Renaissance of the coordination chemistry of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT). Part II: new insights into the reaction of TPymT with Pb(NO₃)₂†

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Reaction of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT) with Pb(NO₃)₂ in aqueous medium leads to the formation of a mixture of two pseudopolymorphs, \([\text{Pb}_2(\text{TPymT})(\text{H}_2\text{O})(\text{NO}_3)_4]\cdot\text{H}_2\text{O}\), 1 and \([\text{Pb}_2(\text{TPymT})(\text{NO}_3)_4]\), 2, where TPymT molecules are coordinated with two PbII ions in a bridging bis-terpyridine fashion. We demonstrate that fast evaporation of the solvent leads exclusively to the formation of 1, while 2 was formed upon slow evaporation. The two pseudopolymorphs can be interconverted by dissolving in water upon heating and controlling the evaporation rate.

Since the discovery of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT) by Case and Koft,¹ numerous attempts have been made to employ this multidentate chelate in coordination chemistry. Despite the fact that TPymT has three coordination pockets that resemble the terpyridine ligand, the majority of attempts to coordinate TPymT to metals failed due to the hydrolytic decomposition of the ligand in the presence of metal ions.² Although there have been a few reports on the successful synthesis of TPymT complexes with RuII,³ PbII,⁴ Ti⁴⁺ and UO₂II,⁴a only two crystal structures have been described: that of a 1D polymeric chain \([\text{Pb}_2(\text{TPymT})(\text{H}_2\text{O})(\text{NO}_3)_4]\cdot\text{H}_2\text{O}\), 1, comprising Pb₂ heteroleptic building blocks,⁴a and a that of a discrete Pb₂ supramolecular aggregate \([\text{Pb}_6(\text{TPymT})_2(\text{Lig})_3(\text{OTf})_{12}\text{ (Lig} = 4,6\text{-bis(4-(propylthio)-2,2′-bipyridin-6-yl)pyrimidine})\).⁴b Furthermore, the limited number of studies on the coordination properties of TPymT might also be explained by low yields of the ligand. However, since TPymT has great potential as an intriguing ligand for coordination chemistry as terpy or pyrimidine,⁵ we have recently focused our attention on the synthesis and study of TPymT-based coordination compounds. As a first successful result we have reported on the unprecedented dinuclear CdII complex, \([\text{Cd}_2(\text{TPymT})(\text{H}_2\text{O})_3(\text{SO}_4)_3]\cdot\text{H}_2\text{O}\), which is the third structurally characterized example of a metal complex of TPymT and the first example of such a complex involving a d-metal cation.⁶

In continuation of our research into isolating stable coordination complexes with TPymT, we have focused our attention on lead complexes. Herein we report the reaction of TPymT with Pb(NO₃)₂ in water. Although this reaction was first described by Lerner and Lippard,⁴a we have found that the formation of the final product strongly depends on the solvent evaporation conditions. Interestingly, two pseudopolymorphs can be interconverted by controlling the evaporation rate of the solvent.

Reaction of TPymT with Pb(NO₃)₂ in water (Scheme 1, for details see ESI†) yielded a mixture of two pseudopolymorphs...
upon solvent evaporation (20 mL, ~1.5 weeks): large pale orange needles of [(Pb₂(TPymT)(H₂O)(NO₃)₄]H₂O n, and colourless plates of [Pb₂(TPymT)(NO₃)₄]n, 2 (Fig. 1). Pure compounds 1 and 2 can be obtained using fast (20 mL, ~6 days) or slow (20 mL, ~4 weeks) evaporation of the solvent, respectively. In addition to traditional characterization methods such as FTIR, Raman, diffuse reflectance, TG/DTA, and powder X-ray diffraction analyses, both complexes were characterized using ²⁰⁷Pb solid-state magic-angle spinning (MAS) NMR spectroscopy. Such a unique study allows us to visualize subtle differences in local coordination environment in both complexes. Single crystal X-ray diffraction (SCXRD) reveals 1 exhibits the same structure as the reported compound; ⁴ however, SCXRD data for 2 expose how through careful control of crystallization a second pseudopolymorph 2 can be isolated.

The observed FTIR and Raman spectra of 1 and 2 are similar (Fig. S1 and S2 in ESI†). The main difference is the presence of characteristic broad bands at about 625, 1300, and 3380 cm⁻¹ in the FTIR spectrum of 1, which correspond to water molecules. The former two bands are overlapped with bands from the organic ligand⁵ and/or the NO₃⁻ anions.⁷

To establish the origin of the different colours of 1 and 2 as well as to study their electronic properties, diffuse reflectance spectra were recorded on pure samples (Fig. S3 in ESI†). The spectrum of 2 exhibits a broad absorption band with two main maxima in the range of 200 to 500 nm, corresponding to intra-ligand transitions of TPymT⁶ and ligand-to-metal or metal-to-ligand charge transfer. The same bands were found in the spectrum of 1 but were accompanied by an intense shoulder centred at about 440 nm, which can be explained by the presence of π-···π interactions⁸ between the neighbouring TPymT ligands in the crystal structure.⁴ Appearance of this band in the spectrum of 1 explains the pale orange colour of the compound.

²⁰⁷Pb solid-state NMR is a sensitive probe of the local environment of Pb⁰ ions, and lead chemical shifts are known to range over 10 000 ppm.⁹ Bloch decay ²⁰⁷Pb MAS NMR spectra of powdered samples of 1 and 2 were obtained in a magnetic field of 4.7 T (Fig. 2). Two crystallographically unique sites are identified for 1, and one unique site is identified for 2, consistent with the crystal structures (vide infra). The spinning sideband manifolds were analysed to determine the lead chemical shift tensor magnitudes (Table S1 in ESI†). The isotropic chemical shifts of −3005 ppm and −2920 ppm for 1 and −2973 ppm for 2 are reasonably close to that of lead nitrate. The chemical shift tensor spans of 570 ppm for 2 and 370 ppm and 550 ppm for sites 1 and 2 of 1, respectively (Table S1 in ESI†), suggest that site 1 in 2 features a similar coordination environment to that found in 2, i.e., nine coordinate (vide infra). Site 2 in 1 is attributed to the eight-coordinate site.

The thermal properties of 1 and 2 in an air atmosphere were studied by means of simultaneous TG/DTA analyses in order to determine their respective stabilities (Fig. S4 and S5 in ESI†). The molecule of 1 is stable up to about 100 °C and decomposes in two clearly defined steps (Fig. S4 in ESI†). The first step corresponds to the loss of water molecules with an endothermic effect centred at about 95 °C. Surprisingly, although the structure of 1 contains the bridging μ-O-coordinated and crystal water molecules, both solvent molecules are evaporated during the same single decomposition step. The second decomposition step is an extremely abrupt exothermic effect at ~350 °C. Compound 2 is stable up to about 350 °C and decomposes in a very similar manner as 1 after the latter complex completely loses its water molecules (Fig. S5 in ESI†). Thus, compound 1 can be converted to 2 after heating between 120 and 320 °C. This was further confirmed by the means of X-ray powder diffraction analysis (see below).

Crystals of 1 and 2 suitable for a single-crystal X-ray analysis were obtained after synthesis on standing with fast or slow evaporation of the solvent, respectively. The molecular structure of 2 is shown in Fig. 3, whereas the crystal and structure refinement data are given in ESI†.

According to the X-ray data, 2 crystallizes in the orthorhombic space group Pccn and forms an infinite polymeric 2D sheet (Fig. 4). The structure of 1 was refined in the monoclinic space group P2₁/n.⁴ The molecular unit in 2 is composed of...
nine-coordinated distorted monocapped square antiprismatic \(\text{[Cd}_2\text{(TPymT)}(\text{H}_2\text{O})_6\text{(SO}_4\text{)}_2]\) 1D polymeric chain or 2D polymeric sheet (Fig. 4) is observed

coordination mode (Fig. 3). As a result, the formation of a 2

\(\text{NO}_3\)

bis-terpyridine ligand, exhibiting a bridging coordination mode. The same type of coordination was found for a TPymT ligand coordinated to two \(\text{Pb}^{II}\) atoms and acts as a

packing or molecular structures.

Coordination environments in both polymorphs are completed by oxygen atoms of the \(\mu-O, O'\)-coordinated \(\text{NO}_3\) anions. The \(\text{Pb}^{II}\)–\(\text{Pb}^{II}\) separation between two oxygen bridged metal atoms in 1 is about 4.15 Å, while the same separation between two \(\mu-O\)-bridged cations in 2 is ~4.87 Å. Other shortest \(\text{Pb}^{II}\)–\(\text{Pb}^{II}\) separations in the latter complex are about 5.60 and 6.54 Å. The \(\text{Pb}–\text{N}\) and \(\text{Pb}–\text{O}\) bond lengths in 2 (Table S2 in ESI†) are in the same range as in 1.\(^4\)a These values are in agreement with those found for the sum of the ionic radius of \(\text{Pb}^{II}\) and the van der Waals radii of nitrogen and oxygen, being 2.77 and 2.67 Å, respectively.9 All \(\text{NO}_3\) anions in 2 were found in their expected planar trigonal geometry with the \(\text{N}–\text{O}\) bond lengths and \(\text{O}–\text{N}–\text{O}\) bond angles being 1.225(4)–1.263(5) Å and 118.1(3)–122.0(4)°, respectively (Table S2 in ESI†). The torsion angles between the planes formed by the triazine and bridging and non-bridging pyrimidine rings in two polymorphs are about 9.5 and 4.1°–10.7° in 1, and 13.1 and 1.9° in 2, respectively. The same angles between the bridging and non-bridging pyrimidine planes are ~12.8–15.9° (1) and ~14.4° (2).\(^4\)a Thus, the TPymT ligand in 2 is more planar than in 1. Furthermore, these angles are lower than those in the structure of a discrete \(\text{Cd}^{II}\) analogue,\(^3\) and exhibit a higher distortion of the TPymT ligand in the structure of the latter one. The bond lengths and bond angles within the TPymT ligand in the structures of both polymorphs are similar and almost the same found for those in the structure of the \(\text{Cd}^{II}\) derivative.\(^3\) A closer inspection of the crystal structure of 2 revealed no classical hydrogen bonds but further \(\text{H}–\text{X}\) short contacts. However, based on established criteria\(^10\) these weak interactions are not directing the crystal packing or molecular structures.

Bulk samples of 1 and 2 were studied by means of X-ray powder diffraction analysis (Fig. S6 and S7 in ESI†). The experimental X-ray powder patterns are in full agreement with the calculated ones obtained from SCXRD. This validates a single phase of the raw materials of 1 and 2. Furthermore, the relative intensities of the peaks at \(2\theta = 8.6\) and 17.3° in the X-ray powder pattern of 2 are significantly higher in the experimental powder pattern compared to those in the calculated one (Fig. S7 in ESI†). These \(2\theta\) values correspond to the \(hkl = (002)\) and \(004\) planes, testifying to a preferred orientation of layers along the \(0c\) axis. Thus, the crystallographic layers are orthogonal to the \(ac\) plane. This is in agreement with the layered structure of 2, obtained by SCXRD (Fig. S8 in ESI†).

We have also annealed the raw sample of 1 at 200 °C for 10 min. The obtained material was studied by the means of X-ray powder diffraction analysis (Fig. S7 in ESI†), which testified to the exclusive formation of a single phase of 2. Furthermore, keeping solid powder of 2 in water for two weeks at ambient conditions did not result in the formation of 1. Thus, the solid state-to-solid state transformation of 1 to 2 is irreversible.

Loss of coordinated water molecule in 1 leads to a drastic rearrangement of molecules with a change in coordination number for a \(\text{Pb}^{II}\) atom and a change in coordination mode...
of one of the terminal NO$_3^-$ anions. This finding supports a crucial role of solvent molecules in the supramolecular aggregation of coordination systems.$^{11}$ Furthermore, the role of the NO$_3^-$ anion in the 1D to 2D structural transformation resembles the recently published findings observed for the complexes of Pb(NO$_3$)$_2$ with 8-hydroxyquinoline.$^{12}$ The driving force of the solid state-to-solid state transformation to the irreversible solid state-to-solid state transformation of 1 to 2 upon annealing is due to the increased volatility of the coordinated water molecule at higher temperatures. The structural change is further supported by the polydentate nature of one of the terminal nitrate anion which can substitute the bridging water molecule in 1 and promote the transformation.$^{13}$

In summary, although it has been established that the reaction of TPymT with Pb(NO$_3$)$_2$ in water leads to the formation of a 1D polymeric chain $\left[\left(\mathrm{Pb}_2\mathrm{TPymT}\right)\left(\mathrm{H}_2\mathrm{O}\right)\left(\mathrm{NO}_3\right)\mathrm{H}_2\mathrm{O}\right]_n$, 1, we have now found that a mixture of 1 and $\left[\mathrm{Pb}_2\mathrm{TPymT}\right]\left(\mathrm{NO}_3\right)_n$, 2, is formed. Pure samples of 1 and 2 can be formed upon fast or slow evaporation of the solvent, respectively. The pseudopolymorphs can be interconverted by dissolving in water upon heating and controlling the evaporation rate. Annealing of 1 between 120 and 320 °C under ambient conditions leads to the irreversible solid state-to-solid state transformation to 2. Furthermore, the formation of 1D and 2D polymeric structures for 1 and 2, respectively, resulted in different solid-state optical properties, that were studied by diffuse reflectance spectroscopy. At the same time both complexes exhibit very similar thermal properties with an abrupt exothermic decomposition step at ~350 °C without any explosion. Thus, these pseudopolymorphs might be intriguing samples for thermal fuse formation.

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Notes and references