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New Reversible Crystal-to-Crystal Conversion of a Mixed-Ligand Lead(II) Coordination Polymer by De- and Rehydration

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A reversible crystal-to-crystal transformation of a new 2D lead(II) coordination polymer with the ligand 4-pyridinecarboxylic acid (4-Hpyc), $[Pb(4\text{-}pyc)(Br)(H_2O)]_n$ (**1**) to $[Pb(4\text{-}pyc)(Br)]_n$ (**2**) by de- and rehydration, has been observed, and the structures of **1** and **2** have been determined by single-crystal X-ray diffraction. 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 batch powder samples and leads to monophasic products.

The study of metal coordination polymers has gained great recognition as an important interface between synthetic chemistry and materials science and provides a solid foundation to help in the understanding of how molecules can be organized and how functions can be achieved.[1] To develop further our understanding of the supramolecular architecture, it is challenging to continue the investigations on the crystal-to-crystal transformations involving coordination polymers and networks.[2−15] There are several types of structural transformations that are primarily influenced by the expansion of coordination numbers, thermal association, condensation, rearrangement of bonds, or the removal/exchange of solvents.[16] During the course of the syntheses of the mixed-ligand lead(II) coordination polymers, in this case 4-pyridinecarboxylate (4-pyc) and bromide anions, we isolated two lead(II) coordination polymers that do novel reversible solid-state thermal desolvation conversion of a 2D into a 3D framework by heating and desolvation, $[Pb(4\text{-}pyc)(Br)(H_2O)]_n$ (**1**) to $[Pb(4\text{-}pyc)(Br)]_n$ (**2**).

1 was prepared by a branched tube method.[17] This white compound converts upon heating at 115−120 °C into a new brown compound, **2**, which was characterized by single-crystal X-ray diffraction techniques. Figure S1 in the Supporting Information shows the structures of the basic polymeric building blocks of compounds **1** and **2**. Crystals of **1**, allowed to stand in air at 115−120 °C for 3 days, undergo a reversible transformation to yield **2**. This process is accompanied by a color change from white to brown (Figure 1). While the white phase crystallizes in the orthorhombic $P2_12_12_1$ space group, a monoclinic $C2/c$ cell is found for the brown compound, providing us with one of the rare examples of crystal-to-crystal conversion.[18]

Single-crystal X-ray diffraction analysis (Tables S1 and S2 in the Supporting Information) of compound **1** shows that the complex is a 2D neutral metallopolymer bridged by Br^- and 4-pyc^- ligands, thus forming an infinite framework, as illustrated in Figure 1, top. There is one coordinated water molecule. The structure of compound **1** may also be considered as a coordination polymer of lead(II), with Br^- and 4-pyc^- anions bridging two lead(II) ions. The coordination number in **1** is 6, and each lead atom is coordinated by two oxygen and one nitrogen atoms of the 4-pyc^- ligand, one oxygen atom of the water molecule, and two bromide ions (Figure S1a in the Supporting Information).

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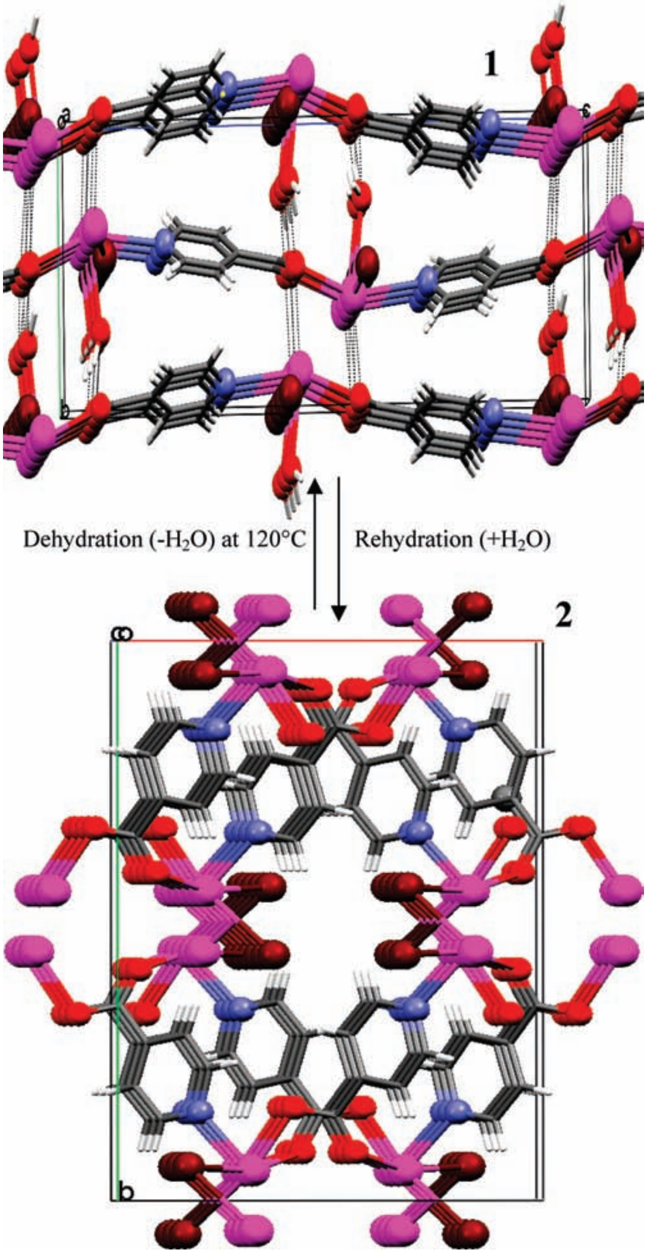

Figure 1. Schematic diagram illustrating the structural conversion of 2D−3D coordination polymeric structures by thermal de- and rehydration.

The 4-pyc$^-$ anions act as bridging ligands via a bidentate chelating carboxylate group and the pyridyl nitrogen atom. The 2D coordination polymer of compound **1** interlinked by water hydrogen atoms with oxygen atoms of 4-pyc$^-$ ligands, $O{-}H_{water}\cdots O_{carboxylate}$ hydrogen bonds, and secondary $Pb\cdots O_{carboxylate}$ interactions form a 3D supramolecule (Figure 1, top).

Upon heating at 115−120 °C, the white compound **1** changes to a brown compound **2**, and the X-ray structure determination of the brown compound reveals a number of unique features. Determination of the structure of **2** by X-ray crystallography (Tables S1 and S3 in the Supporting Information) showed that the complex is a 3D polymeric network in the solid state (Figure 1, bottom). The coordination number in **2** is 6, and each lead atom is coordinated by three oxygen and one nitrogen atoms of the 4-pyc$^-$ ligand as well as two bromide ions (Figure S1b in the Supporting Information).

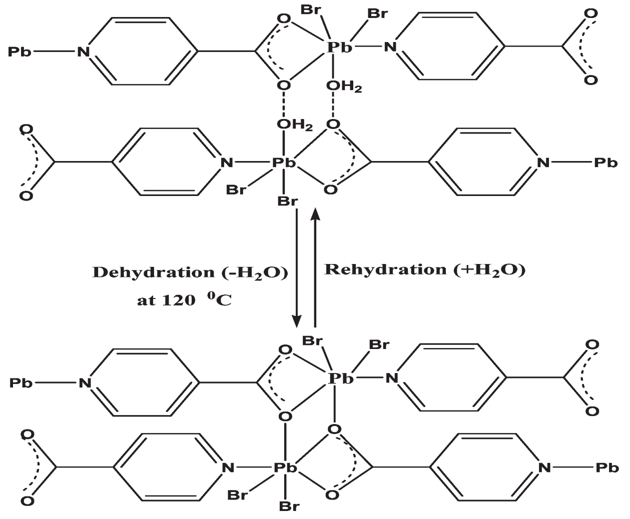

Figure 2. Schematic representation of the solid-state structural conversion of **1** to compound **2**.

On the other hand, the structure may be considered a coordination polymer of lead(II) consisting of 1D linear chains, running parallel to the *c* axis, with a building block of [$PbBr_2$]. The Br$^-$ anions bridge two lead(II) ions. The intrachain $Pb\cdots Pb$ distances within the $[PbBr_2]_n$ chains are 4.349 Å, and those bridged by the 4-pyc$^-$ anions are 8.554 and 9.783 Å.

The carboxylate moiety of the 4-pyc$^-$ ligand now acts as both bidentate and bridging groups (totally tridentate) in a μ-1,3 mode, where two oxygen atoms of the carboxylate group bidentately coordinate to a lead(II) ion, creating a four-membered chelate ring. One of the oxygen atoms from the 4-pyc$^-$ ligand also bridges two adjacent lead(II) ions, thus again chains of lead ions bridged by oxygen atoms but this time with $[Pb\mu(O_{pyc})_2)]_n$ repeating units. Parallel chains are now bridged via the nitrogen and oxygen atoms of all 4-pyc$^-$ ligands (Figures 1 and 2).

As expected for this type of lead compound with 6-coordination, both of the compounds exhibit irregular coordination geometry and coordination around the lead atoms is hemidirected with sterically active lone pairs (Figure S1 in the Supporting Information).[19]

Reversible crystal-to-crystal conversion 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 (Figure S2 in the Supporting Information). Acceptable matches were observed between the pattern simulated from single-crystal X-ray data (Figure S2a in the Supporting Information) and that measured by powder X-ray diffraction for the bulk crystalline sample as obtained from the synthesis of compound **1** (Figure S2b in the Supporting Information). Transformation by thermal treatment of compound **1** (Figure S2a−d in the Supporting Information) results in a significant change of the powder pattern (Figure S2d in the Supporting Information),

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which now matches the pattern of compound **2**, as calculated from the single-crystal X-ray data (Figure S2c in the Supporting Information). The powder X-ray diffraction pattern of the resolvated species (Figure S2e in the Supporting Information) shows that the sample regains the original structure and is reestablished and vice versa (Figure S2b in the Supporting Information). These facts clearly indicate that the structure of compound **1**, which responds toward desolvated or resolvated by a reversible change of its framework, is quite flexible and dynamic.

To further confirm the removal and reabsorbing of the coordinated water molecules by compound **1**, IR spectra were recorded for a fully solvated sample and for the same sample after heating experiments as well as the resolvated sample (Figures S3 in the Supporting Information). The IR spectrum of **1** shows characteristic absorption bands for the 4-pyc$^-$ ligand and water (Figures S3a in the Supporting Information). The absorption bands with variable intensity in the frequency range 1400−1580 cm^{-1} correspond to ring vibrations of the py moiety of the 4-pyc$^-$ ligand. The symmetric and asymmetric vibrations of the carboxylate group are observed at 1350 and 1569 cm^{-1}. The $\Delta(\nu_{\mathrm{asym}}-\nu_{\mathrm{sym}})$ value of 219 cm^{-1} indicates that the carboxylate groups coordinate to the lead(II) centers in a bridging mode.[20] The $\nu_{\mathrm{O-H}}$ vibration of the coordinated water molecule is observed as a strong band centered at 3250 cm^{-1}.

No such band was observed for the sample after heating (Figures S3b in the Supporting Information), and the large broad band attributable to the O−H stretching vibrations is also significantly reobserved for the resolvated sample (Figures S3c in the Supporting Information).

To confirm the transformation of compound **1** to compound **2** upon heating and dehydration, thermal gravimetric and differential thermal analyses (TGA and DTA) were recorded for the original sample and the same sample after 3 days of heating to 120 °C (Figure S4 in the Supporting Information). Compound **1** is stable up to 120 °C, at which temperature the water molecules begin to be removed (Figure S4a in the Supporting Information). The TGA and DTA curves show a mass loss of ca. 4.30% and an endothermic effect of around 110 °C. The solid residue formed at around 120 °C is suggested to be the water-free compound [Pb(4-pyc)(Br)]. Above a temperature of 120 °C, the graphs of compounds **1** and **2** are basically superimposable (Figure S4a,b in the Supporting Information).

The coordination geometry of the lead atoms in the polymers of **1** and **2** allows some speculation about the origin and mechanism of the solid-state transformation. The water molecules in **1** are located roughly on top of each other, and removal of the water molecules would create an open channel through the entire crystal, which would allow for relatively easy and nondestructive removal of all of the solvate molecules. The oxygen atoms of the 4-pyc$^-$ anions in **1** are also oriented toward the coordinated water molecule of neighboring units via O−H···O hydrogen bonds (Figure 1, top, and Figure 2, top). One may assume that, upon removal of the water molecules, the Pb···O contacts shorten in the course of the solid-state reaction and turn into bonds with lead(II) atoms by removal of the water molecules, which in the process creates a new 3D network topology (Figure 1, bottom, and Figure 2, bottom).

However, removal of one water molecule from compound **1** in the solid state is accompanied by variation in the packing, metal-centered angles, and the original lead-donor bonds. The formation of new $\mathrm{Pb\cdots O_{carboxylate}}$ bonds takes place along with the removal of $\mathrm{Pb-O_{water}}$, resulting in no change in the coordination number of the lead atoms. This change in network topology started when the crystals of compound **1** are allowed to stand in air at 115−120 °C for 3 days.

In summary, the 2D coordination network **1** dehydrates upon heating of the solid to 120 °C to form a new 3D coordination polymer, **2**.

Syntheses of 1 and 2. 4-Pyridinecarboxylic acid (0.246 g, 2 mmol), sodium bromide (0.205 g, 2 mmol), and lead(II) acetate trihydrate (0.75 g, 2 mmol) were placed in the main arm of a branched tube.[17] Water was carefully added to fill both arms. The tube was sealed and the ligand-containing arm immersed in an oil bath at 60 °C while the other arm was kept at ambient temperature. After 2 days, colorless crystals that deposited in the cooler arm were isolated, filtered off, washed with acetone and ether, and air-dried. Anal. Calcd for $C_6H_6BrNO_3Pb$: C, 16.94; H, 1.41; N, 3.29. Found: C, 17.01; H, 1.53; N, 3.26. IR (selected signals, cm^{-1}): 682m, 708s, 765s, 850s, 998s, 1061s, 1217s, 1391w, 1524w, 1569m, 1636s, 3200w. Crystal data for **1**: orthorhombic space group $P2_12_12_1$, a = 6.0675(3) Å, b = 6.9454(3) Å, c = 19.8525(8) Å, V = 836.61(6) Å^3, Z = 4, T = 293(2) K. The refinement of 1738 parameters on the basis of 1725 independent reflections (of a total of 6378) converged at R1 = 0.0490 and wR2 = 0. 1140.

1 dehydrates upon heating of the solid at 115−120 °C to form **2**. Mp = 98 °C. Anal. Calcd for $C_6H_4BrNO_2Pb$: C, 17.58; H, 0.97; N, 3.42. Found: C, 17.35; H, 1.10; N, 3.60. IR (selected bands, in cm^{-1}): 603m, 701s, 833m, 924w, 120rm, 1414s, 1444m, 1525vs, 1559m, 3020w. Crystal data for **2**: monoclinic space group $C2/c$, a = 11.695(4) Å, b = 17.175(6) Å, c = 7.861(3) Å, β = 91.037(7)°, V = 1578.7(9) Å^3, Z = 8, T = 100(2) K. The refinement of 1932 parameters on the basis of 1932 independent reflections (of a total of 63 368) converged at R1 = 0.0972 and wR2 = 0. 2662.

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Supporting Information Available: ORTEP diagram, XRD patterns, IR spectra, TGA and DTA diagrams, and tables of crystal data and structure refinement and of bond lengths and angles for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for the structures reported in the paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 739062 and 686654 for compounds **1** and **2**, respectively. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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