



Similar to what occurs in biological systems; irreversible replacement of potassium with thallium in coordination polymer nanostructures



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ABSTRACT

Irreversible solid-state structural transformation of two-dimensional K^I coordination polymer nanostructures, prepared by sonochemical procedure, to one-dimensional Tl^I coordination polymer nanoparticles has been observed upon mechanochemical reaction of compound $[K(dcpa)(H_2O)_{0.5}]_n$ (**1**), [Hdcpa = 2,4-dichlorophenoxyacetic acid] with $TlNO_3$. This irreversible exchange is similar to that occurred in biological systems approved the toxicity of thallium. In addition to removal of coordinated H_2O molecule, during this transformation the coordination bonds of 2-chloro substituent and phenoxy oxygen atom of $dcpa^-$ with the potassium ion was broken. The bridging and chelating coordination behavior of $dcpa^-$ between three $K(I)$ ions in **1** is changed to bridging coordination behavior of $dcpa^-$ between two $Tl(I)$ ions in $[Tl(\mu_2-dcpa)]_n$ (**2**). A comparison between crystal data of these two compounds shows that these two compounds have the same crystal system and similar space groups, unit cell dimensions and volume. This similarity may be an assistant factor for possibility of this solid-state conversion.

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1. Introduction

The rational and controlled design of multinuclear coordination polymers (CPs) are still one of the most focused areas of crystal engineering, due to their fascinating architectures [1] and highly promising chemical and physical applications in many fields [2]. The synthesis of thallium(I) coordination polymers is an increasingly active area due to presence of a $6s^2$ electron configuration and stereoactivity of the valence shell lone electron pair and according to directed ligands classify as holodirected and hemidirected. Tl^I usually favors the formation of $Tl \cdots Tl$, $Tl \cdots C$, $Tl \cdots H$ and $Tl \cdots X$ (X = halogen atoms) secondary interactions especially on its vacant coordination site with stereo chemically active electron lone pair which indicates that Tl^I ion has the capacity to act as both a Lewis acid and a Lewis base [3]. To further promote our understanding of supramolecular architecture, it is challenging to continue the investigations on the solid-state structural transformations of coordination polymers [4]. Specially thallium(I) compounds are similar in structure and chemical properties to potassium which makes it easy for us to study their structural transformations in solid-state [5]. The scale and shape of solid materials influence on the chemical and physical properties. By

decreasing the scale of coordination polymers as in nano-scale, surface area would be increased. Hence making coordination polymers in any form in nano-scale is certainly a major step forward toward the technological applications of these new materials [6]. In this paper we would like to describe a simple synthetic sonochemical preparation of nano-structured potassium coordination polymer, $[K(dcpa)(H_2O)_{0.5}]_n$ (**1**) [7], (Hdcpa = 2,4-dichlorophenoxyacetic acid) and then we want to examine the solid-state structural transformation of it with $TlNO_3$ to prepare the $[Tl(\mu_2-dcpa)]_n$ (**2**) coordination polymer. Solid-state reactions are regularly much faster, more efficient and more selective than the analogous reactions in solutions. Consequently, many organic, inorganic and coordination compounds have been prepared by solid-state reactions [8]. Solid-state structural transformations of CPs involve making and breaking of new coordination and/or covalent bonds in more than one direction. The stimuli for the structural transformations are generally heat, light, mechanochemical force, etc. The effects of such actions are manifested in terms of new bond formation or breakage which results in a change of coordination number and geometry, dimensionality, chirality, interpenetration, etc. [9]. Solid-state reactions by manual or mechanical grinding with minimal or no solvent for molecular synthesis have triggered lots of attention [10]. Mechanochemistry, a burgeoning field in CPs, has been utilized to synthesize various CPs from the reactants without solvents or using liquid assisted grinding (LAG) [11]. However, this

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grinding has also been shown to result in various types of structural transformations due to loss or uptake of solvents, pedal-like motion and movements of molecular fragments due to mechanical force. Such transformations by the mechanochemical grinding cannot be investigated directly by single-crystal X-ray crystallography, though structures could be solved from PXRD diffraction data in many cases. Matching of the PXRD patterns of the bulk with those simulated from the single-crystal data from separate synthetic routes has also been utilized successfully [9].

2. Experimental

2.1. Materials and physical techniques

All reagents for the synthesis and analysis were commercially available and used as received. PARSONIC 15S ultrasonic bath (with the frequency 28 kHz) was used for the ultrasonic irradiation. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. 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 ATR form, in the range of 400–4000 cm^{-1} with 4.0 cm^{-1} resolution and the 16 scan's numbers. The molecular structure plot and simulated XRD powder pattern based on single crystal data were prepared using OLEX and Mercury software. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with mono chromatized $\text{Cu K}\alpha$ radiation. The thermal behavior was measured with a PL-STA 1500 apparatus in the static atmosphere of nitrogen. The samples were characterized with a scanning electron microscope (Philips XL 30) with gold coating.

2.2. Synthesis of $[\text{K}(\text{dcpa})(\text{H}_2\text{O})_{0.5}]_n$ (**1**) nanostructure by a sonochemical process

To prepare nano-sized $[\text{K}(\text{dcpa})(\text{H}_2\text{O})_{0.5}]_n$ (**1**), 4 mmol (0.884 g) of the 2,4-dichlorophenoxyacetic acid was dissolved in 15 ml methanol and was mixed and stirred with solution of 4 mmol (0.228 g) KOH in 5 ml H_2O at 100 °C for about 45 min and then this mixture was positioned in an ultrasonic bath. After 3 h white precipitate was obtained which was filtered and dried at room temperature. d.p. = 184 °C, yield: 0.944 g, 88.0% based on final product, IR (selected bands; in cm^{-1}): 463.65 s, 496.05 vs, 535 s, 751 m, 796 m, 866 w, 929 w, 1065 m, 1105 w, 1241 m, 1344 w, 1419 s, 1478 s, 1604 m, 1735 w and 2926–3291 br. *Anal. Calc.* for $\text{C}_8\text{H}_6\text{Cl}_2\text{K}_1\text{O}_{3.5}$: C, 35.83; H, 2.25. Found: C, 35.99; H, 2.30%.

2.3. Mechanochemical reaction of **1** with TlNO_3 in order to prepare $[\text{Tl}(\mu_2\text{-dcpa})]_n$ (**2**)

This reaction was performed between 2 mmol (0.536 g) of $[\text{K}(\text{dcpa})(\text{H}_2\text{O})_{0.5}]_n$ (**1**) nano-structure with 2.5 mmol (0.665 g) of TlNO_3 . These two reactants were mixed in mortar and ground up for 30 min through liquid-assisted grinding (LAG) method by adding a few droplets of water. Then the mixture was four times washed with distilled water until the resulting KNO_3 and unreacted TlNO_3 removed from it and the pure compound was separated. d.p. = 175 °C, yield: 0.806 g, 95.0% based on final product, IR (selected bands; in cm^{-1}): 447 vs, 480 vs, 549 m, 612 m, 688 s, 751 vs, 795 m, 865 m, 935 m, 1059 s, 1105 m, 1159 w, 1240 s, 1340 m, 1375 s, 1416 s, 1476 vs, 1555 m, 1598 w and 1735 w. *Anal. Calc.* for $\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3\text{Tl}$: C, 22.64; H, 1.19. Found: C, 22.73; H, 1.24%.

2.4. Checking the reversibility of this solid-state structural transformation with KNO_3

This reaction was performed between 1 mmol (0.424 g) of **2** with 1.25 mmol (0.126 g) of KNO_3 . These two reactants were mixed in mortar and ground up for 30 min through liquid-assisted grinding (LAG) method by adding a few droplets of water. The XRD pattern of resulting precipitate approved that this transformation is irreversible (Fig. 1f) and $[\text{Tl}(\mu_2\text{-dcpa})]_n$ (**2**) was not converted back to **1** upon solid-state reaction with KNO_3 . IR (selected bands; in cm^{-1}): 446 vs, 481 vs, 550 m, 613 m, 688 s, 751 vs, 796 m, 865

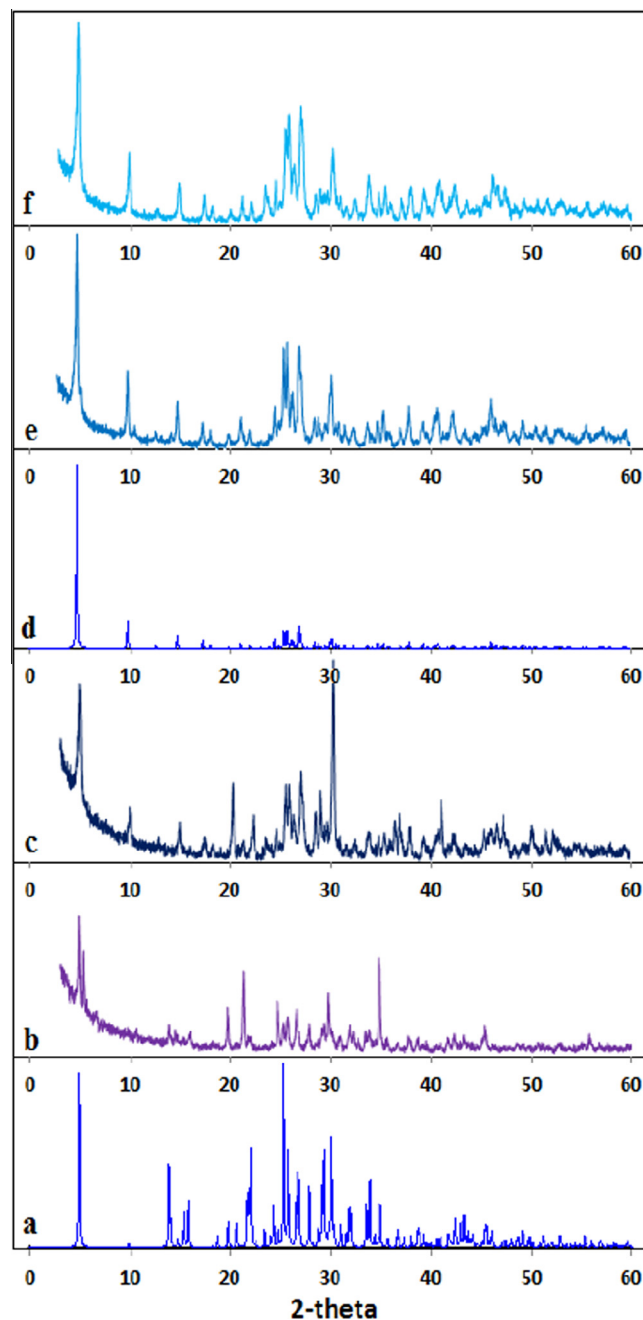


Fig. 1. XRD patterns; (a) simulated pattern based on single crystal data of compound $[\text{K}(\text{dcpa})(\text{H}_2\text{O})_{0.5}]_n$ (**1**), (b) compound **1** nanostructures synthesized under ultrasonic irradiations, (c) compound **1** after solid-state mechanochemical reaction with excess TlNO_3 , (d) simulated pattern based on single crystal data of compound $[\text{Tl}(\mu_2\text{-dcpa})]_n$ (**2**), (e) pure phase of **2** and (f) compound **2** after mechanochemical reaction of it with excess KNO_3 .

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