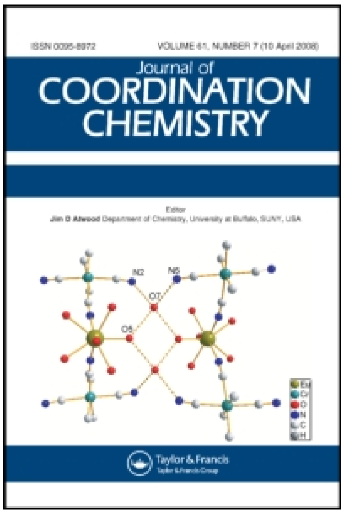

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Spectroscopic, thermal and structural studies of a new mercury(II) one-dimensional coordination polymer, [Hg(3-bpo)$_2$(SCN)$_2$], 3-bpo = 2,5-*bis*(3-pyridyl)-1,3,4-oxadiazole

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A new mercury(II)-organic polymeric complex generated from 2,5-*bis*(3-pyridyl)-1,3,4-oxadiazole (3-bpo) as an angular dipyridyl derivative ligand, [Hg(3-bpo)$_2$(SCN)$_2$], was prepared from reactions of ligand 3-bpo with mercury(II) thiocyanate. The compound was characterized by elemental analysis, IR-, ^{1}H NMR-, ^{13}C NMR-spectroscopy and structurally determined by X-ray single crystal diffraction. The thermal stability of [Hg(3-bpo)$_2$(SCN)$_2$] was studied by thermal gravimetric (TG) and differential thermal analyses (DTA).

Keywords: Mercury(II); 2,5-*bis*(3-pyridyl)-1,3,4-oxadiazole; Crystal structure; Coordination polymer

1. Introduction

Metal-organic frameworks (MOFs) are developed as a new type of functional crystalline material for a wide range of promising applications in separation, storage, exchange, and heterogeneous catalysis due to their high stability and structural diversity [1–3]. Extended systems of a variety of metals have been characterized providing information about supramolecular isomerism. Zn^{2+}, Cd^{2+} and Hg^{2+}, d^{10} metal ions, are particularly suited for construction of coordination polymers and networks. The spherical d^{10} configuration has a flexible coordination environment so that geometries can vary from tetrahedral to octahedral and severe distortions in the ideal polyhedra easily occur. Furthermore, due to the general lability of d^{10} metal ion complexes, the formation of coordination bonds is reversible which enables metal ions and ligands to rearrange during polymerization to give highly ordered network structures.

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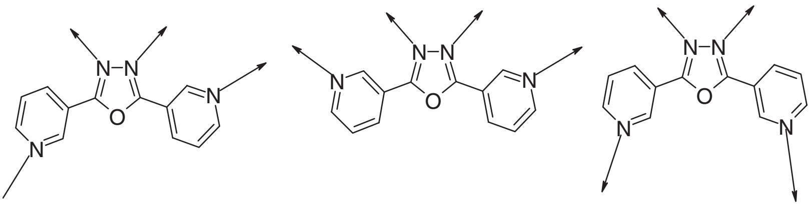

Scheme 1. The general structure of the 2,5-*bis*(3-pyridyl)-1,3,4-oxadiazole (3-bpo) ligand and the possible sites and modes of coordination.

Consequently, Zn, Cd and Hg can readily accommodate different architectures in 1D, 2D and 3D polymers. In contrast to coordination polymers of Zn^{2+} and Cd^{2+} ions, the formation of polymers with Hg^{2+} ion is sparse. Continuing our previous work on Hg^{II} coordination polymers [4–6], we now examine the structural characteristics of the mercury(II) thiocyanate with 2,5-*bis*(3-pyridyl)-1,3,4-oxadiazole (3-bpo) ligand.

The 2,5-*bis*(3-pyridyl)-1,3,4-oxadiazole (3-bpo) ligand, as an angular dipyridyl derivative, is interesting because of the structural chemistry of its multifunctional coordination modes, binding to metal ions from both pyridyl and oxadiazolic nitrogen atoms to form polymeric structures (scheme 1). Oxadiazole-containing ligands binding metal ions simultaneously by $N_{pyridyl}$ and $N_{oxadiazole}$ donors allows access to frameworks of novel topology. Moreover, heteroatoms such as N and O on the (1,3,4)-oxadiazole ring could be considered as potential hydrogen bond acceptors to expand polymeric frameworks with hydrogen bonding interactions [7–13].

2. Experimental

2.1. *Physical measurements*

With the exception of 3-bpo, which was prepared according to the literature procedure [14], all reagents and solvents for the synthesis and analysis were commercially available and used as received. IR spectra were recorded 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. The thermal behavior was measured with PL-STA 1500 apparatus. ^{1}H and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz and all chemical shifts are reported in δ units downfield from Me_4Si. Crystallographic measurements were made at 100(2) K using a Bruker AXS SMART APEX CCD diffractometer. The intensity data were collected using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and orientation matrices were obtained from least-squares refinements using SMART [15] and SAINT [16], and the data were integrated using SAINT [16]. The structures have been solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXTL [17]. All hydrogen atoms were placed geometrically and refined with an isotropic displacement parameter 1.2 times that of the neighboring carbon atom. Crystallographic data and details of the data collection and structure refinement are listed in table 1.

Table 1. Crystal data and structure refinement for $[Hg(3\text{-bpo})_2(SCN)_2]_n$.

Identification code	$[Hg(3\text{-bpo})_2(SCN)_2]_n$
Empirical formula	$C_{26}H_{16}HgN_{10}O_2S_2$
Formula weight	765.20
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	5.7019(6)
b	7.1424(7)
c	16.2794(16)
α	80.694(2)
β	89.951(2)
γ	79.607(2)
Volume (Å^3)	2438.3(6)
Z	1
D_{calcd} (Mg m^{-3})	1.975
Absorption coefficient	6.193
$F(000)$	370
Crystal size (mm^3)	$0.36 \times 0.29 \times 0.24$
θ range for data collection (°)	2.54–28.28
Index ranges	$-7 \leq h \leq 7$ $-9 \leq k \leq 9$ $-21 \leq l \leq 21$
Reflections collected	6668
Independent reflections	3180
Absorption correction	Multi-scan
Max. and min. transmission	0.226 and 0.172
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3180/0/187
Goodness-of-fit on F^2	1.043
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0179$ and $wR_2 = 0.0453$
R indices (all data)	$R_1 = 0.0179$ and $wR_2 = 0.0453$
Largest diff. peak, hole (e Å^{-3})	1.732 and −0.849

The observed anisotropic thermal parameters, the calculated structure factors, and full lists of bond distances, bond angles and torsion angles are given in the supplementary material. X-ray crystal structure and perspective views of the packing are shown in figures 1 and 2.

2.2. *Synthesis of $[Hg(3\text{-bpo})_2(SCN)_2]_n$*

5-*bis*(3-pyridyl)-1,3,4-oxadiazole (3-bpo) (0.5 mmol, 0.112 g) was placed in one arm of the branched tube and mercury(II) thiocyanate (0.159 g, 0.5 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 10 days, white crystals (m.p. = 193°C), deposited in the cooler arm which were filtered off, washed with acetone and ether and air dried (0.121 g, yield 45%). Found: C, 40.40; H, 2.09; N, 18.40%. Calcd for $C_{26}H_{16}HgN_{10}O_2S_2$: C, 40.77; H, 2.09; N, 18.29%. IR (cm^{-1}) selected bonds: $\nu = 704$(s), 827(m), 1057(w), 1275 (m), 1402(m), 1464(m), 1527(m), 1608(w), 2078(vs), 3028(w). ^{1}H NMR ([D$_6$]–DMSO): $\delta = 7.80$ (d, 1H), 8.10 (d, 1H), 8.20 (s, 1H), 8.51 (q, 1H) ppm. ^{13}C{^{1}H} NMR ([D$_6$]–DMSO): $\delta = 121.5$, 125.5, 131.5, 132.5, 151.4 and 163.8.

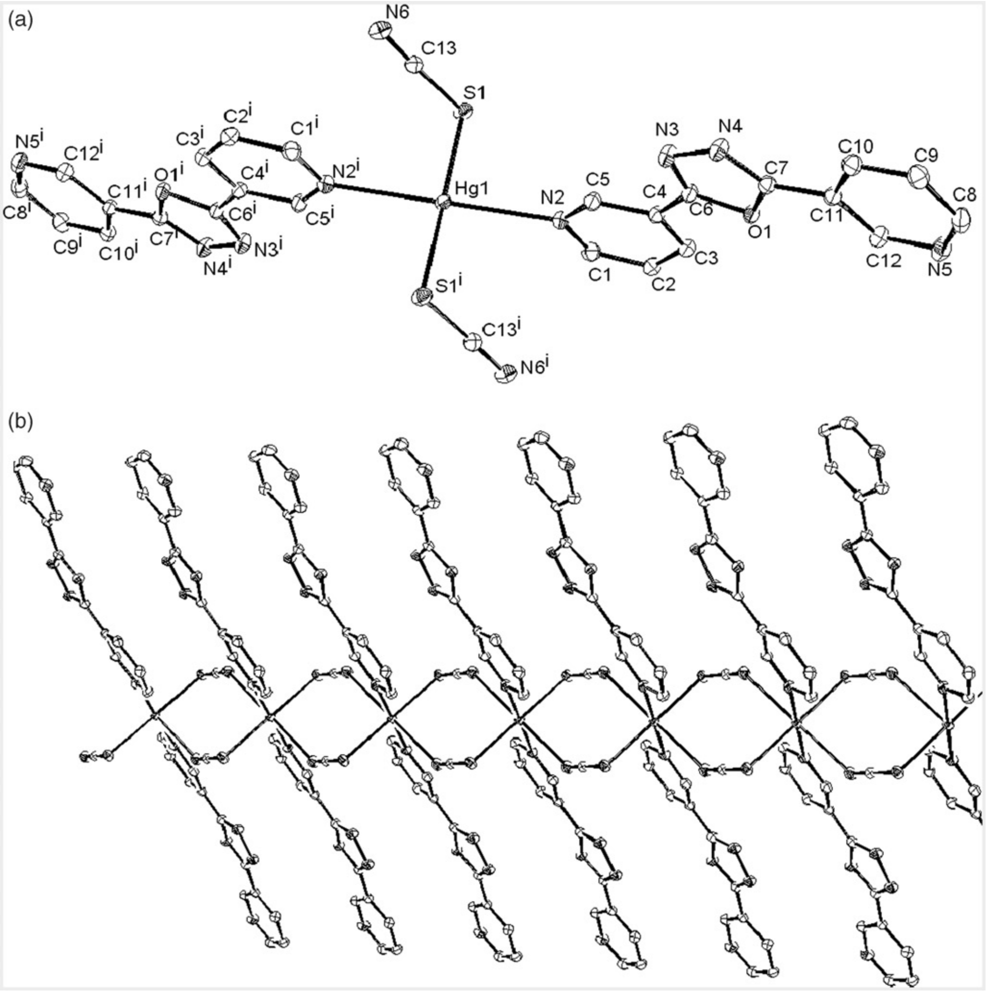

Figure 1. (a) ORTEP diagram of the repeating units in $[Hg(3\text{-bpo})_2(SCN)_2]_n$. Ellipsoids 30% probability, (b) The one-dimensional chain generated from thiocyanate bridging in the $[Hg(3\text{-bpo})_2(SCN)_2]_n$. i: $-x$, $-y+2$, $-z+2$.

3. Results and discussion

Reaction between 3-bpo and mercury(II) thiocyanate provided crystalline materials analyzing as $[Hg(3\text{-bpo})(SCN)_2]_n$. The relatively weak absorption bands around 3025–3035 cm^{-1} in IR spectra are due to the C–H of the aromatic rings. The absorption bands with variable intensity in the frequency range 1404–1600 cm^{-1} correspond to vibrations of the pyridyl and oxadiazole rings. The characteristic band of the thiocyanate anions in $[Hg(3\text{-bpo})(SCN)_2]_n$ are at 2078 cm^{-1}. The ^{1}H-NMR spectrum of the DMSO solution of $[Hg(3\text{-bpo})_2(SCN)_2]$ displays four distinct signals assigned to the aromatic ring protons of pyridyl groups of 3-bpo. The ^{13}C-NMR spectrum (DMSO) of this compound displays six distinct signals assigned to the

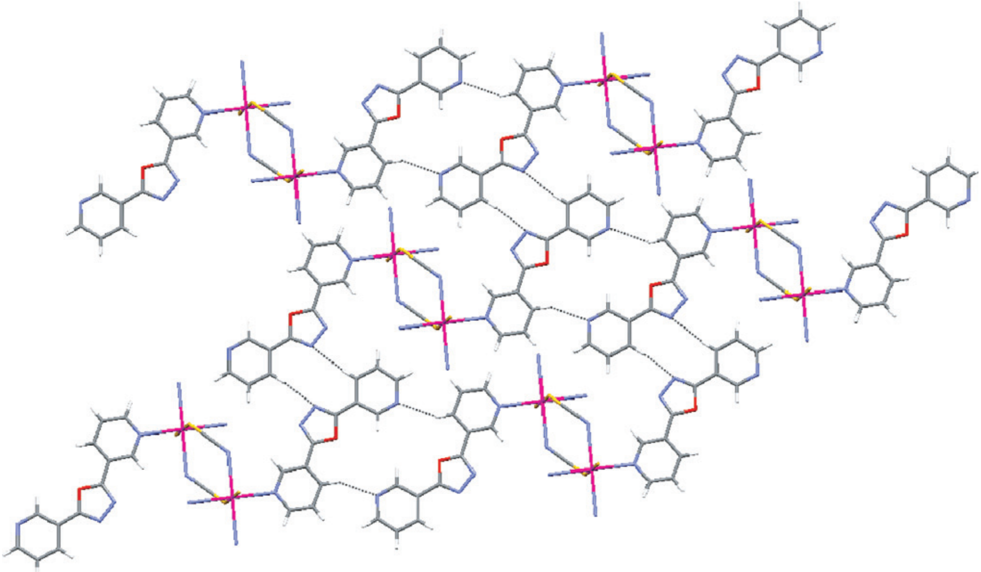

Figure 2. The two-dimensional network and N···HC interactions in $[Hg(3\text{-}bpo)_2(SCN)_2]_n$.

Table 2. Bond lengths [Å] and angles [°] for $[Hg(3\text{-}bpo)_2(SCN)_2]_n$.

Hg(1)–S(1)	2.4515(6)
Hg(1)–S(1)#1	2.4515(6)
Hg(1)–N(2)#1	2.5974(19)
Hg(1)–N(2)	2.5974(19)
N(3)–N(4)	1.403(3)
S(1)–Hg(1)–S(1)#1	180.0
S(1)–Hg(1)–N(2)#1	91.77(5)
S(1)#1–Hg(1)–N(2)#1	88.23(5)
S(1)–Hg(1)–N(2)	88.23(5)
S(1)#1–Hg(1)–N(2)	91.77(5)
N(2)#1–Hg(1)–N(2)	180.00(5)

#1 $-x, -y+2, -z+2$.

aromatic pyridyl and oxadiazole ring carbons of 3-bpo, not significantly different from those of free 3-bpo. The compound may not retain the polymeric structure in DMSO; the NMR data may only be seen as proof of purity with respect to the ligand 3-bpo.

Single crystal X-ray diffraction analysis of $[Hg(3\text{-}bpo)_2(SCN)_2]$ (figure 1) reveals that the mercury(II) ion is coordinated by four thiocyanate anions and two bpo molecules, resulting in a six-coordinate complex, PbN_4S_2 (table 2). Although the coordination geometry around the mercury(II) ion is irregular, presumably associated with the steric constraints arising from the shape of the ligands, it is best described as a distorted octahedron. The S1–Hg1–S2 and N6–Hg1–N5 bonds with SCN^- form the equatorial plane and while the two N atoms of two 3-bpo occupy the axial positions as shown in figure 1b. One nitrogen of 3-bpo is not coordinated to Hg (figure 1b) and the ligand is a less common unidentate ligand [7–13]. The M^{II}–bpo–NCS– system (M^{II}=Co^{II},

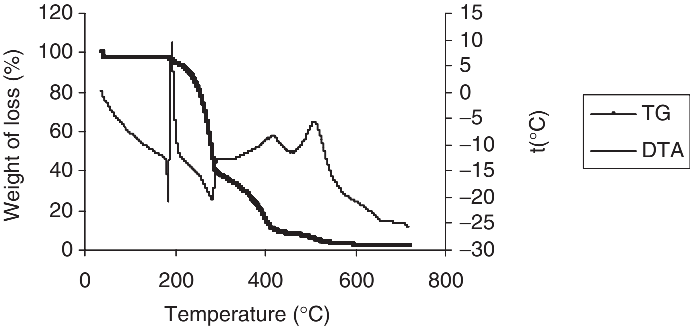

Figure 3. Thermal behavior of $[Hg(3\text{-bpo})_2(SCN)_2]_n$.

Mn^{II}, and Cd^{II}) [18, 19] of general formula $[M(bpo)_2(NCS)_2(H_2O)_2]$ have been reported as monomeric structures (the 3-bpo molecule and NCS^- anion act only as the monodentate terminal ligands) with a hydrogen bonded 3D network.

The structure here may be considered a coordination polymer of mercury(II) consisting of one-dimensional linear chains, running parallel to the *b* axis, with a building block of $[Hg(SCN)_2]$. Two SCN^- anions doubly bridge two mercury(II) ions *via* the N and S atoms. Two Hg–N bond distances in this compound are dissimilar and significantly shorter than found in the reported mercury(II) complexes with thiocyanate. The intrachain $Hg\cdots Hg$ distances within the $[Hg(SCN)_2]_n$ chains are 5.70 Å. The individual polymeric chains are almost parallel to each other and further linked by $N_{oxa}\cdots HC(py)$ and $N_{py}\cdots HC(py)$ interactions (figure 2) with bond distances of $N_{oxa}\cdots HC(py) = 2.46$ Å and $N_{py}\cdots HC(py) = 2.53$ Å, resulting in a two-dimensional framework (figure 2). The coordination polymer obtained from other Hg^{2+} with ligand bpo [12, 13] shows one-dimensional zig-zag motif and in these compounds the Hg^{2+} units connected to each other by bpo through the two pyridyl nitrogens.

In order to examine the thermal stabilities of $[Hg(3\text{-bpo})_2(SCN)_2]$, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 30 and 700°C. The TG curve of $[Hg(3\text{-bpo})_2(SCN)_2]$ indicates that this compound is stable up to 195°C at which temperature it melts. The release of 3-bpo takes place at 220–275°C (observed 59.24%, Calcd 58.54%) with two exothermic events at 205 and 270°C (figure 3). The solid residue formed at 265°C is suggested to be $Hg(SCN)_2$ which is stable up to 285°C and under higher temperature with one exothermic effect at 420°C is decomposed. The solid residue formed at around 410°C is suggested to be HgO that under higher temperature is evaporated.

Supplementary material

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at the Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request quoting deposition number 644399 for $[Hg(3\text{-bpo})_2(SCN)_2]$.

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