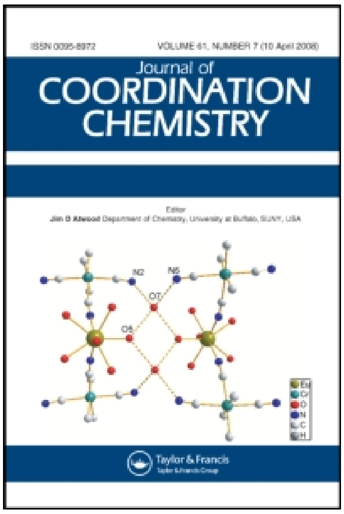

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Synthesis and structural characterization of a one-dimensional coordination polymer, $[Cd(PDPT)(\mu\text{-}SCN)_2]_n$, PDPT = 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine

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A new one-dimensional coordination polymer of cadmium(II) with 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDPT) ligand, $[Cd(PDPT)(\mu\text{-}SCN)_2]_n$ has been synthesized and characterized by elemental analysis, IR- and ^1H NMR spectroscopy. The single crystal X-ray analyses show that the coordination number in this complex is six with two N-donor atoms from one "PDPT" ligand and four of the anionic ligands, CdN_4S_2. Self-assembly of this compound in the solid state via π–π stacking interactions and weak hydrogen bonding is discussed.

1. Introduction

Cadmium is an extremely toxic element that is naturally present in the environment and also as a result of human activities. Its toxicity derives from the fact that it is rapidly localized intracellularly, mainly in the liver, and then bound to metallothionein forming a complex that is slowly transferred to the bloodstream to be deposited in the kidneys. This leads to urinary loss of filterable proteins, calcium and other small molecules, which may produce proteinuria and bone decalcification [1].

The ligand 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine, noted PDPT, has been widely used as a sensitive reagent for the determination of Fe(II) by spectrophotometric methods, in natural and waste waters [2]. Its role as transfer agent for transition metal ions has been shown by electrochemical studies [3]. Some Cu(II) [4, 5], Pb(II) [6] and Zn(II) [7] complexes of this ligand have been isolated and studied structurally and as

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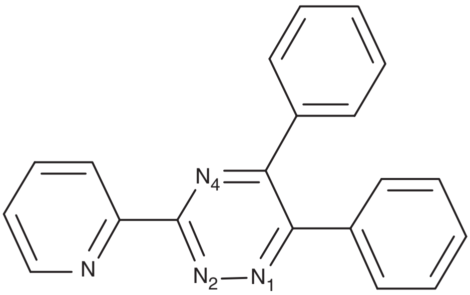

Scheme 1. The 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDPT) ligand.

catalytically active redox agents. The general structure of the ligand PDPT is shown in scheme 1.

The mixed-anion zinc(II) and cadmium(II) complexes of PDPT have recently been reported [8] and in this work, we wish to describe the synthesis and characterization of a new 1D Cd(II) coordination polymer of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine ligand with thiocyanate anions, $[Cd(PDPT)(\mu\text{-}SCN)_2]_n$.

The thiocyanate anion is a versatile ambidentate ligand coordinating through either the nitrogen or the sulfur, or both, giving rise to linkage isomers or polymers. This creates an interesting situation for the Zn–Cd–Hg triad. The tetrahedral Zn(II) complexes tend to be N-bonded and the tetrahedral Hg(II) complexes are almost always S-bonded. Cd(II) becomes 'schizophrenic' [24], exhibiting both (S and N) bonding modes as well as a variety of coordination numbers and forms polymeric compounds [9–12]. 1D anionic cadmium thiocyanate coordination solids are rare [13, 14].

2. Experimental

2.1. *Physical measurements*

IR spectra were recorded as nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz.

2.2. *Preparation of [Cd(PDPT)(μ-SCN)$_2$]*

3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine (PDPT) (0.620 g, 2 mmol) was placed in one arm of a branched tube and $Cd(SCN)_2$ (0.228 g, 1 mmol) in the other. Methanol was carefully added to fill arms, the tube sealed and the ligand-containing arm immersed in a bath at 60°C while the other was at ambient temperature. After 7 days, crystals had deposited in the cooler arm, which were filtered off, washed with acetone and ether, and air dried. (Found: C: 49.30, H: 2.20, N: 15.80%, calculated for $C_{22}H_{14}CdN_6S_2$: C: 48.98, H: 2.59, N: 15.58%). IR (cm^{-1}) selected bonds: 690(m), 760(m), 1265(s),

Table 1. Crystal data and structure refinement for $[Cd(PDPT)(\mu\text{-}SCN)_2]_n$.

Complex	$[Cd(PDPT)(\mu\text{-}SCN)_2]_n$
Empirical formula	$C_{44}H_{28}Cd_2N_{12}S_4$
Molecular weight	1077.82
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*Cc*
a (Å)	14.569(3)
b (Å)	14.262(3)
c (Å)	21.821(4)
β (°)	106.02(3)
V (Å^3)	4358.0(15)
Z	4
D_{Calcd} (g cm^{-3})	1.643
μ (mm^{-1})	1.216
$F(000)$	2144
Crystal size (mm^3)	0.35 × 0.20 × 0.20
θ range (°)	2.04–27.00
Index ranges	$0 \le h \le 18$, $0 \le k \le 18$, $-27 \le l \le 26$
Reflections collected	4914
Independent reflections (R_{int})	4914 (0.0000)
Completeness to theta	99.6%
Data/restraints/parameters	4914/2/560
Goodness-of-fit on F^2	0.986
R [$I > 2\sigma(I)$]	$R_1 = 0.0376$, $wR_2 = 0.0944$
R (all data)	$R_1 = 0.0411$, $wR_2 = 0.0952$
Largest diff. peak and hole (e Å^{-3})	1.502 and −1.219

1442(s), 1511(s), 1590(m), 2040(vs) and 3062(w). ^{1}H NMR (DMSO, δ): 7.60 (m, 10H), 7.70 (t, 1H), 8.21(t, 1H), 8.62(d, 1H), and 8.80 (d, 1H).

2.3. *Crystallography*

Crystallographic measurements were made at 200(2) K using a Siemens R3m/V diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2. Structure solution and refinement was accomplished using SIR97, SHELXL97 and WinGX [15, 16]. All H atoms were positioned geometrically and allowed to ride on their parent atoms. The molecular structure plots were prepared by using ORTEPIII [17].

Crystal data and structure refinement are given in table 1. Selected bond lengths and angles are given in table 2. Anisotropic thermal parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material. ORTEP diagram and perspective views of the packing in the unit cell are shown in figures 1 and 2.

3. Results and discussion

Reaction between PDPT and cadmium(II) thiocyanate provided crystalline materials analyzed as $[Cd(PDPT)(\mu\text{-}SCN)_2]_n$. An IR spectrum shows characteristic absorption

Table 2. Bond lengths (Å) and angles (°) for $[Cd(PDPT)(\mu\text{-}SCN)_2]_n$.

Cd(1)–N(3T)	2.350(7)	Cd(1)–S(2)	2.591(2)
Cd(1)–N(1T′)	2.352(7)	Cd(1)–S(2)	2.68(2)
Cd(1)–N(4)	2.375(6)	Cd(1)–N(1)	2.412(5)
N(3T)–Cd(1)–N(1T′)	174.5(3)	N(4)–Cd(1)–S(2)	155.11(14)
N(3T)–Cd(1)–N(4)	94.0(2)	N(1)–Cd(1)–S(2)	92.81(14)
N(1T′)–Cd(1)–N(4)	83.9(2)	N(3T)–Cd(1)–S(1)	85.48(18)
N(3T)–Cd(1)–N(1)	84.9(2)	N(1T′)–Cd(1)–S(1)	89.73(17)
N(1T′)–Cd(1)–N(1)	98.9(2)	N(4)–Cd(1)–S(1)	96.22(14)
N(4)–Cd(1)–N(1)	68.42(19)	N(1)–Cd(1)–S(1)	161.21(14)
N(3T)–Cd(1)–S(2)	100.65(18)	S(2)–Cd(1)–S(1)	104.83(7)
N(1T′)–Cd(1)–S(2)	83.09(19)		

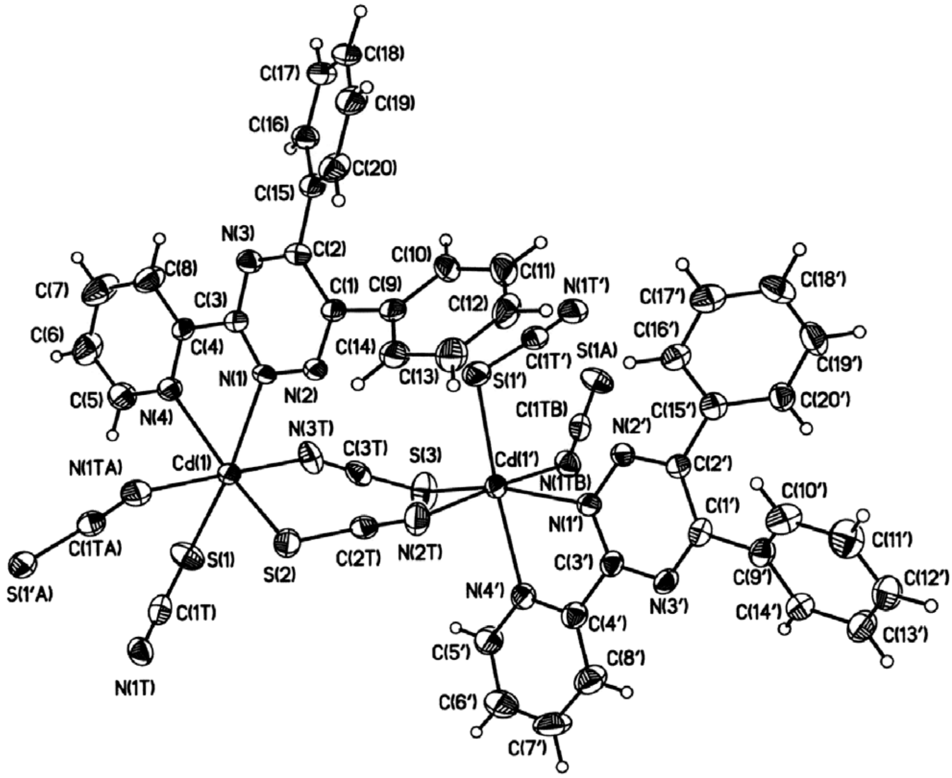

Figure 1. ORTEP diagram of $[Cd(PDPT)(\mu\text{-}SCN)_2]_n$.

bands for PDPT and thiocyanate anions. The relatively weak absorption bands around $3062\,cm^{-1}$ are due to the C–H modes involving the aromatic ring hydrogen atoms. The absorption bands with variable intensity in the frequency range $1400–1580\,cm^{-1}$ correspond to ring vibrations of the ''py'' and ''ph'' moieties of PDPT. The characteristic bands of the thiocyanate anions appear at $2040\,cm^{-1}$. The ^1H NMR spectrum of the DMSO solution of $[Cd(PDPT)(\mu\text{-}SCN)_2]_n$ displays five different protons of ''ph'' and ''py'' groups of the PDPT ligand.

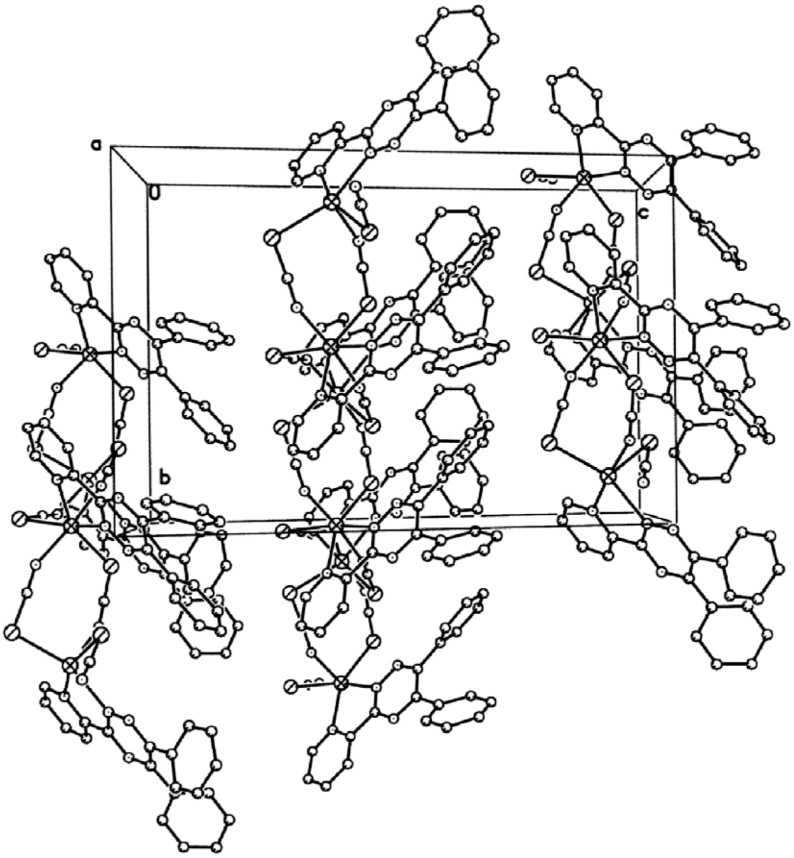

Figure 2. The unit cell and showing 1D chains of $[Cd(PDPT)(\mu\text{-}SCN)_2]_n$.

Single X-ray crystal analysis reveals that $[Cd(PDPT)(\mu\text{-}SCN)_2]_n$ crystallizes in the monoclinic space group *Cc*. The structure of this complex may be considered as a polymer of cadmium(II) coordinated by one PDPT and bridged by two thiocyanate anions (figures 1 and 2). The coordination number of this complex is six with Cd coordinated by two nitrogen atoms from PDPT and two nitrogen and two sulfur atoms from thiocyanate anions. The environment of cadmium atoms is CdN_4S_2, distorted octahedral. The PDPT ligand is a bidentate ligand and uses only two of the four potential donor nitrogen atoms, forming a five-membered metallocycle. In this complex the triazine group of PDPT uses nitrogen from position 2 (scheme 1), due to steric interference of the phenyl group close to nitrogen in position 4. Two sulfur atoms of thiocyanate anions occupy the cis positions [S(2)–Cd(1)–S(1) = 104.83(7)°]. The large distortion of the coordination polyhedron may be the consequence of the small bite angle of PDPT {68.42(19)°}. In this complex the Cd atoms are bridged by thiocyanate anions and produce a one-dimensional coordination polymer (figure 2).

There are π–π stacking interactions [18, 19] between the parallel aromatic rings belonging to adjacent chains as shown in figure 3. The pyridyl and phenyl groups are almost parallel and separated by a distance of about 3.5 Å, close to that of the layers in graphite. Parallel arrays of the planes of the aromatic moieties in this complex indicate

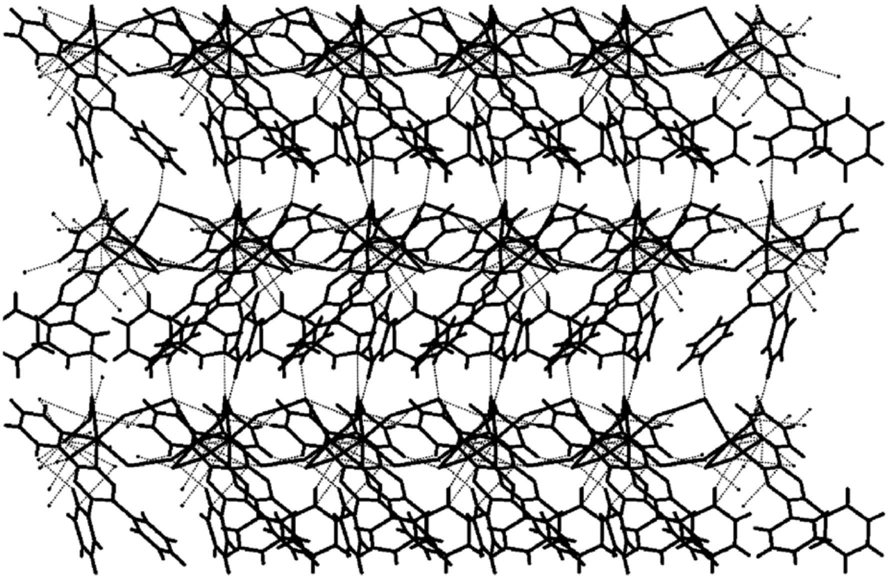

Figure 3. Showing of the C–H $\cdots$ S and C–H $\cdots$ N interactions in the packing of $[Cd(PDPT)(\mu\text{-}SCN)_2]_n$.

that these interactions are of the "face-to-face π-stacking", and "edge-to-edge" types [20, 21]. The interplanar distances for face-to-face and edge-to-edge π-stacking are 3.37 and 3.48 Å, respectively, normal for π–π stacking [22, 23].

A search was also generally made for non-classical C–H $\cdots$ S and C–H $\cdots$ N approaches in this complex and there are both C–H $\cdots$ S and C–H $\cdots$ N interactions, between the hydrogen atoms of ph rings and sulfur and nitrogen atoms of thiocyanate anions belonging to adjacent complexes. In this complex, there are two C–H $\cdots$ S interactions with distances of S $\cdots$ HC(ph) = 2.927–2.947 Å {HC(ph) $\cdots$ S = 3.653–3.655 Å and ∠S $\cdots$ H–C = 136.28–133.89°}. Also there are two C–H $\cdots$ N interactions with distances of N $\cdots$ HC(ph) = 2.609–2.648 Å {HC(ph) $\cdots$ N = 3.400–3.404 Å and ∠N $\cdots$ H–C = 138.85–143.27°}. Consequently, the C–H $\cdots$ S and C–H $\cdots$ N interactions grow the 1D structure into a hybrid two-dimensional network.

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-283536. 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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