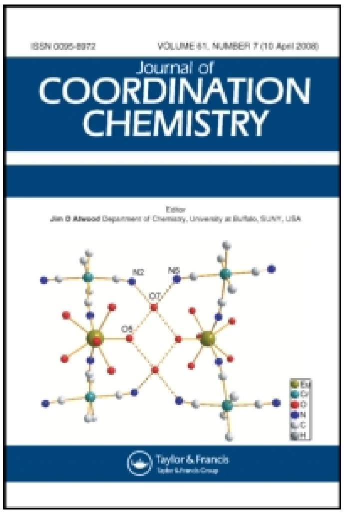

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Zinc(II) and cadmium(II) complexes with PDT: study of the effect of weak interactions on crystal packing

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Zinc(II) and cadmium(II) complexes with PDT: study of the effect of weak interactions on crystal packing

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Two new zinc(II) and cadmium(II) complexes, $[Zn(PDT)_2(NCS)_2]$ (**1**) and $[Cd((PDT)_2I_{1.6}(H_2O)_{0.4}(OH)_{0.4}] \cdot 0.4H_2O$ (**2**) ("PDT" is the abbreviation of 3-(2-pyridyl)-5, 6-diphenyl-1,2,4-triazine), have been synthesized and characterized by elemental analysis, IR, ^{1}H NMR spectroscopy, and studied by X-ray crystallography. Zinc(II) in **1** is six coordinate ZnN_6. **2** is a co-crystal with cadmium(II) being 60% six-coordinated with a CdN_4I_2 environment and 40% seven-coordinated with a CdN_4O_2I environment. The supramolecular features in these complexes are guided/controlled by weak directional intermolecular $S \cdots \pi$, $C–H \cdots \pi$, $C–H \cdots I$, and $\pi \cdots \pi$ interactions.

Keywords: Crystal structure; Zinc(II); Cadmium(II); Intermolecular interactions

1. Introduction

Metal-directed self-assembly has become a powerful tool for construction of systems having cavities or possessing intrinsic physical and chemical properties that are promising for creation of new materials and new metal-containing drugs [1]. More recently, non-covalent weak molecular forces, which can connect these metallic subunits into intriguing, loose supramolecular infrastructures, have been widely investigated in structural chemistry, structural biology and pharmaceutical sciences [2]. Intra- and intermolecular non-bonded $I \cdots X$ and $S \cdots X$ ($X = O, S, N$, etc.) interactions have been investigated for characterization of molecular structures in a large number of compounds [3]. These intra- and intermolecular non-bonded interactions are important in construction of new molecular recognition systems in chemical reactions [4] and medicinal biochemistry [5]; non-bonded $I \cdots H$ [6], $S \cdots H$ [7], $S \cdots O$ [8], $S \cdots N$ [9], and $S \cdots S$ [10] interactions have all attracted interest. The 3-(2-pyridyl)-5, 6-diphenyl-1,2,4-triazine (PDT) ligand, with aromatic rings and ability for forming intermolecular $S \cdots \pi$ and $C–H \cdots I$ non-bonded weak interactions with coordinated

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iodide and thiocyanate groups and C–H $\cdots\pi$, and $\pi\cdots\pi$ interactions with neighboring ligand may be a very good candidate for new zinc(II) and cadmium(II) compounds.

2. Experimental

2.1. *Physical measurements*

All chemicals were reagent grade and used without purification. FT-IR spectra were collected on a Mattson 1000 spectrophotometer using KBr pellets from 4000–450 cm^{-1}. Elemental analyses (CHN) were performed using a Carlo ERBA model EA 1108 analyzer; ^1H NMR spectra were obtained with a Bruker spectrometer at 250 MHz in [D_6]DMSO. Thermal analyses were carried out on a Perkin–Elmer instrument (Seiko Instruments).

2.2. *Preparation of [Zn(PDT)$_2$(NCS)$_2$] (1)*

3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT) (0.310 g, 1 mmol) was placed in one arm of a branched tube and $ZnCl_2$ (0.068, 0.5 mmol) and KSCN (0.097 g, 1 mmol) in the other. Methanol was carefully added to fill both the arm, 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 had deposited in the cooler arm which were filtered off, washed with ether, and air dried, m.p. 275°C. Analysis: Found: C 62.40, H 3.18, N 17.15%, calculated for $C_{42}H_{28}N_{10}S_2Zn$: C 62.82, H 3.49, N 17.45%. IR (cm^{-1}) selected bands: 3024s, 2096vs, 1624w, 1612m, 1593s, 1585s, 1569s, 1423s, 1160w, 1124w, 780w, 755m. ^1H NMR (DMSO, δ): 7.65 (m, 10H, two phenyls), 7.75 (dd, 1H, pyridyl), 8.20 (dd, 1H, pyridyl), 8.60 (d, 1H, pyridyl), and 8.80 (d, 1H, pyridyl).

2.3. *Preparation of [Cd((PDT)$_2$I$_{1.6}$(H$_2$O)$_{0.4}$(OH)$_{0.4}$]$\cdot$0.4H$_2$O (2)*

3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT) (0.310 g, 1 mmol) was placed in one arm of a branched tube and $Cd(OOCCH_3)_2\cdot 3H_2O$ (0.154 g, 0.5 mmol) and KI (0.166 g, 1 mmol) in the other. Methanol and water (ratio of 5 : 1 V) was carefully added to fill both the arm, the tube sealed, and the ligand-containing arm immersed in a bath at 60°C while the other was at ambient temperature. After 1 day, red crystals deposited in the cooler arm were filtered off, washed with ether, and air dried, m.p. 260°C. Analysis: Found C, 50.54; H, 3.12; N, 11.50%, calculated for $C_{40}H_{30}CdI_{1.60}N_8O_{1.20}$: C 50.14, H 3.13, N 11.70%. IR (cm^{-1}), selected bands: 3063s, 1610w, 1584s, 1571s, 1419s, 1161w, 1117m, 1054w, 1016s, 782w. ^1H NMR (DMSO, δ): 7.45 (m, 10H, two phenyl), 7.65 (dd, 1H, pyridyl), 8.08 (dd, 1H, pyridyl), 8.55 (d, 1H, pyridyl), and 8.85 (d, 1H, pyridyl).

2.4. *Crystallography*

Crystallographic data were collected at 100.0(1) K with the Oxford Cyrosystem Cobra low-temperature attachment. The data were collected using a Bruker Apex2 CCD diffractometer with graphite monochromated Mo-Kα radiation at a detector distance of 5 cm and with APEX2 software [11]. The collected data were reduced using SAINT, and the empirical absorption corrections were performed using SADABS [11]. The structures were solved by direct methods and refined by least-squares using the SHELXTL software package [12]. Materials for publication were prepared using SHELXTL [12] and ORTEPIII [13].

3. Results and discussion

Compound **1** was shown by single crystal X-ray diffraction to crystallize in the monoclinic space group *C2* (table 1). Selected bond distances and angles are listed in table 2. Each asymmetric unit contains a Zn(II), a SCN$^-$, and a PDT. Zn lies on a two-fold rotation axis. The coordination geometry of Zn(II) is a distorted octahedron (figure 1), formed by two nitrogens (N5) of two isothiocyanates and four nitrogens

Table 1. Crystal data and structure refinement for **1** and **2**.

Identification code	**1**	**2**
Empirical formula	$C_{42}H_{28}N_{10}S_2$ Zn	$C_{40}H_{30}CdI_{1.60}N_8O_{1.20}$
Formula weight	802.23	957.36
Temperature (K)	100.0(1)	100.0(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*C2*	*P21/c*
Unit cell dimensions (Å, °)		
a	15.6934(4)	8.8349(2)
b	9.1879(3)	22.2590(5)
c	14.4807(4)	18.6147(4)
α	90.00	90.00
β	116.872(2)	98.5010(2)
γ	90.00	90.00
Volume	1862.50(9)	3620.47(14)
Z	2	4
Density (Calcd)	1.430	1.765
Absorption coefficient	0.818	2.013
$F(000)$	824	1874
Crystal size (mm^3)	$0.5 \times 0.26 \times 0.14$	$0.63 \times 0.27 \times 0.14$
θ range for data collection (°)	2.61–30.15	1.44–40.12
Index ranges	$-21 \leq h \leq 21$	$-14 \leq h \leq 16$
	$-12 \leq k \leq 12$	$-33 \leq k \leq 40$
	$-20 \leq l \leq 17$	$-33 \leq l \leq 33$
Reflections collected	11730	98528
Independent reflections	2905[$R_{(int)} = 0.0382$]	22318[$R_{(int)} = 0.0402$]
Completeness to θ	99.6	98.8
Full-matrix least squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2905/1/250	22318/1/488
Goodness-of-fit on F^2	1.102	1.041
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0415$	$R_1 = 0.0401$
	$wR_2 = 0.0958$	$wR_2 = 0.0938$
R indices (all data)	$R_1 = 0.0471$	$R_1 = 0.0583$
	$wR_2 = 0.0987$	$wR_2 = 0.1025$
Largest differene peak and hole (e Å^{-3})	0.747 and −0.734	3.840 and −1.737

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
Zn1–N5	2.097(3)	Cd1–N6	2.393(3)
Zn1–N1	2.125(3)	Cd1–O1W	2.397(7)
Zn1–N2	2.212(3)	Cd1–N2	2.424(3)
		Cd1–N7	2.427(3)
N5^{i}–Zn1–N5	91.92(2)	Cd1–N1	2.428(3)
N5–Zn1–N1^{i}	98.48(1)	Cd1–O1	2.505(8)
N5–Zn1–N1	95.89(1)	Cd1–I1	2.777(4)
N1^{i}–Zn1–N1	159.27(1)	Cd1–I2	2.900(5)
N5^{i}–Zn1–N2	173.13(1)		
N5–Zn1–N2	86.52(1)	N6–Cd1–N7	69.06(1)
N2^{i}–Zn1–N2	95.79(1)	N2–Cd1–N7	84.29(1)
N1–Zn1–N2	75.04(1)	N6–Cd1–N2	87.86(1)
N5–Zn1–N2^{i}	173.13(1)	N2–Cd1–N1	67.65(1)
N1–Zn1–N2^{i}	90.96(1)	N7–Cd1–N1	145.46(1)
		N6–Cd1–I1	174.40(7)
		N2–Cd1–I1	89.56(8)
		N7–Cd1–I1	105.74(7)
		N1–Cd1–I1	94.20(7)
		I1–Cd1–I2	101.633(1)
		O1W–Cd1–O1	72.6(2)
		N7–Cd1–I2	105.79(8)
		N1–Cd1–I2	97.17(7)

Symmetry transformation: i: −*x*, *y*, −*z*.

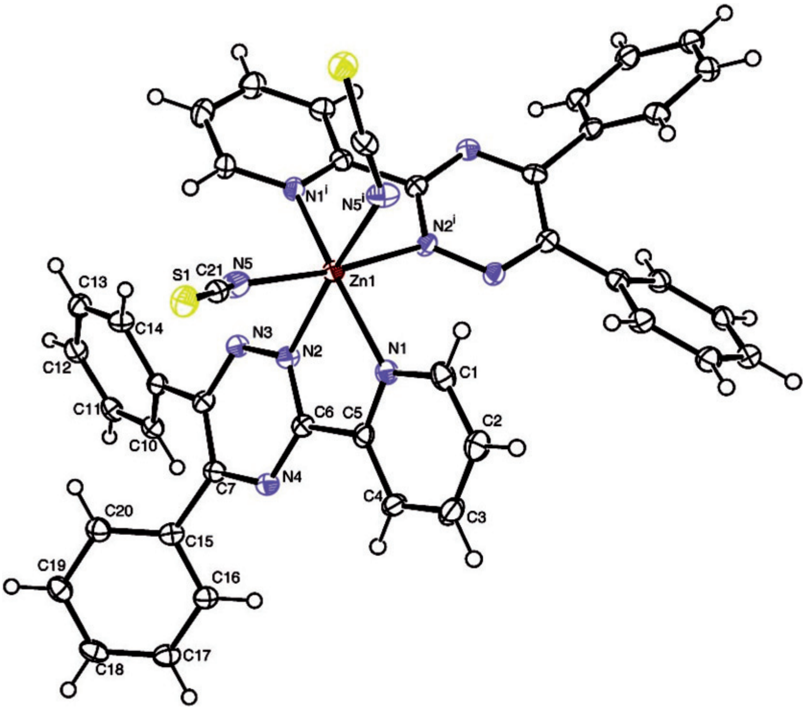


Figure 1. ORTEP diagram of **1**.

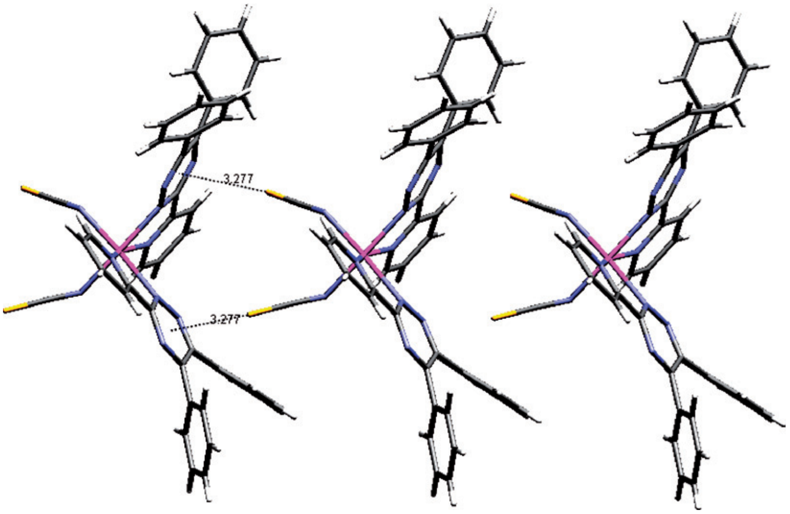


Figure 2. Packing diagram of **1** viewed along *a* showing C–S $\cdots\pi$ interactions.

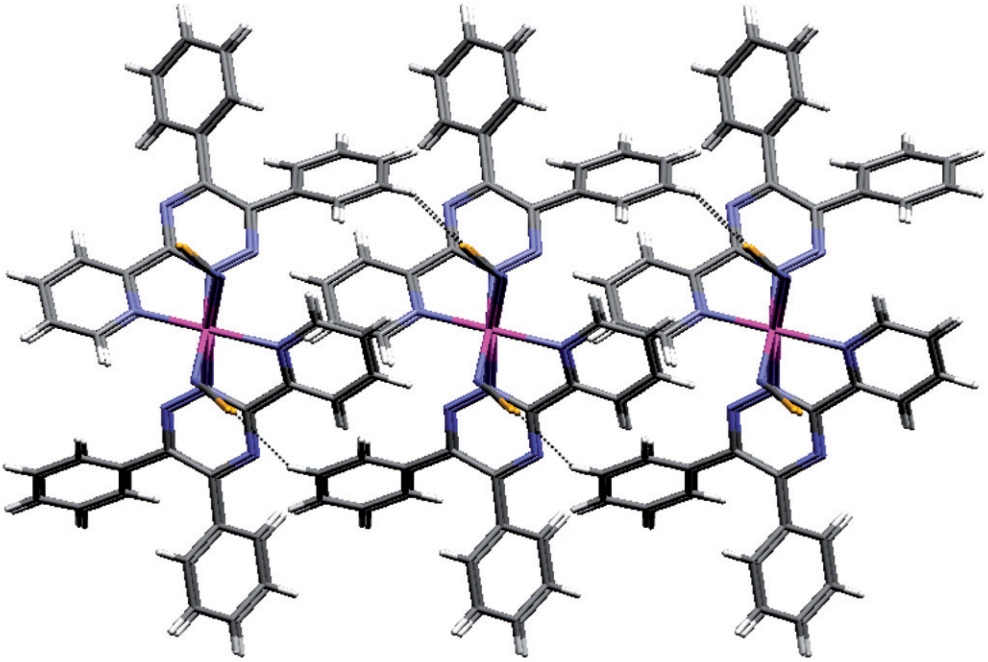
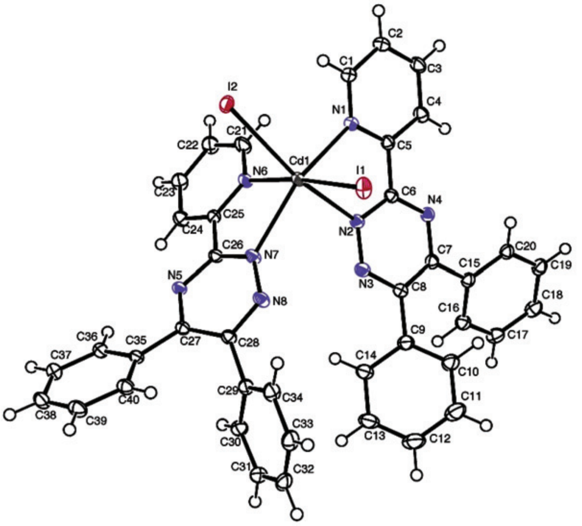
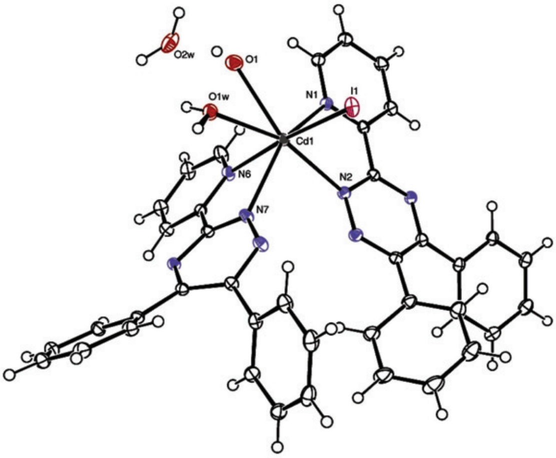


Figure 3. Framework view down *b* of **1** showing C–H $\cdots$ S and $\pi\cdots\pi$ interactions.

(N1 and N2) of two PDT ligands. Every PDT is bidentate. The isothiocyanate is monodentate in a *cis* fashion. The angles around Zn(II) range from 75.04(1) to 98.48(1)°, and the bond lengths around Zn(II) are in the range 2.097(3)–2.212(3) Å. The Zn–N bond distances are comparable to those found in $[Zn(PDT)_2Cl(ClO_4)]$ and



60% composition



40% composition

Figure 4. ORTEP diagram of **2**.

[Zn(PDT)Cl_2] [14]. The isothiocyanate ligands are almost perfectly straight (S–C–N angles = 177.3°), but adopt a significantly bent coordination at Zn (Zn–N–C angles = 138.07°), a possible consequence of the requirements imposed by the supramolecular interactions. Linear *versus* bent coordination for cobalt(II) and nickel(II) isothiocyanate complexes is influenced to a great extent by the local ligand environment [7c, 15]; it is likely that this effect extends into the zinc(II) isothiocyanate systems. An interesting feature in **1** is that there are C–S $\cdots \pi$ interactions (figure 2), with distance of 3.277 Å, suggesting relatively strong interactions within this class of weak non-covalent contacts [16]. There are S $\cdots$ H–C interactions (S3 $\cdots$ H13–C13 at 2.936 Å, H–C $\cdots$ S = 3.771 Å, and S $\cdots$ H–C = 150.20°) [7, 17]. The structure of **1** displays two different π–π stacking edge-to-face of phenyl rings of "PDT" ligands with

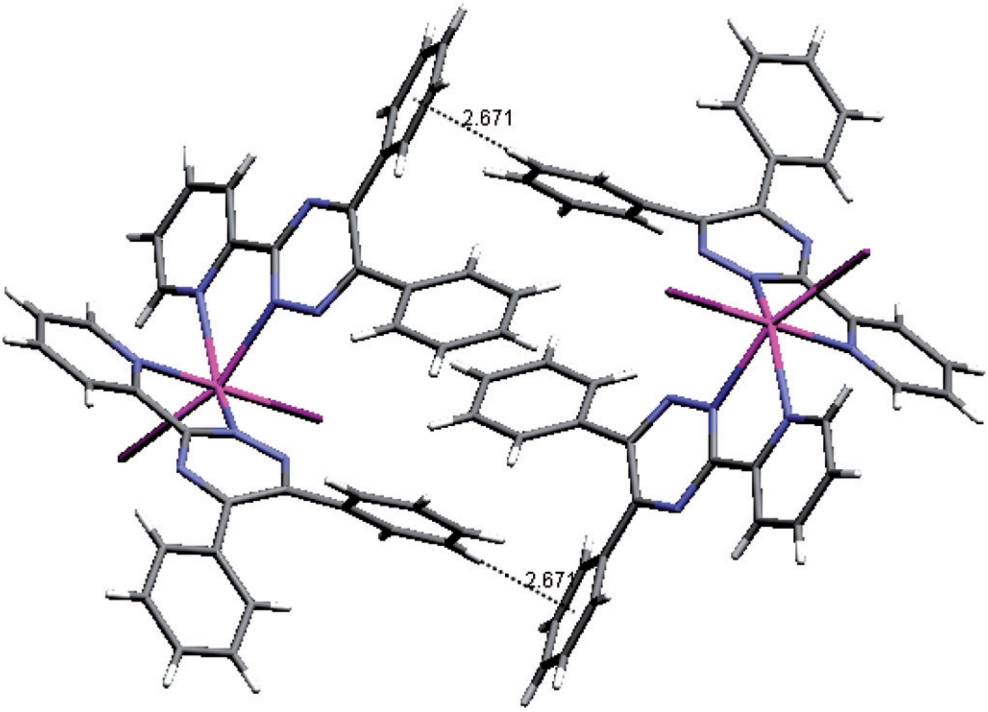


Figure 5. Packing diagram of **2**, down *a*, showing C–H $\cdots\pi$ and $\pi\cdots\pi$ interactions.

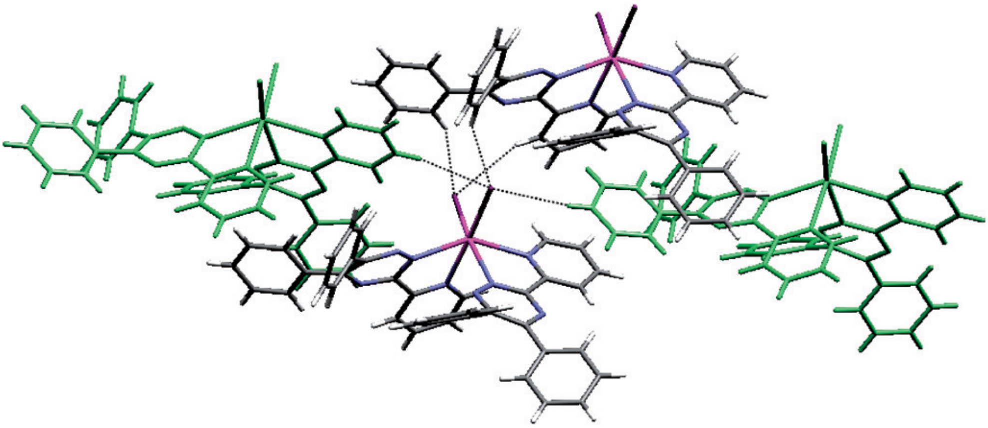


Figure 6. Packing diagram of **2**, down *b*, showing C–H $\cdots$ I interactions.

distance of 3.389 Å (distances of shortest atom $\cdots$ Cg), slipped face-to-face of phenyl rings with pyridyl rings with distance of 3.287 Å (distances between planes), appreciably shorter than the normal intermolecular interactions [18]. These interactions also allow the complex to form a hybrid 2-D network (figure 3).

Table 3. Intermolecular interactions in crystals of **2**.

A···H–B	A···H/Å	A···B/Å	A···H–B(°)
I1···H3A–C3	3.094	3.993	163.14
I1···H30A–C30	3.017	3.853	150.34
I1···H38A–C38	3.070	3.941	156.60
I2···H24A–C24	3.123	3.972	152.48
I2···H36A–C36	3.131	3.982	153.02

An ORTEP drawing of **2** is shown in figure 4. Selected bond distances and angles are listed in table 2. Single crystal analysis reveals that $[Cd((PDT)_2I_{1.6}(H_2O)_{0.4}(OH)_{0.4}]\cdot 0.4H_2O$ crystallizes in the monoclinic space group *P21/c* (table 1). There are two iodides, one coordinated to cadmium and another sharing a position with coordinated and uncoordinated water and hydroxide. The results show 40% of these positions occupied by two water and hydroxide and 60% by iodide. Cadmium is also bonded to four nitrogens of two *cis* "PDT" ligands. Therefore, cadmium(II) in **2** is 60% six, CdN_4I_2, and 40% seven, CdN_4O_2I, coordinate. In **2** there are C–H···π interactions among the weak interactions (figure 5), C33-H33A···π(C15–C20) with distance of 2.671 Å, relatively strong interactions within this class of weak non-covalent contacts [19]. The packing diagram of this complex has self-assembled structural topologies *via* three different π–π stacking interactions (slipped face-to-face) with distance of 3.198, 3.339, and 3.353 Å (distances between planes) shorter than normal intermolecular interactions [20]. The supramolecular features in this complex are guided/controlled by weak directional intermolecular I···H–C interactions (figure 6, table 3) [21].

4. Conclusion

Using various anions with PDT and metal ions, we isolated complexes with two kinds of coordination topologies. Different and interesting patterns of molecular recognition involving sulfur and iodide are shown in this article. Among these interactions are C–H···S, C–S···π, C–H···π, C–H···I, and aromatic self-assemblies which lead to supramolecular structures. Further studies on the mapping of the charge density distributions followed by a topological analysis of these interactions are currently in progress.

Supplementary material

Crystallographic data for the structure reported in the article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-689713 and 689738 for **1** and **2**, respectively. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44–1223/336033; Email: deposit@ccdc.cam.ac.uk).

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