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## COMMUNICATION

# Reversible crystal-to-crystal transformation of a 3D–3D coordination polymer by solid state anion-replacement with no change in nano-particle morphology†

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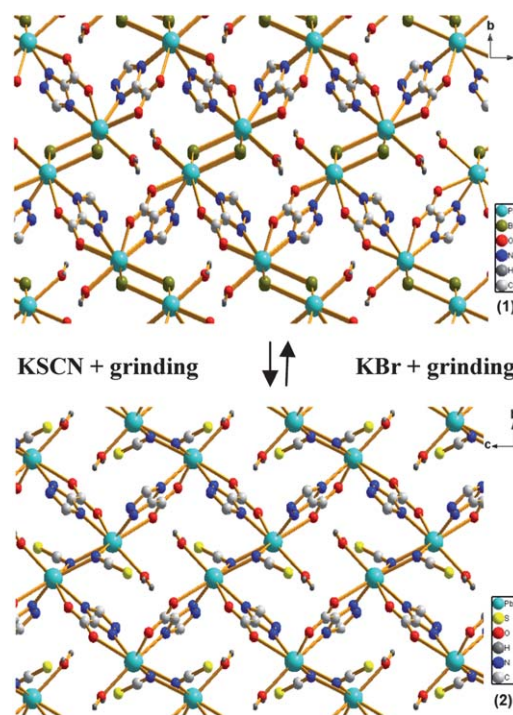
A reversible crystal-to-crystal transformation of a 3D lead(II) coordination polymer with the ligand 1*H*-1,2,4-triazole-3-carboxylic acid (HL), from  $[\text{Pb}(\text{L})(\mu_2\text{-Br})(\text{H}_2\text{O})]_n$  (**1**) to 3D  $[\text{Pb}(\text{L})(\mu_{1,1}\text{-NCS})(\text{H}_2\text{O})]_n$  (**2**) by solid state anion-replacement, has been observed. The thermal stabilities of compounds **1** and **2** were studied by thermal gravimetric and differential thermal analyses. Powder X-ray diffraction experiments showed that the structural transformation occurs in the powder samples and leads to monophasic products. Nano-particles of compound **1** were synthesized by a sonochemical process and characterized by scanning electron microscopy (SEM), powder X-ray diffraction, IR spectroscopy, elemental analyses, thermal gravimetric and differential thermal analyses. The SEM images showed that no morphology change occurs during this solid state anion-replacement.

During the last two decades, the rational design and syntheses of novel coordination polymers have made considerable progress in the field of supramolecular chemistry and crystal engineering,<sup>1–5</sup> not only because of the intriguing structural motifs of the coordination polymers but also because of their potential applications in catalysis, molecular adsorption, magnetism, nonlinear optics, luminescence, and molecular sensing. Structural transformations with the retention of single-crystal character directly reflect the relationship between the solids involved. These conversions are rare, and normally occur merely through minor movements of atoms in the crystal. 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.<sup>6–26</sup> There are several types of structural transformations that are primarily influenced by the expansion of coordination numbers, thermal association, condensation, and rearrangement of bonds or the removal/exchange of solvents.<sup>27</sup> However structural transformation along with anion-replacement is an interesting type of solid state reactions. During the course of the syntheses of the coordination polymers from ligand 1*H*-1,2,4-triazole-3-carboxylic acid (HL) in our laboratory, we isolated

two lead(II) coordination polymers that undergo novel solid state reversible anion-replacement,  $[\text{Pb}(\text{L})(\mu_2\text{-Br})(\text{H}_2\text{O})]_n$  (**1**) to  $[\text{Pb}(\text{L})(\mu_{1,1}\text{-NCS})(\text{H}_2\text{O})]_n$  (**2**).†

The  $[\text{Pb}(\text{L})(\mu_2\text{-Br})(\text{H}_2\text{O})]_n$  (**1**) was prepared by a branched tube method<sup>28</sup> and this compound polymerizes by grinding the solid with KSCN to form  $[\text{Pb}(\text{L})(\mu_{1,1}\text{-NCS})(\text{H}_2\text{O})]_n$  (**2**) that has been previously analyzed and reported.<sup>29</sup> Fig. S1† shows the structures of the basic polymeric building block of compounds **1** and **2**. Crystals of **1** grinding with KSCN by hand and for 20 minutes undergo a reversible transformation to yield **2** and this process being accompanied without a color change (Fig. 1).

While the compound **1** crystallizes in the orthorhombic *Pna*2<sub>1</sub> space group, a monoclinic *P*2<sub>1</sub>/*c* cell is found for the compound **2**



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

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providing us with one of the few examples of crystal-to-crystal conversion along with anion-replacement.

Single-crystal X-ray diffraction analysis (Table S1†) of compound **1** shows that the complex is a 3D neutral metallopolymer bridged by  $\text{Br}^-$  and  $\text{L}^-$  ligands, thus forming an infinite framework, as illustrated in Fig. 1, top. There is one coordinated water molecule. The coordination number in **1** is 7, and each lead(II) atom is coordinated by two oxygen and two nitrogen atoms of the  $\text{L}^-$  ligand, one oxygen atom of the water molecule and two bromide ions (Fig. S1a†). The  $\text{L}^-$  anions act as bridging ligands *via* a tetra-donor coordination mode (Fig. S2a†).

Upon grinding the solid with KSCN, compound **1** changes to compound **2**, and its structure determination by X-ray crystallography reveals a number of unique features. The structure of **2** showed that the complex is a 3D polymeric network in the solid state (Fig. 1, bottom). The coordination number in **2** is 7, and each lead(II) atom is coordinated by two oxygen and two nitrogen atoms of the  $\text{L}^-$  ligand as well as one oxygen atom of the water molecule and two  $\mu_{1,1}$ -NCS $^-$  ions (Fig. S1b and S2b†).

Reversible crystal-to-crystal conversion along with anion-replacement between compounds **1** and **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. S3†). Acceptable matches were observed between the pattern simulated from single-crystal X-ray data (Fig. S3a†) and that measured by powder X-ray diffraction for the bulk crystalline sample as obtained from the synthesis of compound **1** (Fig. S3b†). Transformation by solid state anion-replacement of compound **1** (Fig. S3a–d†) results in a change of the powder pattern (Fig. S3d†), which now matches the pattern of compound **2**, as calculated from the single-crystal X-ray data (Fig. S3c†). The powder X-ray diffraction pattern of the reversed species (Fig. S3e†) shows that the sample regains the original structure which shows almost the same XRPD diffractogram as that of the freshly synthesized material (Fig. S3b†). These facts clearly indicate that the structure of compound **1**, which responds toward anion-replacement by a reversible change of its framework, is quite flexible and dynamic.

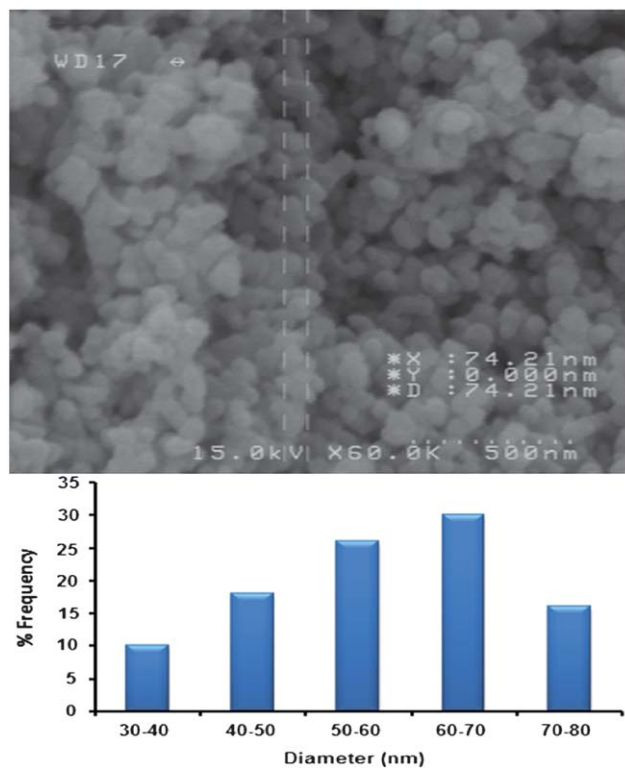
To further confirm the reversible anion replacement between compounds **1** and **2**, IR spectra were recorded for a compound **1** and for the same sample after grinding with KSCN as well as the reversed sample (Fig. S4†). For the IR spectrum of **1**, the triazole out of plane ring absorption can be observed at  $651\text{ cm}^{-1}$ . The symmetric and asymmetric vibrations of the carboxylate group are observed at  $1457$  and  $1606\text{ cm}^{-1}$ . The  $\Delta(\nu_{\text{as}} - \nu_{\text{sym}})$  value of  $149\text{ cm}^{-1}$  indicates that the carboxylate groups coordinate to the lead(II) centers in a bridging mode.<sup>17</sup> The  $\nu_{\text{O-H}}$  vibration of the coordinated water molecule is observed as a strong band centered at  $3370\text{ cm}^{-1}$  (Fig. S4a†). It can be seen clearly that after grinding the solid **1** with KSCN, the characteristic strong stretching absorption band centered at  $2021\text{ cm}^{-1}$ , which originates from the NCS $^-$  anion, appeared in the spectrum of **2** (Fig. S4b†). The solid **2** was ground with KBr to allow reverse anion replacement, and the product **1** was obtained. The band of NCS $^-$  anion disappeared in the IR spectrum. It indicates that the NCS $^-$  anions in compound **2** were completely exchanged by  $\text{Br}^-$  anions (Fig. S4c†).

To confirm the transformation of the compound **1** to compound **2** upon grinding of the sample with KSCN, TGA and DTA were

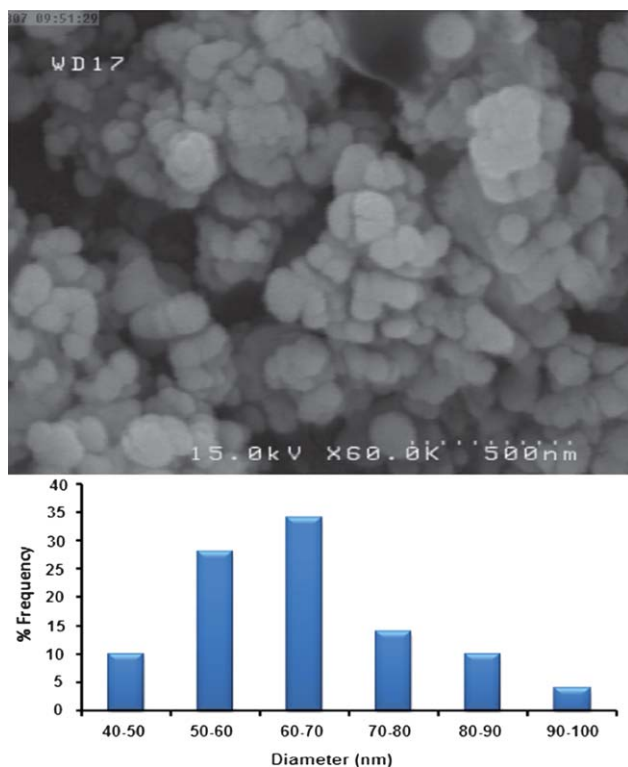
recorded for the original sample and the same sample after anion replacement (Fig. S5 and S6†). Compound **1** is stable up to  $145^\circ\text{C}$  at which temperature the water molecule begins to be removed (Fig. S5†). The solid residue formed at around  $145^\circ\text{C}$  is suggested to be the water-free compound,  $[\text{Pb}(\text{L})(\mu_2\text{-Br})]_n$ . At higher temperatures, the decomposition of the water-free compound occurs to ultimately give a solid that appears to be PbO (observed: 52.04, calcd: 53.50%). The DTA curve of compound **1** indicates the decomposition of the compound takes place with one endothermic effect at  $166^\circ\text{C}$  and three exothermic effects at  $282$ ,  $343$  and  $602^\circ\text{C}$  (Fig. S5†). As it has been shown from Fig. S5 and S6† the thermal behavior of compounds **1** and **2** is similar.

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 (Fig. 2). The corresponding size distribution histogram of these nanoparticles could be observed in Fig. 2.

The elemental analysis and IR spectra of the nanoparticles and of the single crystalline material are indistinguishable (Fig. S7 and S8†). Fig. S8b† shows the XRD patterns of a typical sample of compound **1** prepared by a sonochemical process. Fig. S8a† shows the XRD pattern 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. 3 shows the SEM image and the corresponding size distribution histogram of the compound **2** obtained from transformation of nanoparticles of compound **1** on grinding the sample with KSCN. The size of the nanoparticles obtained using the transformation is the same as that observed in Fig. 2 and no



**Fig. 2** SEM image and the corresponding particle size distribution histogram of compound **1** nanoparticles prepared by a sonochemical process.



**Fig. 3** The SEM image and the corresponding particle size distribution of the compound **2** obtained from transformation of nanoparticles of compound **1** on grinding the sample with KSCN.

morphology change would be observed but the solid state anion-replacement causes the nanoparticles to be agglomerated. The solid state structural transformation is also reversible. XRPD pattern (Fig. S7†) and IR spectrum (Fig. S8†) of compound **2** nanoparticles after grinding with KBr show that the 3D network of **2** is converted back to **1** and this transformation is flexible and dynamic at nano-scale. Fig. S9† shows the SEM image of the reversed species obtained by solid state anion-replacement of compound **2**.

In summary a 3D  $[\text{Pb}(\text{L})(\mu_2\text{-Br})(\text{H}_2\text{O})]_n$  (**1**) polymerizes on grinding the solid by KSCN to form a 3D  $[\text{Pb}(\text{L})(\mu_{1,1}\text{-NCS})(\text{H}_2\text{O})]_n$  (**2**). The morphology and size of the compound **2** nanoparticles are the same as that observed in compound **1**. Attempts to regenerate **2** to give **1** have been successful; therefore, retransformation anion-replacement appears to be reversible for several times.

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## Notes and references

† Single crystals of **1** suitable for X-ray diffraction were prepared by a branched tube method,<sup>28</sup> 1*H*-1,2,4-triazole-3-carboxylic acid (0.117 g, 1

mmol), potassium bromide (0.119 g, 1 mmol) and lead(II) nitrate (0.331 g, 1 mmol) were placed in the arm to be heated. Water was carefully added to fill both arms, and then the arm to be heated was placed in a bath at 60 °C. After 3 days, colorless crystals were deposited in the cooler arm which were filtered off, washed with water and air dried. (0.225 g, yield 54%), mp >300 °C. (Found C, 8.55; H, 0.99; N, 10.43%. Calculated for  $\text{C}_3\text{H}_4\text{BrN}_3\text{O}_3\text{Pb}$ : C, 8.63; H, 0.96; N, 10.07%). IR ( $\text{cm}^{-1}$ ) selected bands: 464(s), 651(s), 1100(s), 1303(m), 1370(m), 1457(vs), 1606(s) and 3370(br). A 3D  $[\text{Pb}(\text{L})(\mu_2\text{-Br})(\text{H}_2\text{O})]_n$  (**1**) polymerizes on grinding the solid with KSCN by hand and for 20 minutes to form a 3D coordination polymer,  $[\text{Pb}(\text{L})(\mu_{1,1}\text{-NCS})(\text{H}_2\text{O})]_n$  (**2**). These crystals separated by washing. (Found C, 12.22; H, 0.79; N, 14.25%. Calculated for  $\text{C}_4\text{H}_4\text{N}_4\text{O}_3\text{PbS}$ : C, 12.19; H, 0.77; N, 14.21%).

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