Renaissance of the coordination chemistry of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT).

Part I: First crystal structure of a TPymT complex with a d-metal cation†

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An unprecedented dinuclear heteroleptic CdII complex was isolated using a stable multitandentate 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT) ligand, which can be seen as a triply fused terpyridine ligand. In the obtained complex, TPymT retains its structural integrity without undergoing oft-observed hydrolysis.

The formation of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT) from 2-cyanopyrimidine, yielding less than 6% on standing for several months, was first described more than 50 years ago by Case and Kort.1 Much later, Lerner and Lippard were able to synthesize TPymT with high yield (~84%) by the trimerization reaction of 2-cyanopyrimidine with stirring for 48 h at 150 °C.2 Although the coordination chemistry of TPymT is extensively promoted by CuII salts with the formation of TPymT in the presence of metal cations under mild conditions, it still remains very poorly explored. This is mainly due to the hydrolysis of the triazine fragment of TPymT in the presence of metal cations under mild conditions, thus breaking down the ligand. In particular, hydrolysis is extensively promoted by CuII salts with the formation of bis(2-pyrimidylcarbonyl)amidate and bis(imino(pyrimidin-2-yl)methyl)amidate anions. However, there have been few reports on the successful synthesis of TPymT complexes with RuII,5 PbII,6,6b TlII,6a and UOII.6a Among them, only two crystal structures were described: a 1D polymeric chain [Pb₂(TPymT)[NO₃]₃]·2H₂O{}_{in}, comprising dillad heteroleptic building blocks,6a and a discrete hexahedral supramolecular aggregate [Pb₆(TPymT)₃(Lig)]₁₂[OTf]₁₂ (Lig = 4,6-bis[4-(propylthio)-2,2′-bipyridin-6-yl]pyrimidine).6b

With this in mind we have turned our attention to the synthesis and study of the unprecedented dinuclear CdII complex, [Cd₂(TPymT)(H₂O)₆(SO₄)₃]·H₂O (1).

Reaction of TPymT with 3Cd(SO₄)₂·H₂O in water (Scheme 1, for details see ESI†) yielded pale orange elongated block-like crystals of the complex in 96% yield. Crystals of 1 are insoluble in common solvents, while TPymT is poorly soluble in DMSO and DMF.

The IR spectrum of TPymT contains bands for the aromatic C–H and C–N stretches at 3060 and 1580 cm⁻¹, respectively (Fig. S1 in ESI†). The aromatic ring chain vibrations were found as bands at 1580, 1430, and 990 cm⁻¹. The same bands were found in the IR spectrum of 1. Wide bands for H₂O moieties in the spectrum of the complex were found at 3200, 1665, and 670 cm⁻¹. The latter band is overlapped with a set of bands for the TPymT ligand in the complex. A strong band at 1065 cm⁻¹ in the IR spectrum of 1 was attributed to the SO₄²⁻ anions.

To shed light on the electronic properties of TPymT and 1, diffuse reflectance spectra were recorded on pure samples. These spectra exhibit a broad absorption band with several maxima, accompanied by a shoulder, in the range 200–600 nm, corresponding to intra-ligand transitions (Fig. S2 in ESI†). The spectrum of the complex additionally contains a band centred at 650 nm. As expected, the CdII cores, featuring a filled d10 electron shell, do not participate in the transitions and the low energy band in the spectrum of the complex might be due to strong π⋯π stacking interactions (see X-ray description below). Appearance of the latter band in the spectrum of 1 explains the pale orange colour of the compound.

Solid-state fluorimetric studies of TPymT and 1 were undertaken to examine their photophysical properties. These spectra were also recorded on pure samples. It was found that both TPymT and its CdII complex show a very similar emission band with maxima at around 450 and 480 nm at λexc = 350 nm (Fig. S3 in ESI†). Excitation spectra of TPymT and 1, recorded at λem = 480 nm, reveal a main contribution from the band centred at about 400–425 nm, which is noted for both compounds. This band can be assigned to the absorption of

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the shoulder at about 415 nm by comparison with diffuse reflectance spectroscopy data (Fig. S2 in ESI†). Thus, the observed emissions of both compounds are contributed by π–π* intra-ligand fluorescence.

The 1H NMR spectrum of TPymT in DMSO-d₆ contains two signals for the pyrimidine fragments: a triplet at 7.82 ppm and a doublet at 9.16 ppm with characteristic coupling constants, J_{HH} = 4.8 Hz. The 113Cd solid-state CP MAS NMR spectrum of powdered 1 shows a single resonance at ~12.6 ppm, consistent with the presence of one crystallographically unique CdII site (Fig. S4 in ESI†). The line width at half-height of 270 Hz suggests some residual dipolar coupling to the three directly-bonded 14N nuclei, although no clear splittings are observed. The signal is less shielded compared to those of the starting material, 3CdSO₄·8H₂O (δ_{113Cd} = 56.4 and ~43.6 ppm for the two crystallographically non-equivalent sites). The 113Cd chemical shift of 1 falls within the known range for 6- and 7-coordinate CdII complexes featuring only oxygen-donating ligands and 7-coordinate complexes featuring both oxygen (4 or 5 oxygen atoms) and nitrogen (2 or 3 nitrogen atoms) donating ligands.⁶

The thermal properties of TPymT and 1 in an air atmosphere were studied by means of TGA (Fig. S5 in ESI†). The ligand TPymT is stable up to 400 °C and decomposed in two clearly defined steps with the final residue corresponding to carbon. 1 is stable up to 60 °C and decomposed in four main steps. The first step corresponds to the loss of six water molecules, while the seventh water molecule evaporates during the second step. The third step corresponds to the burning of the organic ligand with the formation of CdSO₄. The observed final residue of 28.9% is in excellent agreement with the value of 29.8% calculated for CdO.

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

According to the X-ray data, 1 crystallizes in the orthorhombic space group Pbcn and comprises a discrete molecule (Fig. 1). It was found that TPymT in the structure of 1 is coordinated to two CdII atoms and acts as a bis-terpyridine ligand, exhibiting a bridging μν3-coordination mode. The same type of coordination mode of the TPymT ligand was observed in the dilead analogue.⁶d In general, 1 resembles the structure of the monomeric unit of the dilead derivative. However, the latter compound is a polymeric chain, where the [Pb₂(TPymT)₄]⁺ cations are bound together through bridging water molecules and nitrate anions.⁶d Coordination spheres of the CdII atoms in 1 are each filled by four oxygen atoms associated with three water molecules and one sulfate anion. Inspection of the bond lengths and bond angles around the CdII cations (Table S1 in ESI†) shows that the coordination polyhedra are best described as distorted pentagonal bipyramids with the N(1) atom the most displaced from the least-squares plane formed by the equatorial water molecules and nitrate anions.⁶d Sulfate anions exhibit a typical tetrahedral geometry (Fig. 1).

The torsion angles between the planes formed by the triazine and bridging μν3- and non-bridging pyrimidine rings are 8.52(8) and 13.32(12)°, respectively. The same angles between the bridging μν2- and non-bridging pyrimidine planes are 21.81(12)° and 30.59(10)°, respectively. Although the N(5)–N(5)a distance (~4.76 Å) is similar to the N(3)–N(4) distances (~4.64 Å), we believe that coordination of a third CdII atom by the ligand would lead to a more distorted structure of TPymT. This, together with electron density withdrawal by two coordinated CdII atoms, does not favour the coordination of the third CdII atom by the free nitrogen atoms.

![Fig. 1 Molecular structure of 1. Ellipsoids are drawn at the 50% probability level.](Image)
of TPymT. This hypothesis requires a thorough investigation by a number of other crystallographically studied examples and detailed DFT calculations. Both experiments are in progress and the results will be published elsewhere.

As a result, the third coordination site of TPymT in 1 is occupied by the water molecule through the formation of two O–H⋯N hydrogen bonds (Fig. 1, Table S2 in ESI†). The oxygen atom of the same water molecule further serves as an acceptor in the formation of a bifurcated hydrogen bond with two H-atoms from two coordinated water molecules, corresponding to two neighbouring molecules of the complex (Fig. 2, Table S2 in ESI†). This supramolecular interaction presumably led to the stabilization of the TPymT ligand preventing the hydrolysis. As a result of these hydrogen bonds, the formation of two interpenetrated 1D polymeric chains is observed (Fig. 2). The interchain interactions are further stabilized by a number of O–H⋯O hydrogen bonds, formed between the H-atoms of the coordinated water molecules and the O-atoms of the sulfate anions (Table S2 in ESI†), and π⋯π stacking interactions (Table S3 in ESI†). The dichain aggregates are also linked with neighbouring dichain formations through a saturated network of hydrogen bonds and π⋯π stacking interactions (Fig. 3, Tables S2 and S3 in ESI†).

Bulk samples of TPymT and 1 were each studied by means of X-ray powder diffraction analysis (Fig. S6 in ESI†). The experimental X-ray powder pattern of TPymT is very similar to the calculated powder pattern of its close analogue 2,4,6-tris(2-pyridyl)-1,3,5-triazine.9 The latter compound shows a layered structure of the TPymT ligand along the 0a axis.

Thus, the crystallographic layers are parallel to the bc plane. This is in agreement with the layered structure of 1, obtained by single crystal X-ray diffraction (Fig. 3).

In summary, for the first time a dinuclear heteroleptic CdII complex 1 has been synthesized and characterized by means of IR, diffuse reflectance, and 113Cd solid-state CP MAS NMR spectroscopy, and TG and X-ray powder diffraction analyses. The molecular structure of the complex was elucidated by single crystal X-ray diffraction analysis. The luminescence properties of TPymT and 1 were studied in the solid state at room temperature and it was found that both compounds emit in the blue region, due to π⋯π* intra-ligand fluorescence.

The described complex 1, to the best of our knowledge, 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.

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Notes and references