]_n (**2**)

In the same way, suitable single crystals of **2** for X-ray diffraction were obtained using the branched tube method: Sodium azide

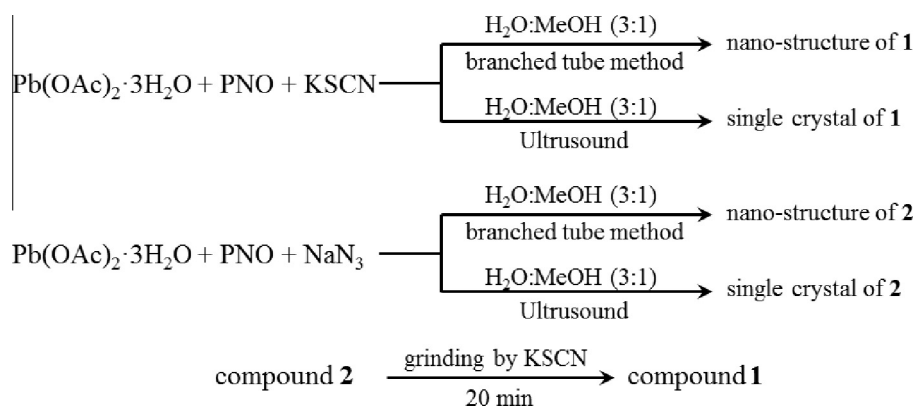
Table 2
Crystal data and structural refinement for **1** and **2**.

Identification code	Compound 1	Compound 2
Empirical formula	C ₇ H ₄ N ₂ O ₃ PbS	C ₆ H ₄ N ₄ O ₃ Pb
Formula weight	403.37	387.32
T/K	298(2) K	298(2)
$\lambda/\text{Å}$	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	P2 ₁ 2 ₁	P2 ₁ /n
Unit cell dimensions	$a(\text{Å}) = 5.5774(2)$ $b(\text{Å}) = 8.7103(4)$ $c(\text{Å}) = 18.6552(8)$	$a(\text{Å}) = 11.1925(3)$ $b(\text{Å}) = 6.4104(2)$ $c(\text{Å}) = 12.7097(3)$
$V/\text{Å}^3$	906.29(7)	829.49(4)
Z	4	4
$D_{calc}/\text{Mg/m}^3$	2.956	3.101
μ (mm ⁻¹)	18.825	20.324
F(000)	728	696
Theta range for data collection	2.18–33.39°	3.17–34.31°
R(int)	0.0719	0.0471
Completeness to theta	99.4%	99.3%
Goodness-of-fit on F^2	1.126	1.142
R ₁ , wR ₂ [$I > \sigma(I)$]	0.040, 0.103	0.014, 0.031
R ₁ , wR ₂ (all data)	0.042, 0.104	0.017, 0.032
CCDC No.	1444348	1444349

(0.049 g, 0.75 mmol) was used instead of potassium thiocyanate, m.p. >300 °C (yield: 65%). C₆H₄N₄O₃Pb: calcd. C, 18.59; H, 1.03; N, 14.46%; found: C, 18.6; H, 1.05; N, 14.48%. FT-IR (KBr cm⁻¹): 670 cm⁻¹ (s, ν (Pb–O)), 770 cm⁻¹ (m, ν_{oop} (C–H)_{ring}), 858 cm⁻¹ (s, ν (C–C)), 1156 cm⁻¹ (m, ν (C–H)_{ring}), 1270 cm⁻¹ (vs ν (N–O)_{N-oxide}), 1355 cm⁻¹ (vs ν_{sym} (CO₂–Pb)), 1431 cm⁻¹ (m, ν (C=C)_{Ar}), 1594 cm⁻¹ (s, ν_{asym} (CO₂–Pb)), 2025 cm⁻¹ (vs ν (N₃)), 3062 cm⁻¹ (w, ν_{sym} (C–H)).

2.4. Synthesis of compounds **1** and **2** nano-structures

Ultrasonic syntheses of **1** and **2** were carried out in an ultrasonic bath at ambient temperature and atmospheric pressure. To prepare the nano-structures, a solution of lead(II) acetate trihydrate with certain concentration in MeOH:H₂O (1:3) were placed in an ultrasonic bath. Into this solution was added a mix-ligand solution of PNO and potassium thiocyanate or sodium azide in MeOH:H₂O (1:3) dropwise. The resulting powders were isolated by centrifugation, washed with acetone and dried in air for characterization. For further studies, these series of experiments were performed in three various concentrations of all reagents (0.01, 0.05 and 0.1 M), three different times (10, 30 and 60 min) and two powers (12 and 24 W) (Table 1).

**Scheme 1.** Schematic graphs of synthetic methods.

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