

# Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



## Journal Name

## ARTICLE

## The renaissance of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT) coordination chemistry

Damir A. Safin,<sup>a</sup> Jamie M. Frost<sup>a</sup> and Muralee Murugesu\*<sup>a</sup>

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

In this perspective we report on recently accumulated data on the synthesis and coordination chemistry of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT). Although a highly attractive ligand, owing to the presence of three fused terpyridine-like coordination pockets, the coordination chemistry of TPymT has something of a chequered past. This can principally be attributed to the hydrolysis of the ligand, which readily occurs under mild conditions. Thus, after first being synthesised in 1959 it had only been used a handful of times to synthesise coordination compounds until we began reinvestigating its chemistry in early 2013. Despite the significant challenges associated with its use, our work over the past two years has demonstrated that coordination chemistry with TPymT is indeed possible. Herein, we describe an overview of this body of work as it stands, and discuss its potential impact in a variety of areas including porous materials, catalysis and crystal engineering.

### Introduction

2,4,6-Tris(2-pyrimidyl)-1,3,5-triazine (TPymT) has been known for almost 60 years.<sup>1</sup> Despite this, its coordination chemistry remains vastly underexplored. This can be explained partly by its general unavailability and poor solubility in common solvents, but, also by the hydrolysis of the central triazine fragment which readily occurs under mild conditions in the presence of appropriate metal cations. As such, developing the coordination chemistry of TPymT constitutes a significant challenge. Indeed, until recently only two coordination compounds of TPymT were known in the literature (both with Pb<sup>2+</sup>).<sup>2,3</sup> With this in mind, we recently turned our attention to the synthesis and study of TPymT-based coordination compounds, initially with a view to creating polymetallic clusters with interesting magnetic and/or optical properties. Herein we discuss our accumulated data on the synthesis and coordination chemistry of TPymT. Undeservedly forgotten by history, its potential to act as an effective ligand for a variety of metals is clearly demonstrated by our results in this area over the past two years. We hope that this perspective will inform more researches about the chemistry of TPymT and boost its adoption as a building platform for cluster synthesis, particularly as a counterpart to terpyridine and pyrimidine-based ligands. Another important avenue of use for TPymT is in the synthesis of coordination polymers such as Metal-Organic Frameworks. Upon coordination TPymT can form molecular 1, 2, or 3 nuclear units that act as well defined nodes for coordination polymers. These potential applications,

along with its unique coordinating ability, means that TPymT represents an important opportunity in materials chemistry based on coordination chemistry.

### Synthesis of TPymT

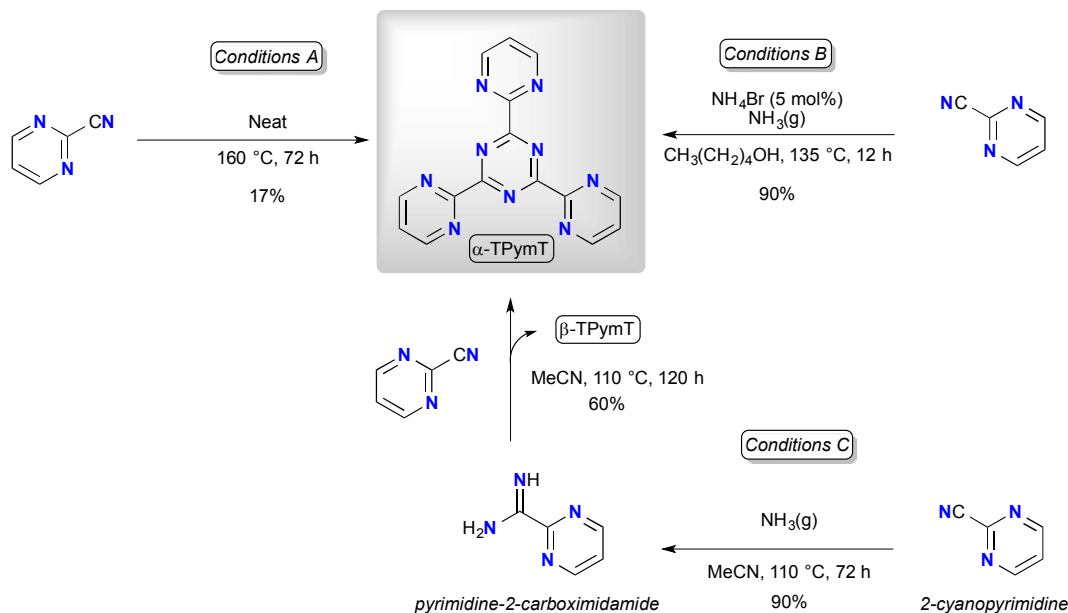
The formation of TPymT from 2-cyanopyrimidine, yielding less than 6% on standing for several months, was first described by Case and Koft in 1959.<sup>1</sup> Much later, Lerner and Lippard were able to synthesise TPymT with a high yield of the crude material (17%) by the trimerisation reaction of 2-cyanopyrimidine, with stirring for 48 h at 150 °C (Scheme 1, *conditions A*).<sup>4</sup> However, the product obtained required a laborious purification procedure, decreasing the final yield by up to 65%. Much later, TPymT was prepared by trimerisation of 2-cyanopyrimidine in the presence of ammonia and a catalytic amount of ammonium bromide, with excellent yield (~90%) (Scheme 1, *conditions B*).<sup>3</sup> The reported tan colour of the formed solid material is indicative of the presence of impurities. Consequently, one can assume that TPymT obtained by this procedure also requires purification.

Surprisingly, our numerous attempts to synthesise TPymT using the simple trimerisation reaction of 2-cyanopyrimidine at high temperature,<sup>4</sup> resulted in significantly lower yields than the literature preparation, regardless of reaction time and temperature.<sup>5</sup> As an alternative, we found that TPymT could be prepared by simply heating 2-cyanopyrimidine under pressure in the presence of pyrimidine-2-carboximidamide, which in-turn is synthesised by heating a solution of 2-cyanopyrimidine and ammonia under pressure, for several days (Scheme 1, *conditions C*). This approach results in significantly higher yields (~60%) and a much cleaner crude material, requiring no further purification. We recently

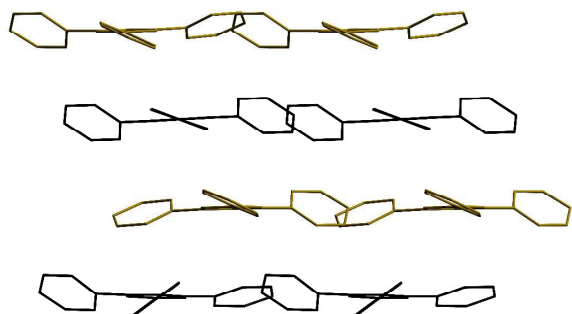
<sup>a</sup> Department of Chemistry and Biomolecular Sciences, University of Ottawa, 10 Marie Curie, Ottawa, ON, Canada K1N 6N5. E-mail: m.murugesu@uottawa.ca; Fax: +1 (613) 562 5170; Tel: +1 (613) 562 5800 ext. 2733.

Journal Name

ARTICLE

**Scheme 1** Synthetic routes for the preparation of TPymT.

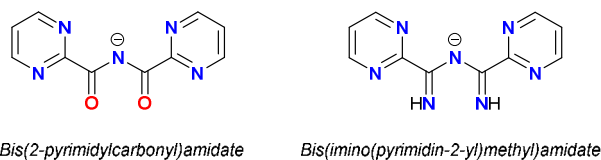
suggested this finding as a highly efficient method for obtaining TPymT.<sup>6</sup> The original trimerisation of 2-cyanopyrimidine method, leads to the formation of a single polymorph,  $\alpha$ -TPymT, (Scheme 1, Fig. 1), whereas the procedure suggested by us affords a mixture of two polymorphs,  $\alpha$ -TPymT and  $\beta$ -TPymT, (Scheme 1).<sup>6</sup> In addition, the first step of our approach allows the isolation of pyrimidine-2-carboximidamide in high yield (~80%). This intermediate compound can be used as a ligand in its own right and also as a potential precursor to react with, for example, derivatised cyanopyridines, to create new asymmetric ligand.

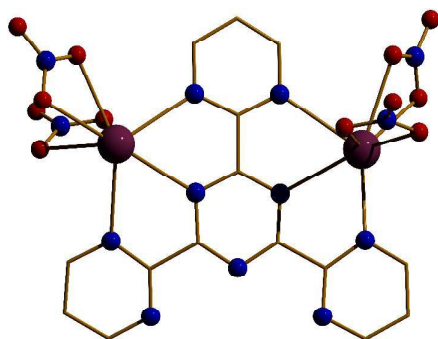
**Fig. 1** Crystal packing of  $\alpha$ -TPymT as viewed along the  $b$ -axis.

### Coordination Chemistry of TPymT

One of the main reasons that the coordination chemistry of TPymT has remained poorly explored for so long is the hydrolysis of the triazine fragment of the ligand (*vide supra*). In particular, hydrolysis is extensively promoted by  $\text{Cu}^{2+}$  salts with the formation of bis(2-pyrimidylcarbonyl)amidate<sup>4,7,8</sup> and bis(imino(pyrimidin-2-yl)methyl)amidate anions (Fig. 2).<sup>9</sup> The former is formed during the reaction in water, whilst the latter results from triazine fragment cleavage in methanol. Furthermore, bis(2-pyrimidylcarbonyl)amidate is also formed upon reacting TPymT with  $[\text{Ru}(\text{phen})_2]^{2+}$  in methanol, accompanied by the formation of pyridine-2-carboxylic acid amide.<sup>10</sup>

There have been a few reports of the synthesis of TPymT complexes in the literature. More specifically complexes with;  $[\text{Ru}(\text{terpy})]^{2+}$ ,  $[\text{Ru}_2\{\rho\text{-C}_6\text{H}_4(\text{terpy})_2\}(\text{2,2}'\text{-bipy})(\text{H}_2\text{O})]^{4+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ti}^+$ ,

**Fig. 2** Anions formed during the reaction of TPymT with  $\text{Cu}^{2+}$  salts in water (left) and methanol (right).

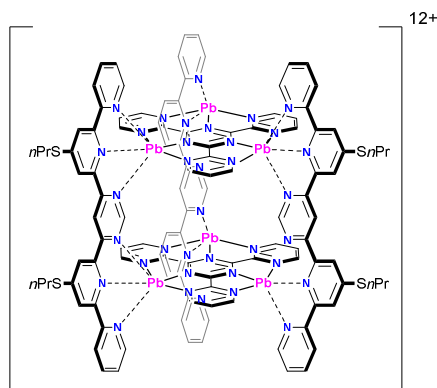


**Fig. 3** Molecular structure of  $\{[\text{Pb}_2(\text{TPyMT})(\text{NO}_3)_4]\}$  as seen in the structure of **1**. H-atoms and  $\text{H}_2\text{O}$  molecules omitted for clarity. Colour code: Pb = purple, C = gold, N = blue, O = red.

**Table 1.** Compilation of the compounds discussed in the text.

Compound	Descriptor	Ref.
$\{[\text{Pb}_2(\text{TPyMT})(\text{NO}_3)_4] \cdot \text{H}_2\text{O}\}_n$ ( <b>1</b> )	Coordination polymer	2
$[\text{Pb}_6(\text{TPyMT})_2(\text{Lig})_3](\text{OTf})_{12}$ ( <b>2</b> )	Discrete molecule	3
$[\text{Cd}_2(\text{TPyMT})(\text{H}_2\text{O})_6(\text{SO}_4)_2] \cdot \text{H}_2\text{O}$ ( <b>3</b> )	Discrete molecule	5
$[\text{Pb}_2(\text{TPyMT})(\text{NO}_3)_4]$ ( <b>4</b> ),	Coordination polymer	6
$\{[\text{Hg}(\text{NCS})_2]_2\text{TPyMT}\}_n$ ( <b>5</b> ),	Coordination polymer	14
$[\text{Ag}_3(\text{TPyMT})(\text{H}_2\text{O})(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$ ( <b>6</b> )	Discrete molecule	15
$\{[\text{AgTPyMT}]\text{C}(\text{ClO}_4)\}_n$ ( <b>7</b> )	Coordination polymer	20
$[\text{Co}(\text{bpca})_2]\text{Cl} \cdot 7.5\text{H}_2\text{O}$ ( <b>8</b> )	Discrete molecule	21
$[\text{Co}(\text{bpca})_2]\text{Br} \cdot 7.5\text{H}_2\text{O}$ ( <b>9</b> )	Discrete molecule	21

and  $\text{UO}_2^{2+}$  have been reported.<sup>2,3,10-12</sup> However, for the majority of these systems no single crystal X-ray diffraction studies could be performed. Therefore, it is impossible to establish if the metal cation is coordinated to TPymT or a co-crystallization product is formed. In fact, among these reported complexes of TPymT, only two crystal structures were described prior to our investigations: a 1D polymeric chain  $\{[\text{Pb}_2(\text{TPyMT})(\text{NO}_3)_4] \cdot \text{H}_2\text{O}\}_n$  (**1**) comprising dilead heteroleptic building blocks (Fig. 3, Table 1),<sup>2</sup> and a discrete hexalead supramolecular aggregate  $[\text{Pb}_6(\text{TPyMT})_2(\text{L})_3](\text{OTf})_{12}$  (**2**) (L = 4,6-bis(4-(propylthio)-2,2'-bipyridin-6-yl)pyrimidine) (Fig. 4, Table 1).<sup>3</sup>

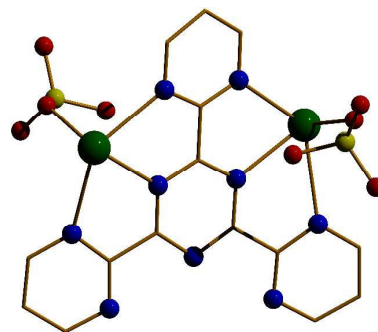


**Fig. 4** Schematic representation of the cation in **2**.

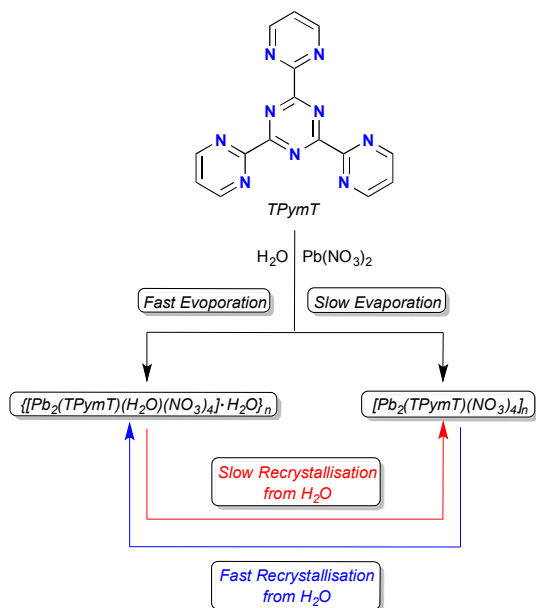
Our first successful synthesis of a TPymT complex was the system  $[\text{Cd}_2(\text{TPyMT})(\text{H}_2\text{O})_6(\text{SO}_4)_2] \cdot \text{H}_2\text{O}$  (**3**) (Fig. 5), obtained from the reaction of TPymT with three equivalents of  $\text{CdSO}_4$  in water. The resulting pale-orange block-like crystals yielded just the third structurally characterised example of a TPymT complex and the first involving a *d*-block metal cation.<sup>5</sup>

Each TPymT ligand in the structure of **3** is coordinated to two  $\text{Cd}^{2+}$  atoms, acting as a  $\mu$ -bridging bis-terpyridine ligand. The same type of coordination mode is observed in the dilead analogue **1**.<sup>2</sup> The coordination sphere of each  $\text{Cd}^{2+}$  ion is completed by three water molecules and a single sulphate anion, with the coordination geometry in each case best described as a distorted pentagonal bipyramid. The intramolecular  $\text{Cd}^{2+} \cdots \text{Cd}^{2+}$  distance of 6.53 Å is approximately 0.5 Å shorter than the analogous metal-metal separation seen in **1** and **2**.<sup>2,3</sup> The third coordination site of TPymT in **3** is occupied by a single  $\text{H}_2\text{O}$  molecule through the formation of two  $\text{O} \cdots \text{H} \cdots \text{N}$  hydrogen bonds. The O atom of the same  $\text{H}_2\text{O}$  molecule further serves as a H-bond acceptor, forming interactions with  $\text{H}_2\text{O}$  molecules coordinated to neighbouring TPymT ligands. One can only speculate that it was this supramolecular interaction that led to the stabilisation of the TPymT ligand, thus preventing hydrolysis. This extensive H-bonding network leads to the formation of what is effectively, two interpenetrated 1D polymeric chains. In-turn significant inter-chain interactions are promoted by a number of  $\text{O} \cdots \text{H} \cdots \text{O}$  contacts, formed between the H-atoms of coordinated water molecules and the O-atoms of the sulphate anions, in addition to  $\pi \cdots \pi$  stacking interactions between the aromatic rings of the TPymT ligands. Solid-state fluorometric studies revealed both TPymT and **3** show an emission band with maxima at around 450 and 480 nm at  $\lambda_{\text{exc}} = 350$  nm, with the observed emissions of both contributed strongly to, by  $\pi \cdots \pi^*$  intra-ligand fluorescence.

We next turned our attention to complexes of  $\text{Pb}^{2+}$ .<sup>13</sup> Although the reaction of TPymT with  $\text{Pb}(\text{NO}_3)_2$  was first described by Lerner and Lippard in 1977,<sup>2</sup> we found that the formation of the product reported by them strongly depends on the solvent evaporation conditions employed. In particular, we found that two pseudopolymorphs can be interconverted by carefully controlling the evaporation rate of the solvent (Scheme 2).



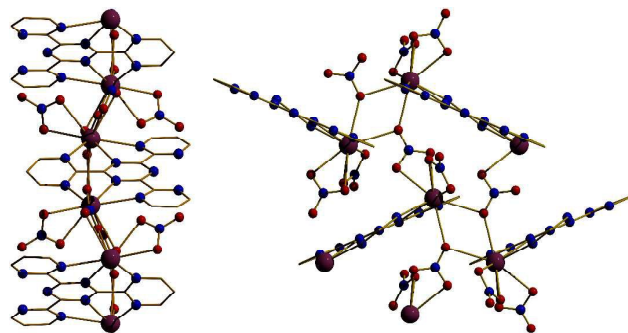
**Fig. 5** Molecular structure of **3**. H-atoms and  $\text{H}_2\text{O}$  molecules omitted for clarity. Colour code: Cd = green, C = gold, N = blue, O = red, S = yellow.



**Scheme 2** Synthetic pathways for the isolation of  $[\text{Pb}_2(\text{TPymT})(\text{NO}_3)_4 \cdot \text{H}_2\text{O}]_n$  (**1**) and  $[\text{Pb}_2(\text{TPymT})(\text{NO}_3)_4]_n$  (**4**).

The reaction of TPymT with  $\text{Pb}(\text{NO}_3)_2$  in a  $\text{H}_2\text{O}$  solvent yields a mixture of two pseudopolymorphs upon solvent evaporation; large pale orange needles of  $[\text{Pb}_2(\text{TPymT})(\text{NO}_3)_4 \cdot \text{H}_2\text{O}]_n$ , **1**, (Fig. 3, Table 1) and colourless plates of  $[\text{Pb}_2(\text{TPymT})(\text{NO}_3)_4]_n$ , **4**, (Fig. 6, Table 1). Pure compounds of both can be obtained using fast (20 mL, ~6 days) or slow (20 mL, ~4 weeks) evaporation of the solvent respectively. It should be noted that **1** can be converted to **4** by heating to between 120–320 °C. This was confirmed by means of simultaneous thermogravimetric and differential thermal analyses and further supported by X-ray powder diffraction studies.

The molecular unit in **4** is composed of a single TPymT ligand coordinated to two  $\text{Pb}^{2+}$  ions, with TPymT again behaving as a  $\mu$ -bridging bis-terpyridine ligand (Fig. 6). The intramolecular metal-metal separation in both polymorphs is almost identical (6.95 in **1** vs. 6.98 Å in **4**).<sup>6</sup> Each  $\text{Pb}^{2+}$  ion in the structure is 9-coordinate and in distorted monocapped square anti-prismatic



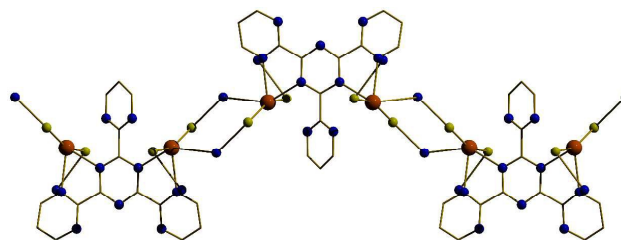
**Fig. 6** Molecular structure of **4** as viewed along the  $a$ -axis (left) and the bridging modes of the  $\text{NO}_3^-$  ligands (right). Colour code: Pb = purple, C = gold, N = blue, O = red.

geometry. The six remaining coordination sites not taken up by TPymT are occupied by one terminally bound  $\text{NO}_3^-$  anion and two bridging  $\text{NO}_3^-$  anions, which are involved in linking  $[\text{Pb}_2\text{TPymT}]^{4+}$  units together. Both bridging  $\text{NO}_3^-$  anions exhibit identical  $\eta^1:\eta^1:\eta^2:\mu_3$  coordination modes, resulting in the formation of a 2D polymeric sheet of interconnected  $\text{Pb}^{2+}$  ions (Fig. 6).

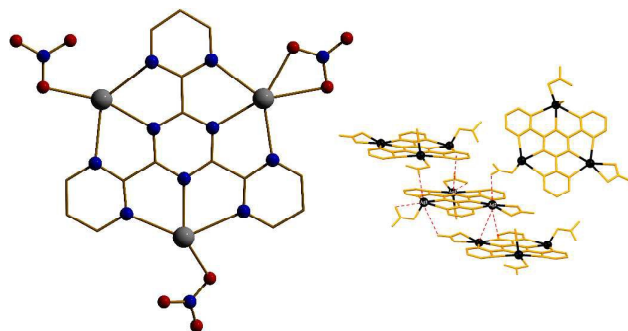
Having re-explored the coordination chemistry of  $\text{Pb}^{2+}$  and successfully synthesised a  $\text{Cd}^{2+}$  complex of TPymT, we turned our attention to cadmium's larger brother,  $\text{Hg}^{2+}$ . Reaction of a stoichiometric mixture of TPymT,  $\text{HgCl}_2$  and  $\text{NH}_4\text{NCS}$  in  $\text{H}_2\text{O}$  yields another coordination polymer,  $[\text{Hg}(\text{NCS})_2]_2\text{TPymT}]_n$  (**5**, Fig. 7, Table 1).<sup>14</sup> Although TPymT again coordinates two  $\text{Hg}^{2+}$  ions here, unusually it is bidentate, acting as what is best described as a  $\mu$ -bridging bis(2,2'-bipyridine)-type ligand. Indeed, this is the first known case of TPymT exhibiting such a coordination mode. Interestingly, a search of the CCDC database reveals 6 hits for 2,4,6-tris(pyridin-2-yl)-1,3,5-triazine (TPymT's closest known analogue) exhibiting exactly the same coordination mode with  $d$ -block metal ions.

Each  $\text{Hg}^{2+}$  ion is five-coordinate by virtue of two S-bonded  $\text{SCN}^-$  and one N-bonded  $\text{NCS}^-$  ligands in addition to the N-coordination from TPymT. One of the S-bonded  $\text{SCN}^-$  ligands is terminally bound, whilst the remaining two are  $\mu$ -bridging. The geometry around each metal centre is best described as significantly distorted square-based pyramid. The bridging  $\text{NCS}^-$  and  $\text{SCN}^-$  ligands double link  $[\text{Hg}_2\text{TPymT}]_4^+$  units together through both  $\text{Hg}^{2+}$  ions to form 1D zig-zag coordination polymers, which are then packed on top of one another. The  $\text{Hg}^{2+} \cdots \text{Hg}^{2+}$  separation between two metals of the same TPymT ligand is ~6.93 Å, with the analogous  $\text{Hg}^{2+} \cdots \text{Hg}^{2+}$  separation between bridged  $[\text{Hg}_2\text{TPymT}]_4^+$  units slightly shorter at ~5.94 Å. Again, it was found that  $[\text{Hg}(\text{NCS})_2]_2\text{TPymT}]_n$  exhibits a very similar emission band to that of the parent TPymT ligand<sup>5</sup> with maxima at around 460 and 495 nm at  $\lambda_{\text{exc}} = 350$  nm. The observed emission again attributed to  $\pi-\pi^*$  intra-ligand fluorescence.

Encouraged by these initial results with TPymT,<sup>5,6,11,12</sup> and the known coordination versatility of  $\text{Ag}^+$ , we sought to combine the two. Reaction of TPymT with three equivalents of  $\text{AgNO}_3$  in a boiling  $\text{H}_2\text{O}$  results in colourless block-like crystals of  $[\text{Ag}_3(\text{TPymT})(\text{H}_2\text{O})(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$ , **6**, (Fig. 8, Table 1) after cooling to room temperature. This complex was the first known example of a system featuring a triply coordinated TPymT ligand.<sup>15</sup>



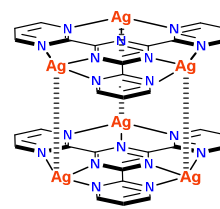
**Fig. 7** Three repeating units of the coordination polymer **5**. Colour code: Hg = orange, C = gold, N = blue, O = red, S = yellow.



**Fig. 8** Molecular structure of **6** (left) and a schematic representation of the  $\text{Ag}^+\cdots\text{O}(\text{NO}_2)$ ,  $\text{Ag}^+\cdots\eta^2[\text{Cg}(\text{C}-\text{N})$ ,  $\text{Pym}$ ],  $\text{Ag}^+\cdots\pi(\text{Pym})$  and  $\text{Ag}^+\cdots\text{Ag}^+$  short contacts of a single molecule (right). Colour code: Ag = silver, C = gold, N = blue, O = red.

Each TPymT in the structure is coordinated to three distinct  $\text{Ag}^+$  ions and acts as a  $\mu_3$ -bridging tris-terpyridine ligand. One of the  $\text{Ag}^+$  ions is four-coordinate whilst the remaining two are five-coordinate. More specifically two of the  $\text{Ag}^+$  sites feature  $\text{NO}_3^-$  ions, which are terminal monodentate. One of these sites features an axial  $\text{H}_2\text{O}$  molecule, whilst the other does not. The remaining  $\text{Ag}^+$  contains no coordinated  $\text{H}_2\text{O}$  but instead features a terminal bidentate  $\text{NO}_3^-$  ligand thus rendering it five-coordinate. The geometry of the four-coordinate site is best described as distorted tetrahedral due to the significant displacement ( $\sim 1.08$  Å) of the coordinating O-atom of the  $\text{NO}_3^-$  ligand, from the mean  $[\text{AgN}_3]$  plane of the coordination pocket. The geometry of the  $\text{Ag}^+$  ion featuring the bidentate  $\text{NO}_3^-$  is essentially planar, with the remaining five-coordinate  $\text{Ag}^+$  site extremely close to an ideal square-based pyramid (the basal plane being defined by the three TPymT nitrogen and  $\text{NO}_3^-$  oxygen atoms). Analysis of the crystal packing of **6** reveals that the molecules are packed parallel with respect to one another, with the average inter-planar separation between the planes formed from the TPymT ligands being  $\sim 3.1$  Å.  $\text{Ag}^+\cdots\text{O}(\text{NO}_2)$ ,  $\text{Ag}^+\cdots\pi(\text{Pym})$  and  $\text{Ag}^+\cdots\text{Ag}^+$  short contacts all assist in the formation of 1D chains of molecules, with these chains being stacked on top of one another to create a 2D sheet, with  $\text{H}_2\text{O}$  molecules of crystallisation intercalated between the 1D chains.

Interestingly, isolated crystals of **6** were found to catalyse the direct aziridination of terminal olefins, using  $\text{PhI}=\text{NTs}$  as a nitrene source.<sup>15</sup> The observed catalytic properties of **6** can be explained by the formation of a hexanuclear supramolecular aggregate (Fig. 9), which assembles through weak argentophilic  $\text{Ag}^+\cdots\text{Ag}^+$  and/or  $\pi\cdots\pi$  stacking interactions of the TPymT ligands, together with the easily accessible coordination sites of the metal centres. This aggregation provides three disilver(I) cores, each of which can potentially react with  $\text{PhI}=\text{NTs}$ . Evidence for this hexa-nuclear aggregate came from electrospray ionisation mass spectrometry studies, which revealed an intense peak corresponding to the mass of the hexanuclear ion  $[(\mathbf{6}-2\text{H}_2\text{O})_2 + \text{H}]^+$ , accompanied with a peak for the ion  $[(\mathbf{6}-2\text{H}_2\text{O})_2 - \text{NO}_3]^+$ . Of course, it must be acknowledged that this only gives an indication that such a hexanuclear structure might be stable in solution, and one can



**Fig. 9** Schematic representation of the hexanuclear aggregate formed from  $[\text{Ag}_3(\text{TPymT})(\text{H}_2\text{O})(\text{NO}_3)_3]$  units in aqueous solution of **6**.

have a debate about the extent to which mass spectrometry studies are a reliable probe for the existence of molecular species in the solution phase.

Nevertheless, it is worth noting that such dinuclear  $\text{Ag}^+$  units seem to be favourable for aziridination reactions of olefins as, was recently suggested for the complex  $[\text{Ag}_2(\text{tBu}_3\text{py})_2(\text{NO}_3)](\text{NO}_3)$ .<sup>16</sup> Although the nature of the reactive intermediate(s) in this disilver system remains unclear, short metal-metal interactions and accessible coordination sites at the terminal positions are known to be crucial factors for catalytic activity.

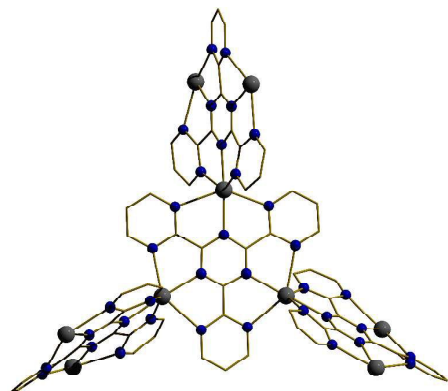
In the last decade, anion- $\pi$  interactions have received significant attention from scientists working across a range of disciplines, due to their fundamental role in biological and chemical applications.<sup>17</sup> Whilst the electron donating nature of anions might typically be expected to result in repulsion with aromatic  $\pi$ -systems, if there is some degree of electron deficiency in the aromatic, then such interactions can be stabilised (typical interaction energy  $\sim 20$ – $50$  kJ mol<sup>-1</sup>). Consequently, harnessing these interactions can facilitate the creation of coordination networks where the nature of the anions (e.g. size, shape, charge, etc.) can be utilised as a driving force for structure formation.

Recently, it was reported that the nature of the anions ( $\text{PF}_6^-$ ,  $\text{BF}_4^-$  and  $\text{ClO}_4^-$ ) in the corresponding  $\text{Ag}^+$  salts controls the self-assembly of the metal cation with TPymTs close analogue 2,4,6-tris(2-pyridyl)-triazine (TPT).<sup>18,19</sup> With this in mind, we intended to see if we could observe analogous structure directing behaviour with TPymT. However, only one such reaction yielded crystalline material. Reacting a hot aqueous solution of  $\text{AgClO}_4$  with TPymT yields pale yellow crystals of the 3D framework,  $\{[\text{AgTPymT}]\text{c}(\text{ClO}_4)\}_n$ , **7**, (Table 1) after slow evaporation of the mother liquor over two days.<sup>20</sup> The system features an unprecedented two-fold interpenetrating coordination network, with anion- $\pi$  interactions between  $\text{ClO}_4^-$  and the electron deficient aromatic fragments of TPymT, playing a crucial role in the self-assembly of the superstructure.

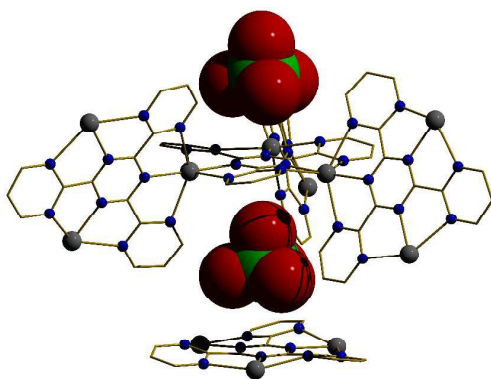
In the structure of **7**, TPymT is coordinated to three  $\text{Ag}^+$  ions acting as a  $\mu$ -bridging tris-terpyridine ligand (Fig. 10). Each  $\text{Ag}^+$  ion is six-coordinate and in significantly distorted octahedral geometry, courtesy of two TPymT ligands, which are close to perpendicular with respect to one another. Within each trinuclear unit, the  $\text{Ag}^+\cdots\text{Ag}^+$  separation is  $\sim 6.20$  Å, which is  $0.24$ – $0.29$  Å shorter than those found in the discrete trinuclear analogue **6**. The presence of anion- $\pi$  interactions between

$\text{ClO}_4^-$  anions and the electron deficient triazine fragment of TPymT (as evidenced by their short contacts), leads to the formation of a 3D network. The  $\text{ClO}_4^-$  anions are situated directly above the triazine rings with distances between the oxygen atoms of  $\text{ClO}_4^-$  and the centroids of the triazine rings being 3.21 and 3.87 Å. Through these interactions, a 1D chain of alternating anion- $\pi$  moieties are formed (Fig. 11). Since each TPymT coordinates to three  $\text{Ag}^+$  ions and each  $\text{Ag}^+$  ion in turn coordinates two TPymT ligands, this leads to a complex 2-fold interpenetrating 3D coordination network. This network exhibits a (10,3)- $\alpha$  topology, with each TPymT ligand acting as a three-connected node and each  $\text{Ag}^+$  cation as a linker. A comparison of the structures of **6** and **7** reveals the vital templating role of the  $\text{ClO}_4^-$  vs.  $\text{NO}_3^-$  anions here. The former serves as a driving force in the formation of the 2-fold interpenetrating network,<sup>20</sup> whilst the latter yields a discrete trinuclear molecule.<sup>15</sup>

As aforementioned, the hydrolysis of the triazine fragment of TPymT in the presence of metal cations under mild conditions, is one of the main reasons for the very limited data on its coordination chemistry. Although it had been established that hydrolysis is extensively promoted by  $\text{Cu}^{2+}$  salts,<sup>9</sup> no direct proof of hydrolysis by other metal cations had been established prior to our investigations. With this in mind,



**Fig. 10** Molecular structure of the  $[\text{Ag}_9\text{TPymT}_4]^{9+}$  segment in **7**. Colour code: Ag = silver, C = gold, N = blue.



**Fig. 11** Ball and stick and spacefill representation of the  $\text{ClO}_4^-$ - $\pi$  system interactions seen in **7**. Colour code: Ag = silver, C = gold, N = blue, O = red, Cl = green.

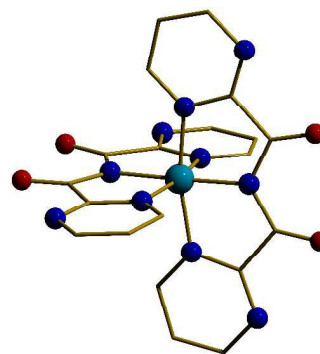
in an effort to better understand (and thus gain control over) the coordination behaviour of TPymT with first row transition metals, we began reacting TPymT with metal salts of  $\text{Co}^{2+}$ .

We found that reacting  $\text{CoX}_2$  ( $X = \text{Cl}^-, \text{Br}^-$ ) with TPymT in aqueous solution yields the isostructural complexes  $[\text{Co}(\text{bpca})_2]\text{X}\cdot 7.5\text{H}_2\text{O}$  ( $X = \text{Cl}^-$  (**8**),  $\text{Br}^-$  (**9**)) (Fig. 12, Table 1). These molecules appear to be formed through the metal cation promoted hydrolysis of TPymT, with  $\text{Co}^{2+}$  being oxidised to  $\text{Co}^{3+}$  and subsequently coordinated by the resulting bis(2-pyrimidylcarbonyl)amidate (bpca) anions.<sup>21</sup> Each complex features a central six-coordinate  $\text{Co}^{3+}$  ion in distorted octahedral geometry, with two bpca ligands (approximately perpendicular to one another) coordinating in a  $\kappa^3$ - $N,N',N''$  fashion. The C=O moieties remain uncoordinated. The unit cell of the system contains seven and a half  $\text{H}_2\text{O}$  molecules of crystallisation per complex.

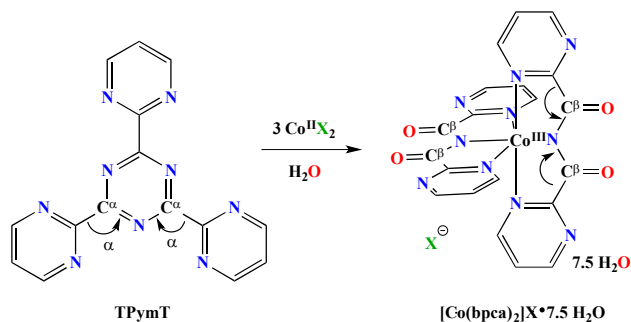
Alkyl and aryl substituted triazines are known to undergo hydrolysis,<sup>22–26</sup> but these reactions often require harsh conditions.<sup>27</sup> This is also true in the case of TPymT, where hydrolysis can occur when it is heated in 6M HCl.<sup>4</sup> Thus, it is safe to assume that the  $\text{Co}^{2+}$  ion likely assists the hydrolysis of the TPymT triazine ring here. It seems improbable that the hydrolysis is caused by the metal acting solely as a Schiff acid, since TPymT is stable in mineral acids of moderate concentration.

We suggest that destabilisation of the triazine ring upon coordination is likely the main reason for hydrolysis here. When  $\text{Co}^{2+}$  binds to one of the tridentate sites of TPymT, it induces angular strain at the carbon atoms of the triazine ring which allows for nucleophilic attack by  $\text{OH}^-$  or  $\text{H}_2\text{O}$ . The angles,  $\alpha$ , at the carbon atoms ( $\text{C}^\alpha$ ) are of  $120^\circ$  for  $sp^2$  hybridization, which is consistent with the free ligand. Within the chelate rings in **8** and **9** the angles,  $\alpha$ , are compressed to  $110^\circ$ . The angles,  $\beta$ , at the carbon atoms ( $\text{C}^\beta$ ) are very close to the values expected for the tetrahedral intermediate of the hydrolysis by nucleophilic attack of  $\text{OH}^-$  or  $\text{H}_2\text{O}$  at the  $\text{C}^\alpha$  atoms (Fig.13).

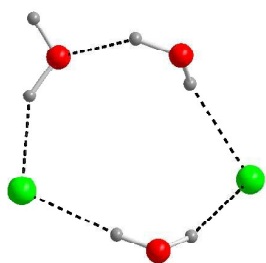
As a result of the carbon-nitrogen bond cleavage, the coordinated imide is formed. After hydrolysis,  $\text{C}^\beta$  are no longer in the triazine ring and  $\beta$  angles are significantly decreased. This allows the pyrimidine fragment to come closer to the metal center, which results in shorter M–N distances (as observed here). It is interesting to note that the previously



**Fig. 12** Molecular structure of the cation  $[\text{Co}(\text{bpca})_2]^+$  in **8** and **9**. Colour code: Co = cyan, C = gold, N = blue, O = red.



**Fig. 13** Preparation of  $[\text{Co}(\text{bpca})_2]\text{X}\cdot 7.5\text{H}_2\text{O}$  ( $\text{X}=\text{Cl}$ , **8**;  $\text{Br}$ , **9**). The angles  $\alpha$  in TPymT (left) and  $\beta$  in bpca (right) referred to in the text.



**Fig. 14** A hydrogen bonded  $[(\text{Cl}/\text{Br})_2(\text{H}_2\text{O})_3]^{2-}$  cluster as seen in the crystal structures of **8** and **9**. Colour code: Cl/Br = green, H = grey, O = red.

reported structure with Cu and bpca features the metal in the 2+ oxidation state, whereas the Co ion here is present as  $\text{Co}^{3+}$ . It is possible that the bpca anions coordinate to  $\text{Co}^{2+}$  with the metal centre subsequently being oxidised. This is similar to the situation encountered in hexamminecobalt(III) salts, which are formed upon reacting cobalt(II) salts with  $\text{NH}_3$ ,<sup>28</sup> and  $\text{NH}_3$  is known to be released during the hydrolysis of TPymT.<sup>29</sup> This is mere speculation of course.

The structures of both complexes are stabilised by a myriad of intermolecular H-bonds formed between C=O groups, the non-coordinated nitrogen atoms of the pyrimidine moieties,  $\text{H}_2\text{O}$  molecules and halide counter ions. These interactions result in the formation of a complex 2D sheet of H-bonded species, which comprise 1D polymeric chains constructed from pentagonal  $[(\text{Cl}/\text{Br})_2(\text{H}_2\text{O})_3]^{2-}$  clusters, separated from one another by a network of H-bonded  $\text{H}_2\text{O}$  molecules (Fig. 14). Such clusters have not previously been observed.

## Conclusions and Outlook

Although the number of reported complexes built from TPymT has quadrupled in the last two years, there remains much more work to be done. Both in terms of the synthesis and characterisation of new complexes and the exploration of their applications. The catalytic properties of complex **6** are particularly interesting and this is one avenue ripe for future exploitation – specifically the area of C–H bond activation. Currently, there exists no reported example of a TPymT complex with a paramagnetic metal. Indeed, we initially became interested in the ligand as a means of synthesising

magnetically frustrated  $\text{M}_3$  triangles and Single-Molecule Magnets; however, as yet, this has not come to fruition. Efforts towards this remain on-going. It is quite amazing, given the diverse structural chemistry that we have already witnessed working with TPymT (and just a handful of metal ions), that such a unique ligand could remain forgotten in the literature for so long. This begs the exciting question; what other ligand systems are out there waiting to be rediscovered in the annals of coordination chemistry?

## Acknowledgements

We thank the University of Ottawa, NSERC (Discovery and RTI grants), CFI for their financial support. We also acknowledge Dr. Amélie Pialat for useful discussions.

## References

- 1 F. H. Case and E. Koft, *J. Am. Chem. Soc.*, 1959, **81**, 905.
- 2 E. I. Lerner and S. J. Lippard, *Inorg. Chem.*, 1977, **16**, 1537.
- 3 A. M. Garcia, D. M. Bassani, J.-M. Lehn, G. Baum and D. Fenske, *Chem. Eur. J.*, 1999, **5**, 1234.
- 4 E. I. Lerner and S. J. Lippard, *J. Am. Chem. Soc.*, 1976, **98**, 5397.
- 5 D. A. Safin, Y. Xu, I. Korobkov, D. L. Bryce and M. Murugesu, *CrystEngComm*, 2013, **15**, 10419.
- 6 D. A. Safin, N. A. Tumanov, A. A. Leitch, J. L. Brusso, Y. Filinchuk and M. Murugesu, *CrystEngComm*, 2015, **17**, 2190.
- 7 E. I. Lerner and S. J. Lippard, *Inorg. Chem.*, 1977, **16**, 1546.
- 8 D. Cangussu de Castro Gomes, H. O. Stumpf, F. Lloret, M. Julve, V. González, H. Adams and J. A. Thomas, *Inorg. Chim. Acta*, 2005, **358**, 1113.
- 9 T. Glaser, H. Theil, I. Liratzis, T. Weyhermuller and E. Bill, *Inorg. Chem.*, 2006, **45**, 4889.
- 10 C. Metcalfe, S. Spey, H. Adams and J. A. Thomas, *J. Chem. Soc., Dalton Trans.*, 2002, 4732.
- 11 C. Metcalfe, C. Rajput and J. A. Thomas, *J. Inorg. Biochem.*, 2006, **100**, 1314.
- 12 E. Jakubikova, R. L. Martin and E. R. Batista, *Inorg. Chem.*, 2010, **49**, 2975.
- 13 D. A. Safin, K. M. N. Burgess, I. Korobkov, D. L. Bryce and M. Murugesu, *CrystEngComm*, 2014, **14**, 3466.
- 14 D. A. Safin, R. J. Holmberg, K. M. N. Burgess, K. Robeyns, D. L. Bryce and M. Murugesu, *Eur. J. Inorg. Chem.*, 2015, 441.
- 15 D. A. Safin, A. Pialat, I. Korobkov and M. Murugesu, *Chem. Eur. J.*, 2015, **21**, 6144.
- 16 Y. Cui and C. He, *J. Am. Chem. Soc.*, 2003, **125**, 16202.
- 17 B. L. Schottel, H. T. Chifotides and K. R. Dunbar, *Chem. Soc. Rev.*, 2008, **37**, 68.
- 18 X.-P. Zhou, D. Li, T. Wu and X. Zhang, *Dalton Trans.*, 2006, 2435.
- 19 X.-P. Zhou, D. Li, T. Wu and X. Zhang, *Inorg. Chem.*, 2006, **45**, 7119.
- 20 D. A. Safin, A. Pialat, A. A. Leitch, N. A. Tumanov, I. Korobkov, Y. Filinchuk, J. L. Brusso and M. Murugesu, *Chem Commun.*, 2015, **51**, 9547.
- 21 D. A. Safin, P. M. J. Szell, A. Keller, I. Korobkov, D. L. Bryce and M. Murugesu, *New J. Chem.*, 2015, **39**, 7147.
- 22 S. Cloez, *Justus Liebigs Ann. Chem.*, 1860, **115**, 23.
- 23 E. Frankland and J. Evans, *J. Chem. Soc.*, 1860, **37**, 563.
- 24 A. Weddige, *J. Prakt. Chem.*, 1874, **10**, 208.
- 25 R. Otto and K. Voigt, *ibid.*, 1887, **36**, 78.
- 26 J. Miller, *Ber.*, 1889, **22**, 2797.



## ARTICLE

Journal Name

- 27 E. M. Smolin and L. Rapoport, *S-Triazines and Derivatives*, Interscience. New York, N. Y., 1959, 163.
- 28 J. Bjerrum and J. P. McReynolds, *Inorg. Synth.*, 1946, **2**, 216.
- 29 T. R. G. Simões, R. V. Mambri, D. O. Reis, M. V. Marinho, M. A. Ribeiro, C. B. Pinheiro, J. Ferrando-Soria, M. Déniz, C. Ruiz-Pérez, D. Cangussu, H. O. Stumpf, F. Lloret and M. Julve, *Dalton Trans.*, 2013, **42**, 5778.