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Crystal to Crystal Transformation of Nano Lead(II) Coordination polymer by Solid State Anion-replacement

*Ali Morsali[1)] and Vahid Safarifard[2)]

[1), 2)] *Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, Tehran, Islamic Republic of Iran*
[1)] *morsali_a@modares.ac.ir*

ABSTRACT

Irreversible crystal-to-crystal transformation of 3D lead(II) coordination polymer with the ligand 1H-1,2,4-triazole-3-carboxylic acid (HL), $[Pb(L)(\mu_2\text{-}Br)(H_2O)]_n$ (**1**) to 3D supramalecular compound $[Pb(L)(\mu_2\text{-}I)]_n$ (**2**) by solid state anion-replacement have been studied. Structural determination of compound **2** reveals the Pb(II) ion is five coordinated with hemidirected geometry, bonded to one nitrogen atom, two oxygen atoms from the L^- ligand and two iodide ions. The irreversible solid state structural transformations of compounds **1** to compound **2**, by anion-replacement processes under mechanochemical reaction have been verified by PXRD measurements. Nanoparticles of compound **1** was synthesized by sonochemical process and characterized by scanning electron microscopy (SEM), powder X-ray diffraction, IR spectroscopy and elemental analyses. The SEM images showed that no morphology change occur during this solid state anion-replacement.

1. INTRODUCTION

During the last two decades, design and synthesis of novel metal–organic coordination polymers are attracting more attention, not only for their interesting molecular topologies, but also for their potential applications in catalysis, molecular adsorption, magnetism, ions exchange, nonlinear optics, luminescence, and molecular sensing (Janiak 2003). Solid state reactions by manual or mechanical grinding with minimal or no solvent for molecular synthesis have triggered lots of attention. Mechanochemistry, a burgeoning field in coordination polymers, has been utilized to synthesize various coordination polymers from the reactants without solvents or using liquid or ionic liquid assisted grinding (ILAG) (Nagarathinam 2012). Solid state crystal-to-crystal transformations of coordination polymers are interesting since they involve breaking and forming of coordination bonds in more than one direction. These kinds of solid-state structural transformations with the retention of crystalline character directly reflect the relationship between the solids involved. To develop further our understanding of the supramolecular architecture, it is challenging to continue the investigations on the crystal-to-crystal transformations involving anion-replacement.

[1)] Professor
[2)] Graduate Student

There are several types of structural transformations that are primarily influenced by the expansion of the metal coordination numbers, thermal dissociation/association, condensation, rearrangement of bonds or the removal/exchange of solvents (Vittal 2007). However structural transformation along with anion-replacement is interesting type of solid state reactions.

During the past decade, coordination polymers based on 1,2,4-triazole and its derivatives have drawn considerable attention in the development of novel functional materials (Safarifard 2011). During the course of the syntheses of the coordination polymers from ligand 1H-1,2,4-triazole-3-carboxylic acid (HL) in our laboratory, we isolated two lead(II) coordination polymers that undergo interesting solid state anion-replacement, $[Pb(L)(\mu_2\text{-}Br)(H_2O)]_n$ (**1**) to $[Pb(L)(\mu_2\text{-}I)]_n$ (**2**), which are verified by X-ray powder diffraction identification. The 3D coordination polymer **1** polymerized by grinding the solid with KI to form 3D supramalecular compound **2**. In order to study the morphology change of compound **1** nanoparticles under transformation to compound **2**, compound **1** was prepared by a sonochemical process.

2. EXPERIMENTAL SECTION

Syntheses of $[Pb(L)(\mu_2\text{-}Br)(H_2O)]_n$ (1). Single crystals of **1** were prepared by a branched tube method, 1H-1,2,4-triazole-3-carboxylic acid (0.117 g, 1 mmol), lead(II) nitrate (0.331 g, 1 mmol) and potassium bromide (0.119 g, 1 mmol) were placed in the bottom main of a branched tube. Water was carefully added to fill both arms, and then the arm to be heated was placed in oil bath at 60 °C. After 7 days, colorless crystals were deposited in the cooler arm which were filtered off, washed with water and air dried. (0.225 g, yield 54%), m.p. >300 °C. (Found C 8.55, H 0.99, N 10.43%. calculated for $C_3H_4BrN_3O_3Pb$; C 8.63, H 0.96, N 10.07%). IR (cm^{-1}) selected bands: 464(s), 651(s), 1100(s), 1303(m), 1370(m), 1457(vs), 1606(s) and 3370(br).

Syntheses of $[Pb(L)(\mu_2\text{-}I)]_n$ (2). Single crystals of $[Pb(L)(\mu_2\text{-}Br)(H_2O)]_n$ (**1**) upon grinding with solid KI for 20 min in an agate mortar and pestle, lead to formation of compound $[Pb(L)(\mu_2\text{-}I)]_n$ (**2**). The new yellow product, compound **2**, was separated from the unreacted KI and produced KBr by washing with water and ethanol and drying under vacuum. Anal. calcd. for powder product, compound **2**: C 8.07, H 0.45, N 9.41%; found: C 7.93, H 0.49, N 9.82%. IR (cm^{-1}) selected bands: 453(s), 810(s), 981(s), 1280(m), 1453(m), 1622(vs) and 3102(br). In order to obtain compound **2** single crystals, suitable for X-ray crystallography, we used a branched tube method. Compound **2** were placed in the bottom main of a branched tube. Water was carefully added to fill both arms, the tube sealed and the main arm immersed in oil bath at 60 °C while the branched arm was at ambient temperature. After 10 days, suitable yellow single crystals had deposited in the cooler arm which were filtered off, washed with water and air dried (0.28 g, yield 63%). Anal. calcd. for $C_3H_2IN_3O_2Pb$: C 8.07, H 0.45, N 9.41%; found: C 8.15, H 0.43, N 9.63%. IR (cm^{-1}) selected bands: 462(s), 819(s), 995(s), 1286(m), 1457(m), 1626(vs) and 2926(br).

Sonochemical Syntheses of Compound 1 Nanoparticles. To prepare the nanoparticles of **1**, 50 ml solution of lead(II) nitrate (0.01 M) in water was positioned in a high-density ultrasonic probe, operating at 50 Hz with a maximum power input of 305 W. Into this aqueous solution a 50 ml solution of the ligand 1H-1,2,4-triazole-3-carboxylic acid (0.01 M) and sodium hydroxide (0.01 M) and potassium bromide (0.01 M) were added dropwise. The obtained precipitates were filtered off, washed with water and then dried in air. m.p. > 300 °C. (Found C 8.61, H 0.89, N 10.12%). IR (cm^{-1}) selected bands: 466(s), 661(s), 1106(s), 1309(m), 1373(m), 1465(vs), 1610(s) and 3373(br). In order to prepare compound **2** nanostructures and consider the morphology and size change during the solid state structural transformation, nanoparticles of compound **1** was grinded with KI for 20 min to yield **2** nanoparticles. (Found C 8.21, H 0.51, N 9.29%.). IR (cm^{-1}) selected bands: 459(s), 819(s), 995(s), 1286(m), 1457(m), 1626(vs) and 3109(br).

3. RESULTS AND DISCUSSION

The perspective view and the coordination environment of 3D coordination polymer, $[Pb(L)(\mu_2\text{-}Br)(H_2O)]_n$ (**1**) (L^- = 1H-1,2,4-triazole-3-carboxylate) is shown in Fig. 1a. In polymer **1**, the coordination number is 7 and each Pb^{II} ion is in the holo-directed geometry and coordinated by two oxygen atoms, two nitrogen atoms of the L^- anions act as bridging ligands *via* a tetra-donor coordination mode and one oxygen atom of aqua ligand. Also two bridged bromide ions have coordinated to lead(II) ion, forming quite distorted pentagonal bipyramid geometry, thus forming infinite 3D neutral network as illustrated in Fig. 2a. Upon grinding the compound **1** with KI, colorless single crystals of compound **1** changed to compound **2**, a yellow powder sample.

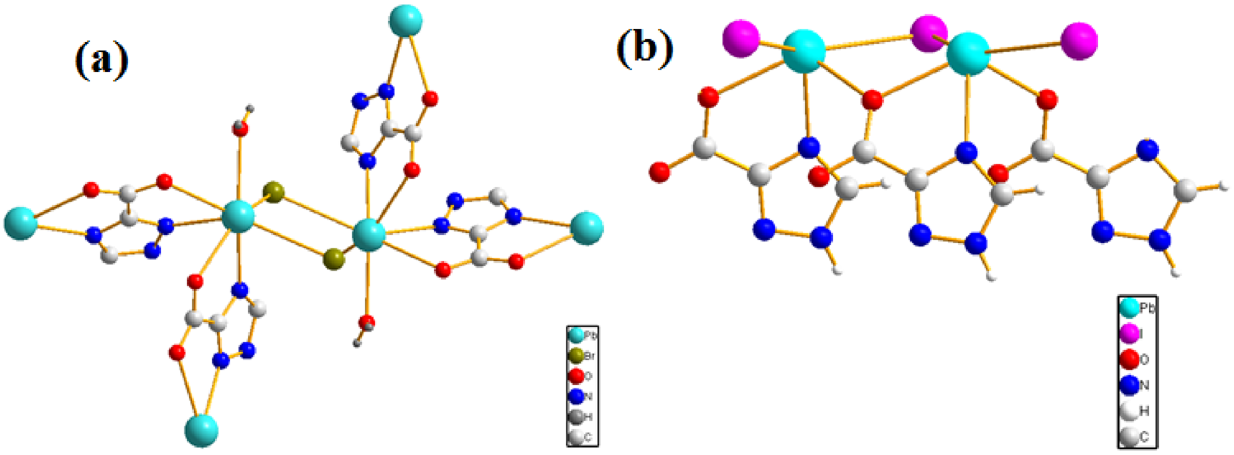

Fig. 1. View of a section of the dimeric units (a) by bridging of the Br^- anions via one sides in **1** and (b) by bridging of the I^- anion and L^- ligand via one sides in **2**.

Single crystals of compound $[Pb(L)(\mu_2\text{-}I)]_n$ (**2**), suitable for X-ray crystallography, were prepared by a branched tube method. The molecular structure of the fundamental building unit for **2** is shown in Fig. 1b. In **2**, the Pb^{II} ion is in the hemidirected geometry and five-coordinated with one nitrogen atom, two oxygen atoms from the L^- anions and two iodide ions. As shown in Fig. 2b, one $\mu_{1,1}$-I^- ligand and the L^- anions act as bridging ligands to join neighboring lead(II) centers to form a 1D linear chain. The Pb…Pb separation bridged by the L^- and μ_2-I^- ligands is 4.1992(10) Å.

The most remarkable and interesting features on the construction of its 3D supramolecular architectures in **2** is that the subtle combination of Pb…I interactions and hydrogen bonding serves to connect these 1D coordination chains to 2D layered networks, and then a 3D supramolecular framework, as shown in Fig. 2b. First, these adjacent 1D coordination chains are mutually interlinked *via* two different Pb…I interactions with distances of 3.58(13) Å and 3.63(14) Å and extended to a 2D layered network. These 2D layers extended to a 3D network, *via* the strong N(2)–H(2)...O(2) hydrogen bonds between the triazole ring and uncoordinated oxygen atom (O(2)) of carboxylate group of L^- ligand with N…O distance of 2.80(2) Å, and N(2)–H(2)...N(3) hydrogen bonds between triazole rings with N...N distance of 3.07(2) Å.

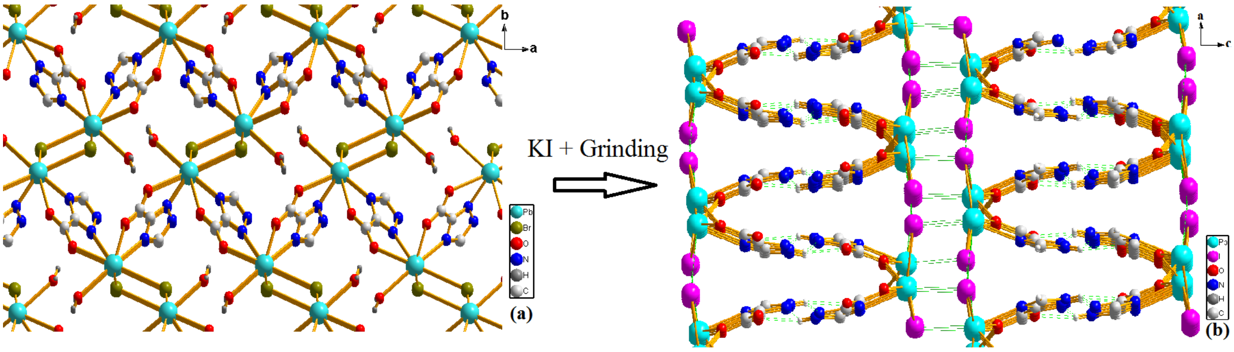

Fig. 2. A schematic diagram illustrating the structural conversions of 3D coordination polymer **1** (a) to a 3D supramolecular compound **2** (b) by solid state irreversible anion-replacement.

Irreversible crystal-to-crystal conversion along with anion-replacement of compound **1** to **2** was confirmed by powder X-ray diffraction patterns. The structures of the bulk materials for the compounds were confirmed by matching their powder X-ray diffraction patterns with those generated from the corresponding single-crystal structures (Fig. 3). Acceptable matches was observed between the pattern simulated from single-crystal X-ray data (Fig. 3a) and that measured by powder X-ray diffraction for the bulk crystalline sample as obtained from the synthesis of compound **1** (Fig. 3b). Transformation by solid state anion-replacement of compound **1** (Fig. 3a-d) results in a change of the powder pattern (Fig. 3d), which now matches the pattern of compound **2**, as calculated from the single-crystal X-ray data (Fig. 3c). The observation of a new pattern of peaks implies complete disappearance of **1** and formation of a new compound **2** during the solid state reaction with KI. This reaction is irreversible and polymer **2** is not converted back to compound **1** by solid state grinding with KBr.

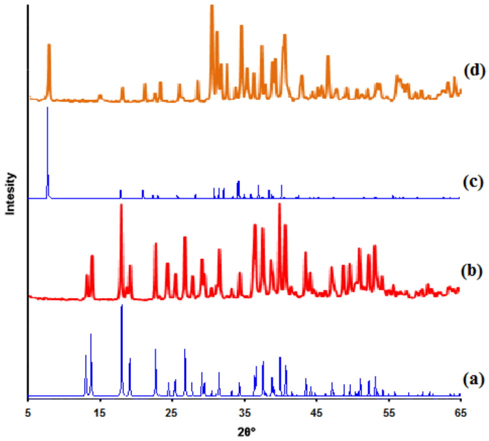

Fig. 3. The XRD patterns of (a) simulated from single crystal X-ray data of compound **1**, (b) bulk materials as synthesized of compound **1**, (c) simulated from single crystal X-ray data of compound **2** and (d) bulk materials obtained by solid state anion-replacement of compound **1**.

To further confirm the irreversible anion replacement between compound **1** and **2**, IR spectra were recorded for compound **1** and the same sample after grinding with KI (Fig. 4). For the IR spectrum of **1**, the triazole out of plane rings absorption can be observed at 655 cm^{-1}. The symmetric and asymmetric vibrations of the carboxylate groups are observed at 1457 and 1606 cm^{-1}. The $\Delta(\upsilon_{as}-\upsilon_{sym})$ value of 149 cm^{-1} indicates that the carboxylate groups coordinate to the lead(II) centers in a bridging mode. The v_{O-H} vibration of the coordinated water molecule is observed as a strong band centered at 1400 cm^{-1}. It can clearly be seen that after grinding the solid **1** by KI, the large broad band attributable to the O-H stretching vibrations is significantly diminished (Fig. 4b).

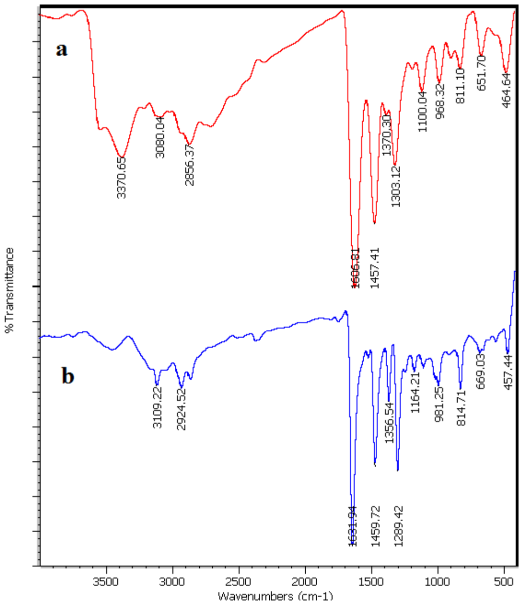

Fig. 4. IR spectra of (a) bulk materials as synthesized of compound **1** and (b) bulk materials obtained by solid state anion-replacement of compound **1** by potassium iodide.

To study the morphology and size of compound **1** nanoparticles under transformation to compound **2**, the nanoparticles of compound **1** were prepared by a sonochemical process. The elemental analysis and IR spectra of the nanoparticles and of the single crystalline materials are indistinguishable (as shown in Fig. 5).

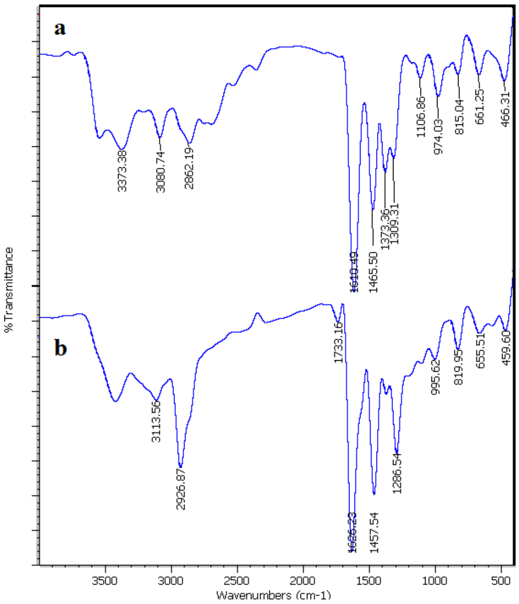

Fig. 5. IR spectra of (a) nanoparticles of compound **1** produced by sonochemical method and (b) nanoparticles of compound **2** obtained by solid state anion-replacement of compound **1**.

Fig. 6b shows the XRD patterns of typical sample of compound **1**, prepared by a sonochemical process. Fig. 6a shows the XRD patterns simulated from the single crystal X-ray data. Acceptable matches are observed for the compound indicating the presence of only one crystalline phase in the sample prepared using the sonochemical process.

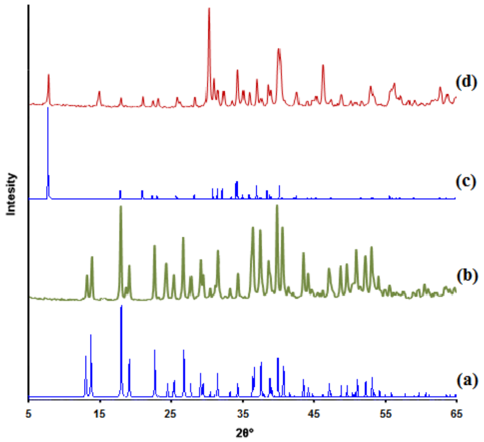

Fig. 6. The XRD patterns of (a) simulated from single crystal X-ray data of compound **1**, (b) nanoparticles of compound **1** prepared by sonochemical process, (c) simulated from single crystal X-ray data of compound **2** and (d) nanoparticles obtained by solid state anion-replacement of compound **1**.

Fig. 7b shows the SEM image and the corresponding size distribution histograms of the compound **2** obtained from transformations of nanoparticles of compound **1** (Fig. 7a). The size of the nanoparticles obtained using the transformation are as the same as that observed in Fig. 7a and no morphology changes would be observed but the solid state anion-replacement causes that the nanoparticles to be agglomerated.

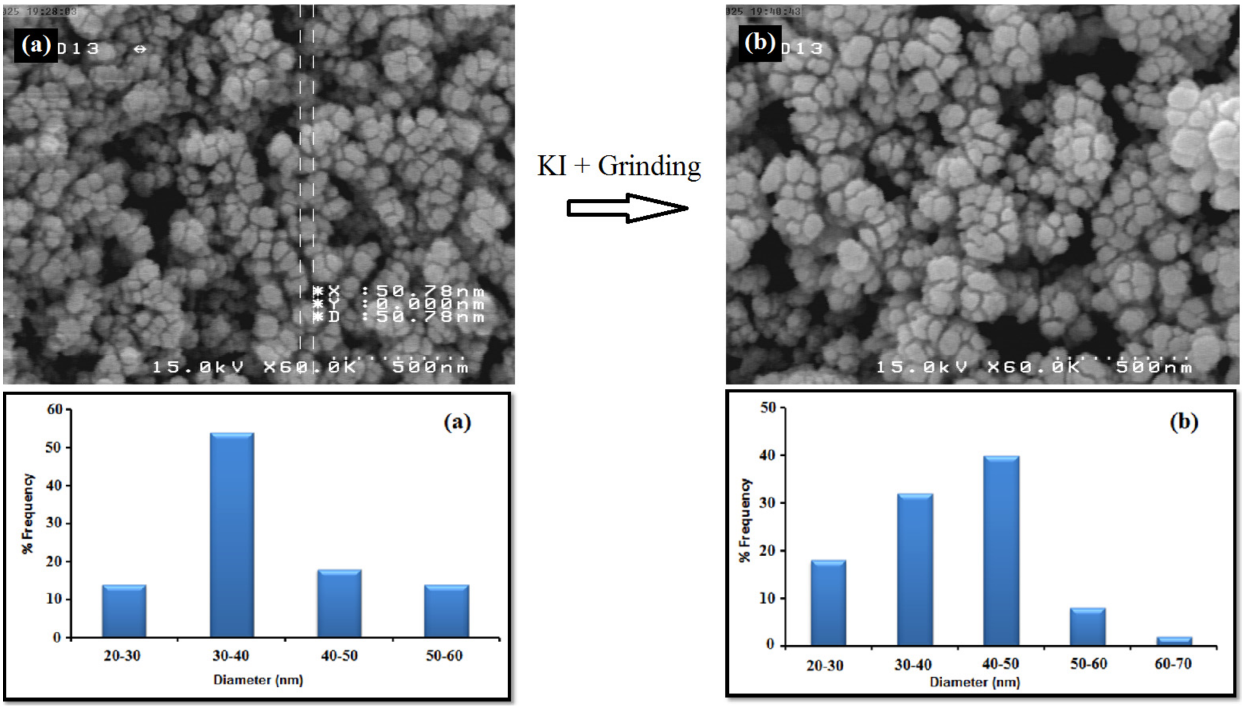

Fig. 7. SEM image and the corresponding particle size distribution histogram of (a) compound **1** nanoparticles prepared by sonochemical process and (b) compound **2** nanoparticles obtained from transformation of nanoparticles of compound **1** on grinding the sample with KI.

CONCLUSION

In summary, 3D lead(II) coordination polymer, $[Pb(L)(\mu_2\text{-}Br)(H_2O)]_n$ (**1**), polymerizes on grinding the solid with KI to form a new 3D supramalecular compound, $[Pb(L)(\mu_2\text{-}I)]_n$ (**2**). In the crystal lattices, bridged bromide ions of compound **1** replace with iodide ion to generate compound **2**. The morphology and size of the compound **2** nanoparticles obtained using solid state anion-replacements are the same as that observed in compound **1** prepared by a sonochemical process. The solid state transformation have been supported by IR spectroscopy and PXRD studies and show that the processes are irreversible and compound **1** cannot be regenerated form **2** upon grinding the solid with KBr. This solid state structural transformation is an example of the mechanochemical reactions for conversion of coordination polymers that take place by manual or mechanical grinding with no solvent. These grinding reactions yielded successful isolation of materials that are otherwise inaccessible in solution.

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