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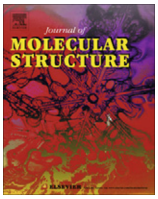

# Synthesis and crystal structures of the first cadmium complexes of 3,5,6-tris(2-pyridyl)-1,2,4-triazine ligand

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## HIGHLIGHTS

- The cadmium complexes were prepared and characterized by spectral and TGA techniques.
- The structures of compounds are determined by X-ray studies.
- The complexes show distorted octahedral and square pyramidal geometries.
- Different intermolecular interactions lead to various crystalline aggregates in **1**–**3**.

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## ABSTRACT

Three new cadmium(II) complexes, $[Cd_2(TPT)_2(SCN)_4]\cdot H_2O$ (**1**), $[Cd(TPT)I_2]$ (**2**) and $[Cd(TPT)Br_2]$ (**3**) ("TPT" is the abbreviation of 3,5,6-tris(2-pyridyl)-1,2,4-triazine), have been synthesized and characterized by elemental analysis, IR, $^1H$ NMR spectroscopy, and studied by thermal gravimetric as well as X-ray single crystal diffraction. Two anions of four thiocyanate anions bridge two $Cd^{II}$ ions to form a dinuclear complex, **1**, and iodide and bromide ions produce two halide-coordinated $[Cd(TPT)X_2]$ complexes (X = I for **2** and Br for **3**). Cadmium(II) in **1** is six coordinate, $CdN_4S_2$ and in **2** and **3** is five coordinate, $CdN_3I_2$ and $CdN_3Br_2$. The supramolecular features in these complexes are guided/controlled by N···O hydrogen bonding (in **1**) and weak directional intermolecular C—H···N, Cg···I, C—H···Br and $\pi$–$\pi$ interactions.

## 1. Introduction

Numerous compounds containing 1,2,4-triazine and 1,3,5-triazine moieties are well known in natural materials and show interesting biological, pharmacological and medicinal properties. Compounds including 1,3,5-triazine moieties are of particular interest because of their potentially large nonlinear optical response [1]. 4-amino-5oxo-3-phenylamino-1,2,4-triazine has a powerful inhibiting effect on the cell wall lignification catalysed by peroxidases, and alters the integrity of chloroplast [2]. Some of the 3,5,6-trisubstituted-1,2,4-triazines can be active as blood platelet aggregation inhibitors and others can exhibit antiviral inhibitory activity (e.g. against influenza viruses), significant activity towards leukaemia and ovarian cancer, and anti-HIV activity. Platinum(II) complexes with N-donor aromatic 3-(pyridyl-2′-yl)-1,2,4-triazine ligands have been reported to possess great potential as anti-HIV microbicides [3]. More recently, it has been revealed that a zinc-dppt complex (dppt = 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine) associated to a biocide could has significant biocidal effects on living cells including those of microorganisms (bacteria and fungi), cell culture system, plants and animals [4]. Another interesting property of the derivatives of 1,2,4-triazine compounds is formation of coloured complexes when coordinated to metal ions. In particular, the ligand 3,5,6-tris(2-pyridyl)-1,2,4-triazine (TPT) has been widely used as a sensitive reagent for the determination of Fe(II) by spectrophotometric methods, in natural and waste waters [5,6]. Some Cu(II) complexes of dppt have been prepared previously and studied as potential catalytically active redox agents [7]. It is obvious that the mode of coordination will have a critical role on the electronic properties of the complexes, e.g. its $\pi$-acceptor properties, because of the localized nature of the double bonds in 1,2,4-triazine [8]. This work focuses on the complexation ability of 3,5,6-tris(2-pyridyl)-1,2,4-triazine (TPT) towards $Cd^{2+}$. Here we present synthesis, spectroscopic and structural data $[Cd_2(TPT)_2(SCN)_4]\cdot H_2O$ **1**, $[Cd(TPT)I_2]$ **2** and $[Cd(TPT)Br_2]$ **3** complexes.

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## 2. Experimental

### 2.1. Materials and physical measurements

3,5,6-tris(2-pyridyl)-1,2,4-triazine was purchased from Aldrich, and the other chemicals were of analytical grade quality. IR spectra was recorded on KBr pellets using Perkin–Elmer 597 and Nicolet 510P spectrophotometers. Elemental analysis was performed with a Heraeus CHN—O-Rapid analyzer. Solution $^1$H NMR spectra was recorded on a BRUKER DRX-250 AVANCE spectrometer at 2500 MHz using d6-dimethylsulfoxide as a solvent. Thermogravimetrical analysis (TGA) was performed in $N_2$ atmosphere with a flow rate of 20 ml/min on a Seiko Instrument thermal analyzer from 20 to 800 °C, with a heating rate of 10 °C/min in the ceramic crucibles.

### 2.2. Preparation of $[Cd_2(TPT)_2(SCN)_4]\cdot H_2O$ (1)

3,5,6-tris(2-pyridyl)-1,2,4-triazine (TPT, 0.312 g, 1 mmol) was placed in one arm of a branched tube [9] and $Cd(CH_3COO)_2\cdot 2H_2O$ (0.133 g, 0.5 mmol) and potassium thiocyanate (0.097 g, 1 mmol) in the other. Methanol and water (2:1 ratio) were carefully added to fill both arms, the tube sealed and the ligand-containing arm immersed in a bath at 60 °C while the other was at ambient temperature. After 2 days, crystals were deposited in the cooler arm and were filtered off, washed with ether, and dried in air. yield: 72%. Analysis: Found: C 43.49%, H 2.10%, N 20.45%, Calculated for $C_{40}H_{26}Cd_2N_{16}OS_4$: C 43.64%, H 2.36%, N 20.36%. IR (cm$^{-1}$) selected bands: 3363br, 3059w, 2131vs, 2085vs, 1581s, 1571s, 1385vs, 1161w, 1117 m, 1054w, 1016s, 782w. $^1$H NMR (DMSO, δ): 7.25(m, 3H, pyridyl), 7.65(m, 3H, pyridyl), 8.00(m, 3H, pyridyl) and 8.90(m, 3H, pyridyl).

### 2.3. Preparation of $[Cd(TPT)I_2]$ (2)

Complex **2** was synthesized in the same way as complex **1** using potassium iodide instead of potassium thiocyanate, yield: 68%. Analysis: Found: C 31.49%, H 2.10%, N 12.45%, Calculated for $C_{18}H_{12}CdI_2N_6$: C 31.83%, H 1.77%, N 12.38%. IR (cm$^{-1}$) selected bands: 3363br, 3073w, 1590s, 1512s, 1479s, 1400vs, 1377vs, 1255w, 1114w, 1010w, 767w. $^1$H NMR (DMSO, δ): 7.20(m, 3H, pyridyl), 7.75(m, 3H, pyridyl), 8.00(m, 3H, pyridyl) and 8.85(m, 3H, pyridyl).

### 2.4. Preparation of $[Cd(TPT)Br_2]$ (3)

Complex **2** was synthesized in the same way as complex **1** using potassium bromide instead of potassium thiocyanate, yield: 65%. Analysis: Found: C 36.83%, H 1.87%, N 14.25%, Calculated for $C_{18}H_{12}CdBr_2N_6$: C 36.95%, H 2.05%, N 14.37%. IR (cm$^{-1}$) selected bands: 3089w, 1595s, 1506s, 1473s, 1406vs, 1377vs, 1253w, 1111w, 1010w, 790w. $^1$H NMR (DMSO, δ): 7.23(m, 3H, pyridyl), 7.70(m, 3H, pyridyl), 8.05(m, 3H, pyridyl) and 8.83(m, 3H, pyridyl).

### 2.5. Crystallography

Data was collected at room temperature with a Bruker APEX II CCD area-detector diffractometer using Mo Kα radiation ($\lambda$ = 0.71073 Å). Data collection, cell refinement, data reduction and absorption correction were performed using multiscan method with Bruker software [10]. The structures were solved by direct method using SIR2004 [11]. The non hydrogen atoms were refined anisotropically by the full matrix least squares method on F$^2$ using SHELXL [12]. All the hydrogen (H) atoms were placed at the calculated positions and constrained to ride on their parent atoms. Details concerning collection and analysis are reported in Table 1.

## 3. Result and discussions

### 3.1. Spectroscopic studies

IR displays characteristic absorption bands of TPT ligands and thiocyanate anions of **1**. The relatively weak absorption bands at

**Table 1**
Crystal data and structure refinement for **1–3.**

| | 1 | 2 | 3 |
|---|---|---|---|
| Identification code | $[Cd_2(TPT)_2(SCN)_2]\cdot H_2O$ | $[Cd(TPT)(I)_2]$ | $[Cd(TPT)(Br)_2]$ |
| Empirical formula | $C_{40}H_{26}Cd_2N_{16}OS_4$ | $C_{18}H_{12}CdI_2N_6$ | $C_{18}H_{12}Br_2CdN_6$ |
| Formula weight | 1099.81 | 678.54 | 584.56 |
| Crystal system | Monoclinic | Monoclinic | Hexagonal |
| Space group | P2(**1**)/c | P2(**1**)/c | P6(5) |
| Unit cell dimensions | $a$ = 13.8503(4) Å | $a$ = 9.6550(2) Å | $a$ = 9.1544(3) Å |
| | $b$ = 9.7728(3) Å | $b$ = 15.0520(4) Å | $b$ = 9.1544(3) Å |
| | $c$ = 15.7437(4) Å | $c$ = 13.7920(4) Å | $c$ = 39.5512(12) Å |
| | $\alpha$ = 90° | $\alpha$ = 90° | $\alpha$ = 90° |
| | $\beta$ = 100.696(1)° | $\beta$ = 91.7020(9)° | $\beta$ = 90° |
| | $\gamma$ = 90° | $\gamma$ = 90° | $\gamma$ = 120° |
| Volume | 2093.98(10) Å$^3$ | 2003.47(9) Å$^3$ | 2870.45(16) Å$^3$ |
| $Z$ | 2 | 4 | 6 |
| Density (calculated) | 1.744 g cm$^{-3}$ | 2.250 g cm$^{-3}$ | 2.029 g cm$^{-3}$ |
| Absorption coefficient | 1.271 mm$^{-1}$ | 4.187 mm$^{-1}$ | 5.333 mm$^{-1}$ |
| $F$(000) | 1092 | 1264 | 1680 |
| $q$ range for data collection | 2.47–28.00 | 2.51–28.00 | 2.57–27.00° |
| Index ranges | $-18 \leqslant h \leqslant 18$ | $-11 \leqslant h \leqslant 12$ | $-11 \leqslant h \leqslant 11$ |
| | $-12 \leqslant k \leqslant 12$ | $-19 \leqslant k \leqslant 19$ | $-11 \leqslant k \leqslant 11$ |
| | $-20 \leqslant l \leqslant 20$ | $-18 \leqslant l \leqslant 18$ | $-50 \leqslant l \leqslant 50$ |
| Reflections collected | 56,270 | 27,156 | 126,189 |
| Independent reflections | 5060 [$R$(int) = 0.0174] | 4835 [$R$(int) = 0.0193] | 4176 [$R$(int) = 0.0368] |
| Completeness to theta | 100.0% | 99.9% | 100.0% |
| Data/restraints/parameters | 5060/0/293 | 4835/0/244 | 4176/1/244 |
| Goodness-of-fit on $F^2$ | 1.100 | 1.038 | 1.254 |
| Final $R$ indices [$I$ > 2s ($I$)] | $R1$ = 0.0236, $wR2$ = 0.0608 | $R1$ = 0.0181, $wR2$ = 0.0406 | $R1$ = 0.0387, $wR2$ = 0.0864 |
| Indices (all data) | $R1$ = 0.0277, $wR2$ = 0.0676 | $R1$ = 0.0222, $wR2$ = 0.0430 | $R1$ = 0.0390, $wR2$ = 0.0865 |
| Largest diff. Peak, hole | 0.62, −0.50 e Å$^{-3}$ | 0.62, −0.71 e. Å$^{-3}$ | 0.83, −0.72 e. Å$^{-3}$ |