Journal of Organometallic Chemistry 861 (2018) 105–111

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Solid-state conversion of thallium(I) coordination polymer nanoparticles with cubic cage units to an organometallic silver(I) coordination polymer

Zarin Moghadam [a], Kamran Akhbari [a, *], Anukorn Phuruangrat [b]

[a] School of Chemistry, College of Science, University of Tehran, Tehran, Iran
[b] Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla, Thailand

ARTICLE INFO

Article history:
Received 10 January 2018
Received in revised form
21 February 2018
Accepted 23 February 2018
Available online 26 February 2018

Keywords:
Coordination polymer
Mechanochemical
Thallium
Silver
Organometallic
Nanostructure

ABSTRACT

Solid-state structural transformation of three-dimensional Tl(I) coordination polymer nanoparticles with cubic cage Tl_4O_4 unit, prepared by sonochemical procedure, to three-dimensional organometallic Ag(I) coordination polymer nanostructures has been observed upon mechanochemical reaction of compound $[Tl_4(\mu_8\text{-B-4-hps})_2]_n$ (**1**), [H_2B-4-hps = bis(4-hydroxyphenyl) sulfone] with $AgNO_3$. During this conversion, compound **2** with higher symmetry in its unit cell is formed. Although B-4-hps^{2-} in both compounds has μ_8 coordination modes but these two modes are different from each other. These nanostructures were characterized by Scanning Electron Microscopy (SEM). IR spectroscopy, X-ray powder diffraction (XRD) and thermo gravimetry and differential thermal analyses (TG-DTA), indicated that this conversion is irreversible. The irreversibility of this transformation is due to the formation of stronger Ag-O and Ag-C bonds (in **2**) in comparison with initial Tl-O bonds in **1**.

1. Introduction

Coordination polymers (CPs) represent an area of growing interest in chemistry and material science [1,2]. The design of CPs is the current interest in the field of supramolecular chemistry and crystal engineering due to their wide properties, which include magnetism, catalysis, nonlinear optics, and molecular sensing [3,4]. CPs consist of repeating ligands interconnected by metallic nodes. CPs can be made either as highly crystalline structures, often referred to as metal–organic frameworks (MOFs), or amorphous structures. So far, one-dimensional, two-dimensional and three-dimensional coordination polymers of different metals has been characterized providing very interesting information about supramolecular isomerism [5]. In addition, they can be made in macroscopic forms or as dispersible nano and micro particles, which have distinct properties from their macroscopic counterparts. the different methods for synthesizing coordination polymer have been developed [1]. The need for environmentally friendly procedures leads to developing new methods such as sonochemistry [6–13], microwave reactions and reactions induced by mechanical force, also known as mechanochemical reactions. These methods are cleaner and more material efficient than existing, solvent based ones [14–16]. The liquid (solvent) free reactions have been successfully applied to the covalent synthesis of molecules and formation of supermolecules based on non-covalent interactions [17,18]. Mechanochemistry can be as simple as grinding two reactants in a pestle and mortar. Ball mills, however, have the merit of requiring no physical effort, supplying greater power and being programmable, allowing more systematic studies of the process [19,20]. The synthesis of thallium(I) coordination polymers is an increasingly active area of research as a result of the presence of a $6s^2$ electron configuration and the stereoactivity of the valence shell lone pair of electrons. Based on the directed ligands, these polymers are classified as holodirected or hemidirected [21]. Tl usually favours the formation of Tl … Tl, Tl … C, Tl … H and Tl … X (X = halogen atoms) secondary interactions, especially on its unoccupied coordination site with a stereochemically active lone pair of electrons, which indicates that the Tl(I) ion can act as either a Lewis acid or a Lewis base [22]. It is interesting to study thallium(I) compounds' structural transformation in the solid state, because they are similar in structure and chemical properties to silver(I) compounds, which

* Corresponding author.
E-mail address: akhbari.k@khayam.ut.ac.ir (K. Akhbari).

https://doi.org/10.1016/j.jorganchem.2018.02.041
0022-328X/

form Ag … Ag, Ag … C, Ag … H and Ag … X (X = halogen atoms) secondary interactions [23–25]. The significant difference between Tl(I) and Ag(I) is the presence of lone pair of electrons in Tl(I) which causes different structure and chemical properties in silver(I) compounds [26]. Study of structural transformations give some valuable information about design and synthesis of novel CPs, because they give key information about the response of CPs to external stimulant such as changes in temperature, mechanical force, solution, reaction time, the presence of guest molecules and electromagnetic irradiation [27–33]. Thus, in this work, it was decided to synthesize Tl(I) nano coordination polymer of bis(4-hydroxyphenyl) sulfone (H_2B-4-hps) by sonochemical process and to study solid-state conversion of ($[Tl_4$ (μ_8-B-4-hps$)_2]_n$) (**1**), [34] to [Ag_2 (μ_8-B-4-hps)]$_n$ (**2**) [35] by mechanochemical reaction with excess amount of $AgNO_3$. The reversibility of this solid-state conversion was also studied.

2. Experimental section

2.1. Materials and physical techniques

All reagents and solvents for the synthesis and analysis were commercially available and were used as received. The molecular structure plots were prepared using Mercury. A PARSONIC 15S ultrasonic bath (with a frequency 28 KHz) was used for the ultrasonic irradiation. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded using an Equinox 55 FT-IR spectrometer (Bruker, Bremen, Germany) in the ATR form, in the range 400–4000 cm^{-1} with a 4.0 cm^{-1} resolution and 16 scans. The thermal behavior was measured with a PL-STA 1500 apparatus between 20 and 1000 °C, with a heating rate of 5 °C min^{-1}, under a nitrogen atmosphere. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer manufactured by Philips with monochromatized Cukα radiation (λ = 1.54056 Å) with a step size of 0.01671 (degree). The X-ray source was operated under a voltage of 40 kV and a current of 30 mA. Bragg-Brentano was used as the source detector geometry with a scintillation detector. Additional attachments or peripheral equipment, such as an anti-scatter slit (1°), divergence slit (1°), monochromator and soller slit (0.04 rad), were also used in this diffractometer. The samples were prepared as fine powders on silicon-based material. Simulated XRD powder patterns based on single crystal data were prepared using the Mercury software. The samples were characterized with a scanning electron microscope (Philips XL 30) with a gold coating.

2.2. Synthesis of [tl_4(μ_8-B-4-hps$)_2]_n$ (1) by a sonochemical process

4 mmol of Bis(4-hydroxyphenyl) sulfone was dissolved in 10 mLof H_2O and 10 Ml of MeCN and was heated and stirred with solution of 8 mmol of KOH in 5 Ml of H_2O for an hour. The solution was placed in ultrasonic bath and then 8 mmol of $TlNO_3$ was added to the solution. After about 5 h, a white precipitate was obtained which was filtered a nd dried at room temperature.

2.3. Mechanochemical reaction of 1 with excess $AgNO_3$ in order to synthesis of [Ag_2(μ_8-B-4-hps)]$_n$ (2)

This reaction was performed between 3 mmol of **1** and 7 mmol of $AgNO_3$. These two reactants were mixed in a mortar and ground up for 30 min, and then the mixture was washed four times with distilled water until the unreacted $AgNO_3$ and produced $TlNO_3$ was removed, and the pure product was separated.

2.4. Checking the reversibility of this solid-state structural transformation with $TlNO_3$

This reaction was performed between 1 mmol of **2** and 2.5 mmol of $TlNO_3$. These reactants were mixed and ground up for 30 min by adding some droplets of water. The XRD pattern of the resulting precipitate (Fig. 1) approved that this transformation is irreversible and **2** was not converted back into **1**.

3. Results and discussion

The reaction between Bis(4-hydroxyphenyl) sulfone (H_2B-4-hps), KOH and $TlNO_3$ in mixture of water and acetonitrile under ultrasonic irradiation results in formation of white powder which was dried at room temperature. A comparison between the XRD patterns simulated from single crystal X-ray data of [Tl_4 (μ_8-B-4-hps$)_2]_n$ (**1**) (Fig. 1a) and the prepared powder (Fig. 1b), approved the formation of **1** successfully. Identification the structure of **1** by

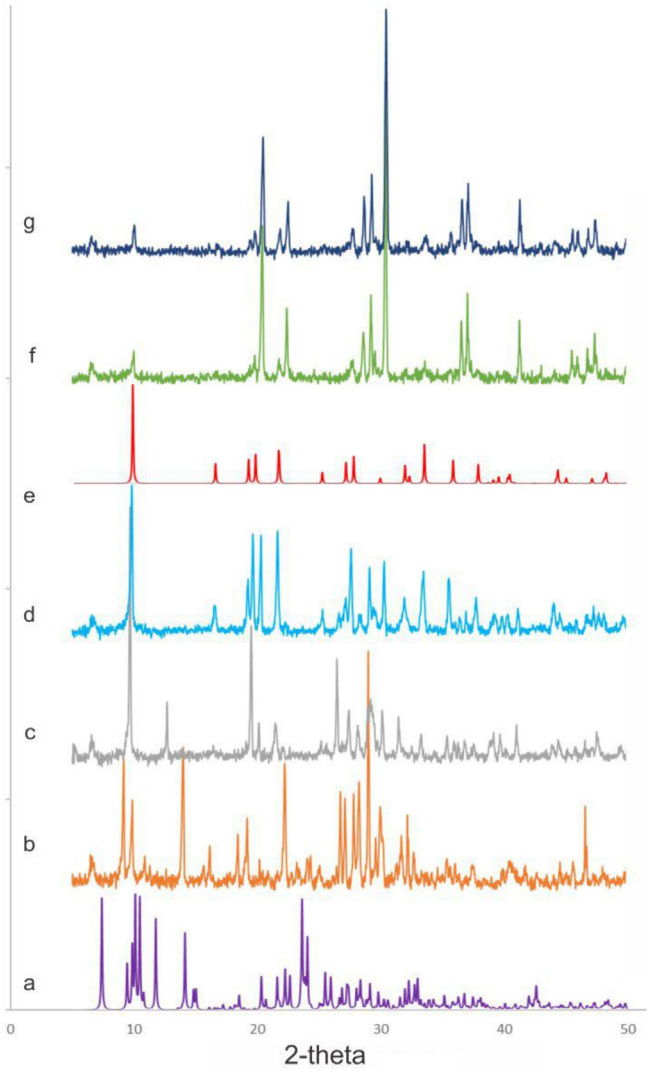

Fig. 1. XRD patterns; a) simulated pattern based on single crystal data of compound [Tl_4 (μ_8-B-4-hps$)_2]_n$ (**1**), b) compound **1** synthesized under ultrasonic irradiations, c) compound **1** after mechanochemical reaction with excess $AgNO_3$, d) the pure phase of compound [Ag_2 (μ_8-B-4-hps)]$_n$ (**2**), e) simulated pattern based on single crystal data of **2**, f) compound **2** nanostructures after mechanochemical reaction with $TlNO_3$ and g) pure phase of compound **2**.