Crystal-to-crystal transformation from a chain polymer to a two-dimensional network by thermal desolvation†

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Received (in Cambridge, UK) 4th January 2008, Accepted 30th April 2008
First published as an Advance Article on the web 9th June 2008
DOI: 10.1039/b800126j

Single-crystal to single-crystal transformation of a new lead(II) coordination polymer with ligands 8-hydroxyquinoline (8-Quin) and nitrate, $[Pb_2(8\text{-Quin})_2(NO_3)_2(MeOH)]$ (1α) to $[Pb(8\text{-Quin})(NO_3)]$ (1β), is reported and the structures of 1α and 1β determined by X-ray crystallography.

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. 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,[1–5] 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. Studies on crystal-to-crystal transformations involving coordination polymers and networks are more recent.[6–26] There are several types of structural transformations that are primarily influenced by the expansion of coordination number, thermal association, condensation, rearrangement of bonds or the removal/exchange of solvents.[27] In this communication we report the thermal desolvation of a one-dimensional chain into a two-dimensional framework by heating and desolvation: $[Pb_2(8\text{-Quin})_2(NO_3)_2(MeOH)]$ (**1α**) to $[Pb(8\text{-Quin})(NO_3)]$ (**1β**), 8-HQuin = 8-hydroxyquinoline.

$[Pb_2(8\text{-Quin})_2(NO_3)_2(MeOH)]$ (**1α**) was prepared by a branched tube method[28]‡ and this light brown compound polymerizes on heating the solid at 165–170 °C to form a new yellow compound, $[Pb(8\text{-Quin})(NO_3)]$ (**1β**) that was also characterized by single-crystal X-ray diffraction techniques. Fig. S1, ESI† shows the structures of the basic polymeric building block of compounds **1α** and **1β**. Crystals of **1α** allowed to stand in air at 160–170 °C for three days undergo a reversible transformation to yield **1β**, this process being accompanied by a color change from brown to yellow (Fig. 1).

While the brown phase crystallizes in the triclinic $P\bar{1}$ space group, a monoclinic $P2_1/c$ cell is found for the yellow phase, providing us with one of the few examples of crystal-to-crystal conversion.

In compound **1α** the structure may be considered as a one-dimensional coordination polymer of lead(II) consisting of tetrameric units with a building block of $[Pb_4(\mu\text{-}8\text{-Quin})_4(MeOH)_2]$. Four 8-Quin$^-$ anions bridge four lead(II) ions *via* the N and O atoms (Fig. S2a, ESI†). The Pb···Pb distances within the $[Pb_4(\mu\text{-}8\text{-Quin})_4(MeOH)_2]$ moieties are 3.963(2) and 4.016(2) Å. The individual tetrameric units are further bridged by bidentate bridging nitrate anions *via* O atoms of this ligand, resulting in a one-dimensional chain as shown in Fig. 1. There are two nitrate anions with different coordination modes. One nitrate ligand acts only as a bidentate chelating group. In the second mode, nitrate anions bridge two lead(II) ions *via* the O atoms with a Pb···Pb separation of 5.767(5) Å.

In compound **1α**, the phenolic oxygen atom of 8-hydroxyquinolate ligand bridges from both sides with distances of 2.642 and 2.668 Å (Fig. S2a).

On heating at temperatures 165–170 °C, brown $[Pb_2(8\text{-Quin})_2(NO_3)_2(MeOH)]$ (**1α**) changes to yellow $[Pb(8\text{-Quin})(NO_3)]$ (**1β**) and the X-ray structure determination of the yellow compound reveals a number of unique features.

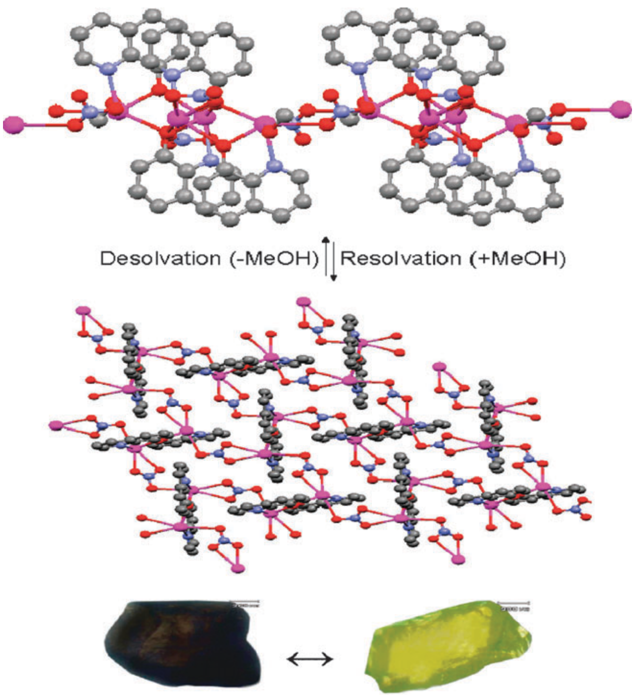

Fig. 1 Schematic diagram illustrating the structural conversion of 1D–2D coordination polymeric structures by thermal desolvation (top), and crystal appearance before (**1α**) and after (**1β**) transformation (bottom).

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† Electronic supplementary information (ESI) available: Experimental section including schematic representations of transformations and ORTEP diagrams. CCDC 670050 (**1α**) and 669855 (**1β**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b800126j

Complex **1β** is a two-dimensional neutral metallopolymer bridged by both NO_3^- and 8-Quin$^-$ ligands, thus forming a two-dimensional infinite framework as illustrated in Fig. 1. On the other hand, the structure may be considered as a coordination polymer of lead(II) consisting of dimeric units with a building block of $[Pb_2(\mu\text{-}8\text{-}Quin)_2]$ across a centre of inversion (Fig. S2a). The NO_3^- anions doubly bridge two lead(II) ions *via* the O atoms. Consequently, the dimer units are grown by the bridging NO_3^- anions into a two-dimensional framework. The Pb···Pb distances within the $[Pb_2(\mu\text{-}8\text{-}Quin)_2]$ moieties are 4.021(2) Å. The intrachain Pb···Pb distances within the $[Pb(NO_3)]_n$ chains are 5.902(2) Å. In compound **1β** the 8-hydroxyquinolate ligand acts as a three-donor ligand whereas this ligand in **1**α acts as a four-donor ligand (Fig. S2, ESI†).

The solid-state transformation starts from the one-dimensional coordination polymer of **1α** (Fig. S3, ESI†). In **1α** unbridging nitrate anions are oriented towards the neighboring one-dimensional units and a schematic representation of this topology is shown in Fig. S4 (top) (ESI†). Dashed lines indicate the shortest nonbonding contacts (3.370(2) Å) between the O atom of nitrate and the lead(II) atoms of its neighbor. One may assume that these contacts shorten in the course of the solid-state reaction and turn into bonds. This approach between the 1D chains is accompanied by variations in the metal-centered angles and by expansion of the originally terminal lead–donor bonds. The rearrangement product $[Pb(8\text{-}Quin)(NO_3)]$ (**1β**) represents a two-dimensional network in which both nitrate anions unsymmetrically bridge metal cations. The forming of an additional $Pb–O_{NO_3}$ bond take place along with removal of $Pb–O_{MeOH}$, so not changing the coordination number of the Pb atoms. This change in network topology from 1D to 2D connectivity is started when solid **1α** is warmed at a temperature of 170 °C with removal of MeOH. The reaction is reversible and polymer **1β** is converted back to **1α** by resolvation.

The structures of the bulk materials for **1α** and **1β** were confirmed by matching their X-ray powder patterns with those generated from the corresponding single crystals (Fig. S5, ESI†). Acceptable matches were observed between the simulated single-crystal X-ray data pattern (Fig. S5a) and those from the experimental powder X-ray diffraction patterns for the bulk crystalline sample as obtained from the synthesis of compound **1α** (Fig. S5b). Transformation by thermal treatment at 170 °C (Fig. S5c,d) results in a significant change of the powder pattern, but acceptable matches were observed between the simulated single-crystal X-ray data pattern (Fig. S5c) and those from the experimental powder X-ray diffraction patterns for the bulk crystalline sample obtained by heating of complex **1α** (Fig. S5d). These facts clearly indicate that the 1D structure of compound **1α** transforms to compound **1β** by heating.

To confirm the transformation of compound **1α** to compound **1β** upon heating of the sample, TGA and DTA were recorded for the original sample and for the same sample after heating for three days at 170 °C (Fig. S6 and S7, ESI†). Compound **1α** is stable up to 165 °C at which temperature the methanol molecule begins to be removed (Fig. S6). The solid residue formed at around 165 °C is suggested to be the methanol-free compound, $[Pb_2(8\text{-}Quin)_2(NO_3)_2]$. At higher temperatures, the decomposition of the methanol-free compound occurs to ultimately give a solid that appears to be PbO (observed mass% 51.70, calc: 52.23). The DTA curve of compound **1α** indicates the decomposition of the compound takes place with one endothermic event at 168 °C and three exothermic events at 315, 425 and 555 °C (Fig. S6). As has been shown from Fig. S6 and S7 the thermal behavior of compounds **1α** and **1β** is very similar and the transformation take places before 168 and is complete by 172 °C; interestingly the DTA analyses shows an endothermic effect at *ca.* 170 °C for **1α**. DSC of compound **1α** was also measured at lower temperature (−100 °C to RT) with no change observed, indicating the absence any transformation at lower temperature.

The most important feature of the crystal of **1**α is that it undergoes a reversible single-crystal-to-single-crystal structural transformation driven by desolvation (**1β**) and resolvation (**1α**). However, when a desolvated sample is exposed to a methanolic medium (*i.e.*, the dry sample is placed in a glass desiccator beside a methanol filled beaker) it reabsorbs some of the lost methanol content and changes from yellow to brown. The XRPD pattern of the resolvated species (Fig. 5Se) shows that the sample regains the original structure which shows almost the same XRPD diffractogram as that of as the freshly synthesized material (Fig. 5Sb). These facts clearly indicate that the structure of **1α**, which responds towards desolvation or resolvation by a reversible change of its framework, is quite flexible and dynamic.

The solid state UV/Vis spectra of compounds **1α** and **1β** as well as of 8-hydroxyquinoline (8-QuinH) were studied. The solid state UV/Vis spectrum of compound **1α** displays an absorption band with maximum intensity at 379.5 nm (Fig. 8Sa, ESI†), whereas compound **1β** displays two absorption bands with maximum intensity at 308.5 and 367.0 nm (Fig. 8Sb, ESI†). The solid state UV/Vis spectrum of 8-hydroxyquinoline itself (Fig. 8Sc, ESI†) does not display any absorption band in this region, indicating that the electronic transitions are mostly of ligand to metal charge-transfer character.

Compounds **1α** and **1β** are photoluminescent in the solid state. **1α** exhibits five fluorescence emission maxima at 423, 433, 484, 505 and 535 nm upon photoexcitation at 370 nm (Fig. S9a, ESI†). Compared to the fluorescence signals of **1β** at 431, 485 and 520 nm (Fig. S9b, ESI†), these emission peaks are slightly red-shifted and exhibit some additional peaks (423 and 505 nm) that are not observed in the spectrum of **1β** (see Fig. S9), indicating the influence of the type of coordination of 8-hydroxyquinolate and structural geometry on photoluminescence in the solid state.

Apart from methanol, as confirmed by the X-ray powder patterns, TGA and elemental analysis we have also explored the possibility of absorbing or coordinating other common solvents (water, ethanol, acetonitrile, dichloromethane, benzene and chloroform) by compound **1β**, but these solvent molecules were not accommodated into its structure.

In summary, brown 1D $[Pb_2(8\text{-}Quin)_2(NO_3)_2(MeOH)]$ (**1α**) polymerizes on heating and desolvation of the solid at 170 °C to form a yellow compound, $[Pb(8\text{-}Quin)(NO_3)]$ (**1β**). In the crystal lattice, one oxygen atom mutually attacks the neighboring Pb(II) center forming a new Pb–O bond in place of methanol and so not expanding the coordination geometry. Attempts to regenerate **1β** to give **1α** have been successful; therefore, retransformation appears to be reversible.

This work was supported by the Tarbiat Modares University.

Notes and references

‡ Single crystals of **1α** suitable for X-ray diffraction were prepared by a branched tube method,[28] 8-hydroxyquinoline (0.290 g, 2 mmol) and lead(II) nitrate (0.331 g, 1 mmol) were placed in the arm to be heated. Methanol was carefully added to fill both arms, and then the arm to be heated was placed in an oil-bath at 60 °C. After 10 days, light brown crystals were deposited in the cooler arm which were filtered off, washed with acetone and air dried (0.233 g yield 54%), mp >300 °C (Found: C, 26.55; H, 1.79; N, 6.55. Calc. for $C_{19}H_{15}N_4O_9Pb_2$: C, 26.60; H, 1.77; N 6.53%). IR (cm^{-1}) selected bands: 730(s), 830(w), 1100(s), 1315(s), 1392(vs), 1461(vs), 1500(s), 3025(w). ^{1}H NMR (DMSO-d_6; δ): 3.15 (d, 3H), 4.09 (q, 1H), 6.67 (d, 1H), 6.69 (d, 1H), 7.49 (t, 1H), 7.74 (q, 1H), 8.44 (d, 1H), 8.92 (d, 1H). ^{13}C{^{1}H} NMR (DMSO-d_6; δ): 49.05 ($^{13}CH_3OH$), 112.31, 117.10, 121.90, 130.64, 132.30, 139.07, 144.00, 146.74, 165.17. Brown 1D [Pb_2(8-Quin)$_2$(NO_3)$_2$(MeOH)] (1α) polymerizes on heating the solid at 165–170 °C to form the yellow 2D coordination polymer, [Pb(8-Quin)(NO_3)] (1β) (Found: C, 26.50; H, 1.40; N, 6.55. Calc. for $C_9H_6N_2O_4Pb$; C, 26.13 H, 1.45; N, 6.77%). Single crystals of 1α to be transformed into crystals of 1β without any significant change in crystal quality and *vice versa*.

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