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From discrete to infinite 3D coordination polymer: Sonochemical syntheses and structural characterization of a new nano flower lead (II) coordination compound

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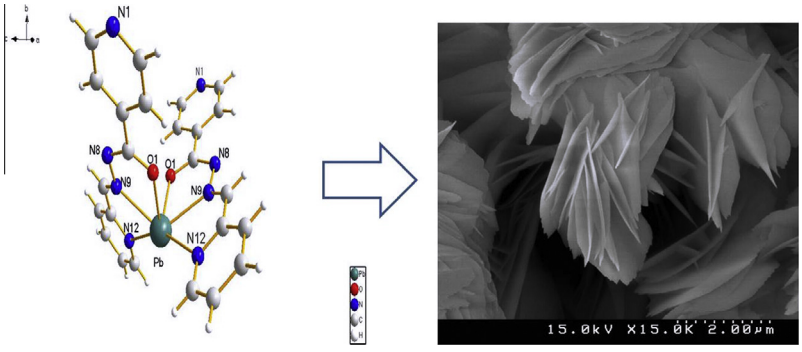
HIGHLIGHTS

- Nanostructures of a Pb (II) coordination compound were synthesized sonochemicaly.
- The lead (II) complex thermolysis leads to formation of PbO nano-particles.
- The morphology of Pb (II) coordination compound is cross-sheets.
- The calculated HOMO–LUMO gap via DFT calculations is 9.629 eV.

GRAPHICAL ABSTRACT



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ABSTRACT

Nano flower of a new discrete Pb (II) coordination compound, $[Pb(pcih)_2]$ (**1**), (pcih = 2-pyridinecarbaldehyde isonicotinoylhy-drazonate), have been synthesized by a sonochemical process and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), FT-IR spectroscopy and elemental analyses. Structural determination of compound **1** reveals the Pb (II) ion is six coordinated, bonded to four nitrogen and two oxygen atoms from two "pcih" ligands. Through strong π–π interactions, the overall structure of 1 is 1D supramolecular chain and with other directional intermolecular interactions, it is further extended into a three dimensional (3D) supramolecular structure. Density functional theory calculations (B3LYP functional) have been performed on complex **1** to provide a qualitative theoretical interpretation of their structural parameters, charge distributions and IR spectra. PbO nanoparticles are obtained by thermolysis of **1** at 180 °C with oleic acid as a surfactant.

Introduction

The design of self-assembled coordination architectures is of current and ongoing scientific investigation due to the potential applicability of these solid-state materials to many areas of science including magnetism, separation science, catalysis [1–4] and for their deceptive variety in building up developed structures [5–8].

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Table 1
Selected experimental FT-IR frequencies (cm^{-1}) for [Pb(pcih)$_2$], compared with the theoretical frequencies obtained from DFT calculations together with free ligand frequencies.

Assignment	Experimental	Calculated	Free ligand [18]
ν (C—H) aliphatic	2923*m*	2992	3007
ν (C—H)	699*m*	702	742
ν (CC)	1565, 1601*s*	1580, 1620	1572, 1610
ν (C=N)	1461*m*	1485	1473

A contemporary theme often exploited for the design and synthesis of extended coordination tectons centers upon the principle of "crystal engineering". This concept was originally introduced to intellectually describe crystal packing in solid-state molecules [9]. Although this interpretation pertained exclusively to organic chemistry, the idea was that both physical and chemical properties of solids were inherently dependent upon the arrangement of molecular entities and the properties associated with the individual components. Since the inception of the concept of crystal engineering, there has been a continuing effort to understand and properly predict patterns accountable for formation, orientation, and connectivity in molecular systems [10,11]. The organic part of a coordination polymer exhibits interestingly steric and electronic effects on the self-assembly of coordination polymers. Organic aromatic ligands are good candidates for spacer part of organic–inorganic materials, because not only they can act as hydrogen-bonding acceptors or donors, but also can provide recognition sites for π–π stacking interactions to form interesting supramolecular structures when coordinating to metal ions. Polynuclear d^{10} metal complexes and coordination polymers have attracted extensive interest in recent years, since they exhibit appealing structures [12–15]. In the field of crystal engineering, the anions not only balancing the charges of cationic species but also impart their influence on the structure of a given supramolecular system through coordinative bonding to metal ions or through weak interaction with organic ligands [16].

In contrast to inorganic materials, the specific syntheses of nano-structured supramolecular compounds seem to be surprisingly sparse. Equally the use of organometallic supramolecular compounds as precursors for the preparation of inorganic nanomaterials has not yet been investigated thoroughly. Sonochemistry is one method that can be used to control the growth of particles and in recent years many such materials have been prepared using this method. Sonochemistry is the research area in which molecules undergo a reaction due to the application of powerful ultrasound radiation (10 kHz–20 MHz) [17].

In this paper, we report the preparation and crystal structure of a novel lead (II) coordination compound in the presence of 2-pyridinecarbaldehyde isonicotinoylhydrazone schiff-base ligand together with theoretical studies, and describe a simple synthetic sonochemical preparation of nano-structures of this coordination polymer and its use in the preparation of PbO nanoparticles.

Experimental

Physical property measurements

2-pyridinecarbaldehyde isonicotinoylhy-drazone ligand (Hpcih) was synthesized according to a literature method [18]. All other chemicals were obtained from Sigma–Aldrich and used without further purification. An Elementar Vario Microanalyzer CHN–O-Rapid Analyzer was used for C, H and N elemental analyses of the samples. The IR spectra were performed on a Bruker Vector 22 FT-IR spectrometer by using KBr disks in the 4000–400 cm^{-1} range. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer manufactured by the PANalytical, with monochromatized Cu Kα radiation. Simulated XRD powder patterns based on single crystal data were prepared using mercury [19]. The crystallite sizes of selected samples were estimated using the Scherrer formula. The morphology of samples after gold coating was investigated using a scanning electron microscope (S-4200, Hitachi, Japan) and transmission electron microscop. 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 at room temperature for 1 h, was used for the ultrasonic irradiation. The crystallite sizes of selected samples were estimated using the Scherrer formula.

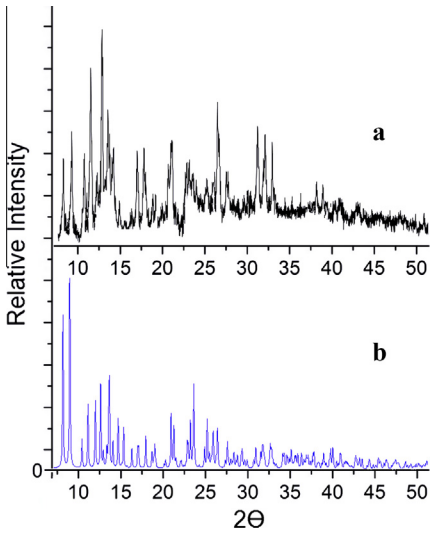

Fig. 1. The XRD patterns of (a) computed from single crystal X-ray data of compound **1**; (b) nano-structure of compound **1**.

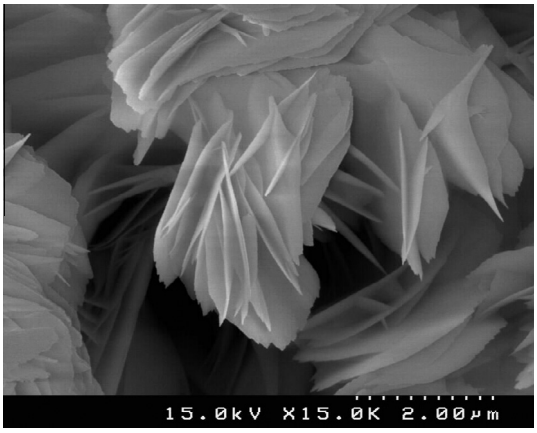

Fig. 2. SEM photographs of [Pb(pcih)$_2$] (**1**) nano flowers.

*Preparation of [Pb(pcih)$_2$] (**1**)*

To prepare the nano-flowers structure of [Pb(pcih)$_2$] (**1**), a solution of $Pb(NO_3)_2$ (25 mL of a 0.1 M) in H_2O was positioned in a high-density ultrasonic probe operating at 20 kHz with a maximum power output of 600 W. 50 mL of a 0.1 M of the ligands