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ARTICLE TYPE

# 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 $Pb(NO_3)_2$

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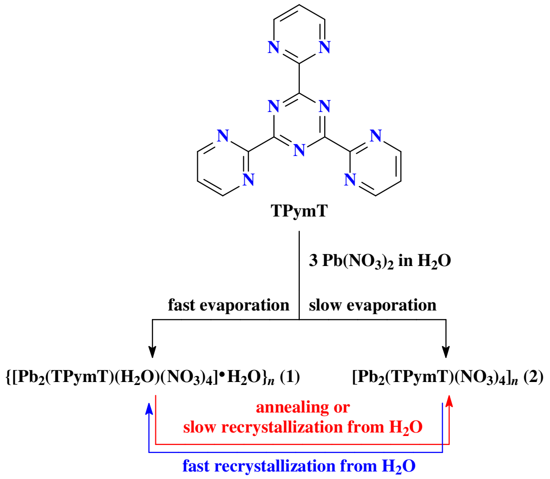
**Reaction of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT) with $Pb(NO_3)_2$ in aqueous medium leads to the formation of a mixture of two pseudopolymorphs, $\{[Pb_2(TPymT)(H_2O)(NO_3)_4]\cdot H_2O\}_n$, 1 and $[Pb_2(TPymT)(NO_3)_4]_n$, 2, where TPymT molecules are coordinated with two $Pb^{II}$ ions 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 TPymT has three coordination pockets that resemble the terpyidine 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 $Ru^{II}$,[3] $Pb^{II}$,[4] $Tl^{I}$,[4a] and $UO_2^{II}$,[4a] only two crystal structures have been described: that of a 1D polymeric chain $\{[Pb_2(TPymT)(H_2O)(NO_3)_4]\cdot H_2O\}_n$, **1**, comprising $Pb_2$ heteroleptic building blocks,[4a] and a that of a discrete $Pb_6$ supramolecular aggregate $[Pb_6(TPymT)_2(Lig)_3](OTf)_{12}$ (Lig = 4,6-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 $Cd^{II}$ complex, $[Cd_2(TPymT)(H_2O)_6(SO_4)_2]\cdot H_2O$, 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 $Pb(NO_3)_2$ 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 $Pb(NO_3)_2$ 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 $\{[Pb_2(TPymT)(H_2O)(NO_3)_4]\cdot H_2O\}_n$, **1** and colourless plates of $[Pb_2(TPymT)(NO_3)_4]_n$, **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 $^{207}Pb$ 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[4a], however SCXRD data of **2** expose how through careful control of crystallization a second pseudopolymorph **2** can be isolated.



**Scheme 1** Synthetic conditions for the isolation of **1** and **2**.

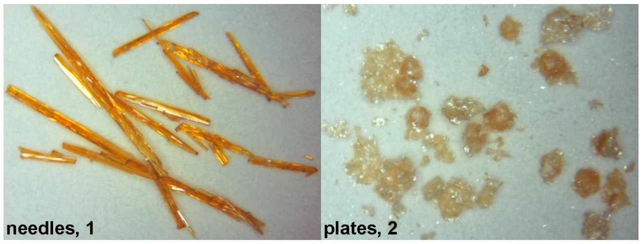


**Fig. 1** Crystal photos of compounds **1** and **2**.

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**,[7] that latter of which corresponds to water molecules. The former two bands are overlapped with bands from the organic ligand[5] and/or the $NO_3^-$ 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 TPymT[5] 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 interactions[6] between the neighbouring TPymT ligands in the crystal structure.[4a] Appearance of this band in the spectrum of **1** explains the pale orange colour of the compound.

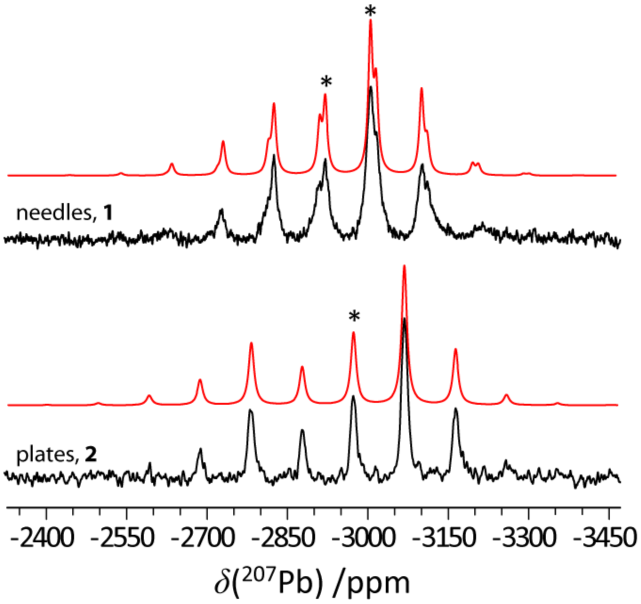


**Fig. 2** Solid-state $^{207}$Pb MAS NMR spectra of compounds **1** and **2** obtained at 4.7 T (black). Analytical simulations of the spinning sideband patterns are shown in red. Isotropic resonances are marked with asterisks.

$^{207}$Pb solid-state NMR is a sensitive probe of the local environment of Pb$^{II}$ ions, and lead chemical shifts are known to range over 10000 ppm.[7] Bloch decay $^{207}$Pb 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 **1** 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 *endo*thermic 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 *exo*thermic 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 Figure 3, whereas the crystal and structure refinement data are given in ESI†.

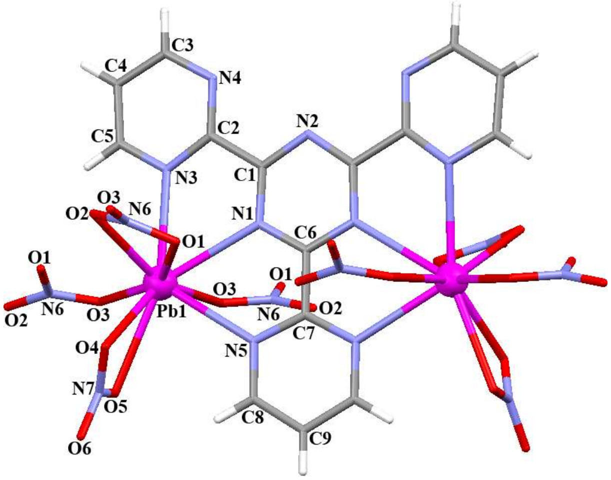


**Fig. 3** Molecular structure of the centrosymmetric compound **2**. Labels on the hydrogen atoms were omitted for clarity.

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 $P2_1/n$.[4a] The molecular unit in **2** is composed of a TPymT ligand coordinated to two $\mathrm{Pb^{II}}$ atoms and acts as a bis-terpyridine ligand, exhibiting a bridging $\mu_6$-coordination mode. The same type of coordination was found for **1**[4a] and $[\mathrm{Cd_2(TPymT)(H_2O)_6(SO_4)_2]\cdot H_2O}$.[6] The distance between two $\mathrm{Pb^{II}}$ atoms in both $\mathrm{Pb_2}$ polymorphs are very similar and of about 6.95–6.98 Å. However, these distances are about 0.45 Å longer than that in the $\mathrm{Cd_2}$ analogue. The structural motifs $[\mathrm{Pb_2TPymT}]^{4+}$ in **1** are linked through one bridging $\mu_3$-[($\mu$-*O*),*O'*]-coordinated $\mathrm{NO_3^-}$ anion and one bridging $\mu$-*O*-coordinated water molecule, while in **2** the same motifs are linked through oxygen atoms of $\mathrm{NO_3^-}$ anions, each exhibiting a bridging $\mu_4$-[($\mu$-*O,O'*),($\mu$-*O''*)]-coordination mode (Fig. 3). As a result, the formation of a 1D polymeric chain or 2D polymeric sheet (Fig. 4) is observed in **1** and **2**, respectively. $\mathrm{Pb^{II}}$ atoms in **1** are nine- or eight-coordinated, exhibiting a distorted monocapped square antiprismatic and a distorted square antiprismatic coordination geometry, respectively.[4a] All $\mathrm{Pb^{II}}$ atoms in **2** are in a nine-coordinated distorted monocapped square antiprismatic coordination geometry (Fig. 3). Coordination environments in both polymorphs are completed by oxygen atoms of the $\mu$-*O,O'*-coordinated $\mathrm{NO_3^-}$ anions. The $\mathrm{Pb^{II}\cdots Pb^{II}}$ 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 $\mathrm{Pb^{II}\cdots Pb^{II}}$ separations in the latter complex are about 5.60 and 6.54 Å. The Pb–N and Pb–O bond lengths in **2** (Table S2 in ESI†) are in the same range as in **1**.[4a] These values are in agreement with those found for the sum of the ionic radius of $\mathrm{Pb^{II}}$ and the van der Waals radii of nitrogen and oxygen, being 2.77 and 2.67 Å, respectively.[9] All $\mathrm{NO_3^-}$ anions in **2** were found in their expected planar trigonal geometry with the N–O bond lengths and O–N–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 $\mu$- 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 $\mu$- and non-bridging pyrimidine planes are ~12.8–15.9° (**1**) and ~14.4° (**2**).[4a] 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 $\mathrm{Cd_2^{II}}$ analogue,[5] 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 $\mathrm{Cd_2^{II}}$ derivative.[5] A closer inspection of the crystal structure of **2** revealed no classical hydrogen bonds but further H···X short contacts. However, based on established criteria[10] these weak interactions are not directing the crystal packing or molecular structures.

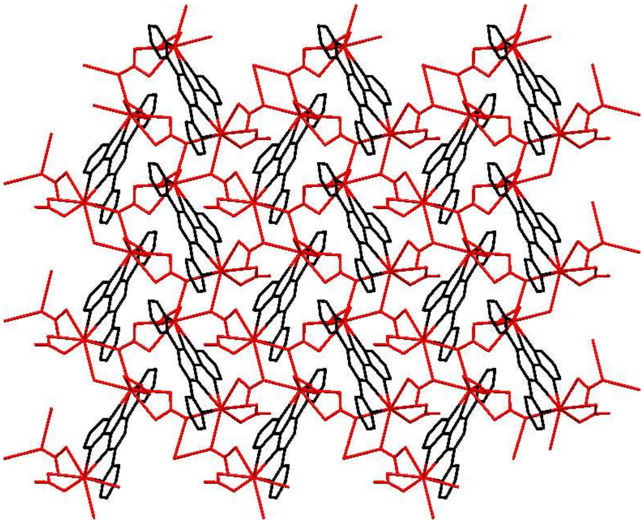


**Fig. 4** Crystal structure of a 2D sheet of **2**. The TPymT molecules are shown in black, while $\mathrm{Pb^{II}}$ and $\mathrm{NO_3^-}$ ions are shown in red.

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 single crystal X-ray diffraction. 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 single crystal X-ray diffraction (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 to the formation of **1**. Thus, the solid state-to-solid state transformation of **1** to **2** is irreversible.

Loosing the coordinated water molecule in the structure of **1** leads to a drastic rearrangement of molecules resulted in the change of both the coordination number of one of the $\mathrm{Pb^{II}}$ atoms and a bridging coordination mode of one of the chelated terminal $\mathrm{NO_3^-}$ anions. This finding supports a crucial role of solvent molecules in the supramolecular aggregation of coordination systems.[11] Furthermore, the role of the $\mathrm{NO_3^-}$ anion in the 1D to 2D structural transformation resembles the recently published findings observed for the complexes of $\mathrm{Pb(NO_3)_2}$ with 8-hydroxyquinoline.[12] The driving force of the solid state-to-solid state transformation of **1** to **2** upon annealing might be in the efficient increasing of volatility of the coordinated water molecule at higher temperatures with its further evaporation. The structural change is further supported by the polydentate nature of one of the terminal chelated nitrate anions, which oxygen atoms in **1** locate in a close environment of the bridging water molecule and, hence, can substitute the latter species upon elimination.[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 $\{[Pb_2(TPymT)(H_2O)(NO_3)_4]{\cdot}H_2O\}_n$, **1**, we have now found that a mixture of **1** and $[Pb_2(TPymT)(NO_3)_4]_n$, **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 *exo*thermic decomposition step at ~350 °C without any explosion. Thus, these pseudopolymorphs might be intriguing samples for the thermal fuse formation.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Additional data, Figures S1–S8, Tables S1 and S2. CCDC reference number 966468 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x

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Reaction of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT) with $Pb(NO_3)_2$ in $H_2O$ leads to a mixture of two pseudopolymorphs, $[\{Pb(NO_3)_2\}_2TPymT\cdot 2H_2O]_n$, **1** and $[\{Pb(NO_3)_2\}_2TPymT]_n$, **2**. It has been established that fast evaporation of the solvent leads exclusively to the formation of **1**, while the polymorph **2** was formed upon slow evaporation of water. The two polymorphs can be interconverted by dissolving in water and controlling the evaporation rate.