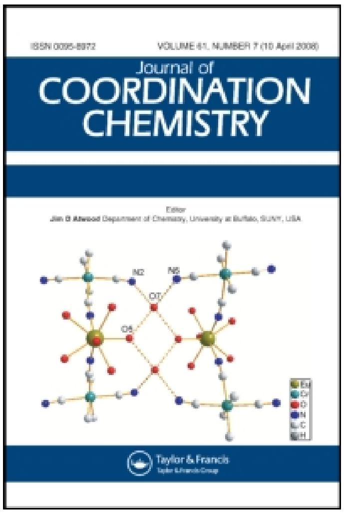

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Syntheses and characterization of three mercury(II) complexes, [Hg(phen)$_2$(SCN)$_2$], [Hg(2,2′-bipy)$_2$(SCN)$_2$] and [Hg(phen)$_2$(NO$_3$)$_2$], thermal and fluorescence studies

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Mercury(II) complexes of 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy), [Hg(phen)$_2$(SCN)$_2$] (**1**), [Hg(2,2′-bipy)$_2$(SCN)$_2$] (**2**) and [Hg(phen)$_2$(NO$_3$)$_2$] (**3**) have been synthesized and characterized by elemental analysis, IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The thermal stability of **1**–**3** were studied by thermal gravimetric (TG) and differential thermal analyses (DTA). The structure of **1** has been confirmed by X-ray crystallography. The complex is a monomer and the Hg atom has an unsymmetrical six-coordinate geometry, formed by four nitrogen atoms of the two phen ligands and two sulfur atoms of the two thiocyanate anions. Solid-state luminescent spectra of phen, 2,2′-bipy and **1**–**3** indicate emission with the maximum intensity at ca 467 nm upon excitation at 295 nm.

Keywords: Mercury(II) complexes; Crystal structure; 10-Phenanthroline; 2,2′-Bipyridine

1. Introduction

The coordination chemistry of mercury(II) with N-donor ligands is of interest due to applications as solid-state materials [1–3]. Hg(II) complexes with bidentate and tridentate ligands have been obtained in which Hg(II) adopts higher coordination numbers such as complexes of 2,2′-bipyridine [4], 1,10-phenanthroline [5], N-substituted pyrazole [6] and tripod ligands containing pyridine and N-methylimidazole [7]. 2,2′-Bipyridine (bipy) and 1,10-phenanthroline (phen) have been widely used in metal complexes [5–8]. Continuing our previous work, we now report the mercury(II) thiocyanate and mercury(II) nitrate complexes with 2,2′-bipyridine and 1,10-phenanthroline (phen), [Hg(phen)$_2$(SCN)$_2$] (**1**), [Hg(2,2′-bipy)$_2$(SCN)$_2$] (**2**) and [Hg(phen)$_2$(NO$_3$)$_2$] (**3**).

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2. Experimental

2.1. *Materials and physical measurements*

Mercury(II) thiocyanate, mercury(II) nitrate, 1,10-phenanthroline and 2,2′-bipyridine were used as received from Aldrich without further purification. IR spectra were obtained from KBr pellets in the range 450–4000 cm^{-1} with 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 and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively. The thermal measurements were performed using a simultaneous TGA-DTA analyzer. The luminescent properties were measured with spectrofluorophotometer, Shimadzu RF-5000.

2.2. *Preparation of [Hg(phen)$_2$(SCN)$_2$] (1)*

1,10-Phenanthroline (0.198 g, 1 mmol) was placed in one arm of a branched tube and Hg(SCN)$_2$ (0.158 g, 0.5 mmol) in the other. Methanol was 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 7 days, crystals deposited in the cooler arm were filtered off, washed with acetone and ether, and air dried. (Found: C, 46.30; H, 2.40; N, 12.60%; Calculated for $C_{26}H_{16}HgN_6S_2$: C, 46.07; H, 2.36; N, 12.40%). IR (cm^{-1}) selected bonds: 625(w), 717(s), 839(s), 1213(m), 1412(s), 1492(s), 1576(m), 2055(vs) and 3025(w). ^{1}H NMR (DMSO; δ): 8.10–8.30 (m, 4H), 8.50–9.00 (m, 2H), 9.20–9.45 (m, 2H). ^{13}C-{^{1}H} NMR (DMSO; δ): 124.30, 127.55, 129.45, 139.30, 144.50, and 149.30.

2.3. *Preparation of [Hg(2,2′-bipy)$_2$(SCN)$_2$] (2) and [Hg(phen)$_2$(NO$_3$)$_2$] (3)*

Complexes **2** and **3** were prepared via the method analogous to that used for **1**.

2.3.1. [Hg(2,2′-bipy)$_2$(SCN)$_2$] (2). Reactant materials: 2,2′-bipy, mercury(II) thiocyanate (2 : 1); white crystals, m.p. = 183–185°C. Yield 0.283 g, 45%. Found: C, 41.50; H, 2.30; N, 13.55; Calculated for $C_{22}H_{16}HgN_6S_2$: C, 41.96; H, 2.54; N, 13.35%. IR (cm^{-1}) selected bands: 760(vs), 1007(m), 1244(w), 1426(s), 1583(s), 2070(vs), and 3070(w). ^{1}H NMR (DMSO; δ): 7.80 (t, 1H), 8.30 (q, 1H), 8.70 (d, 1H), and 7.80 (d, 1H) ppm. ^{13}C-{^{1}H} NMR (DMSO; δ): 117.50, 124.20, 127.60, 149.95, and 150.65 ppm.

2.3.2. [Hg(phen)$_2$(NO$_3$)$_2$] (3). Reactant materials: phen, mercury(II) nitrate, (2 : 1), white crystals, (0.334 g, yield 50%), m.p. 247.5°C. Found: C, 42.30; H, 2.50; N, 12.60; calculated for $C_{24}H_{16}HgN_6O_6$: C, 42.03; H, 2.33; N, 12.25%. IR (cm^{-1}) selected bands: υ = 717(s), 843(s), 1262(m), 1302(s), 1375(vs), 1415(s), 1501(m), and 3055(w). ^{1}H NMR (DMSO): δ = 7.80 (t, 2H), 8.25 (q, 2H), 8.80 (d, 2H), and 7.75 (d, 2H). ^{13}C{^{1}H} NMR (DMSO): δ = 117.50, 124.25, 127.60, 141.60, 149.90, and 150.60.

3. Results and discussion

Reactions between 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) with mercury(II) thiocyanate, as well as between 1,10-phenanthroline (phen) and mercury(II) nitrate, provided crystalline materials analyzing as [Hg(phen)$_2$(SCN)$_2$] (**1**), [Hg(2,2′-bipy)$_2$(SCN)$_2$] (**2**) and [Hg(phen)$_2$(NO$_3$)$_2$] (**3**). The IR spectra of all three complexes show absorption bands resulting from skeletal vibrations of aromatic rings in the 1400–1600 $\mathrm{cm^{-1}}$ range. The IR spectra of **1** and **2** show ν(–CN) of SCN$^-$ at 2055 and 2070 $\mathrm{cm^{-1}}$ respectively, and the IR spectrum of **3** shows ν(NO$_3$) at ca 1380 $\mathrm{cm^{-1}}$. ^{1}H NMR spectrum of the DMSO solution of **1** and **3** displays four signals assigned to protons of aromatic rings of ligand phen and the ^{1}H NMR spectrum of DMSO solution of **2** displays four signals assigned to protons of 2,2′-bipy. The ^{13}C NMR spectra (DMSO) of **1** and **3** display six distinct resonance signals assigned to the aromatic carbons of phen. The ^{13}C NMR spectrum (DMSO) of **1** displays five distinct resonances assigned to 2,2′-bipy.

The structure of **1** was reported [9], but for comparison and thermal and fluorescence studies reported here again. The crystal structure of this compound consists of monomeric units of [Hg(phen)$_2$(SCN)$_2$] (figure 1). Each mercury is chelated by four nitrogen atoms of two 1,10-phenanthroline (phen) ligands and by two sulfur atoms of the thiocyanate anions in distorted octahedral geometry. The structure is closely related to that of [Hg(bipy)$_2$(SCN)](NO$_3$) [10] and [Hg(bipy)(NO$_2$)$_2$] [2]. In [Hg(bipy)$_2$(SCN)](NO$_3$), the structure is also monomeric and the Hg atom has an unsymmetrical five-coordinate geometry with four nitrogen atoms of two bipy ligands and one sulfur atom of the thiocyanate. The [Hg(bipy)(NO$_2$)$_2$] complex is a monomer with an unsymmetrical six-coordinate geometry, formed by two nitrogen atoms of the bipy ligand and four oxygen atoms of the two nitrite anions.

There are some evident similarities in the three mercury(II) complexes. The compounds are packed in layers that are held together by normal van der Waals interactions. Within the layers, the packing of the complexes is characterized by π–π stacking interactions [11–14] between phen and bpy rings of adjacent chains, as shown in figure 2. With the mean molecular planes close to parallel and separated by a distance of ~3.5 Å, this resembles the planes in graphite. The individual monomeric molecules are almost parallel to each other and further linked by N···HC(phen) interactions (figure 2) with bond distances of N···HC(phen) = 2.653 Å, {HC(phen)···N = 3.495 Å and ∠N···H–C = 151.14°}, resulting in a two-dimensional framework.

In order to examine the thermal stabilities of **1**–**3**, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 30 and 700°C. The TG curve of **1** indicates that this compound does not melt and is stable up to 160°C where it begins to decompose with release of two phens between 160–300°C (observed 52.10%, Calcd 53.16%) with one endothermic effect at 285°C (figure 3). The solid residue formed at 300°C is Hg(SCN)$_2$, which is stable up to 315°C; increasing temperature shows two exothermic effects at 360 and 490°C. The TG curve of **2** indicates decomposition and release of two 2,2′-bipys at 192–270°C with two endothermic effects at 196 and 270°C (figure 4). The solid residue formed at 300°C is suggested to be Hg(SCN)$_2$. The TG curve of **3** indicates decomposition takes place at 360–600°C with three exothermic effects at 360, 490 and 595°C (figure 5).

The UV spectra of phen, 2,2′-bipy and **1**–**3** in methanol display intense absorption bands ranging from 220 to 280 nm (figure 6a), indicating that electronic transitions are

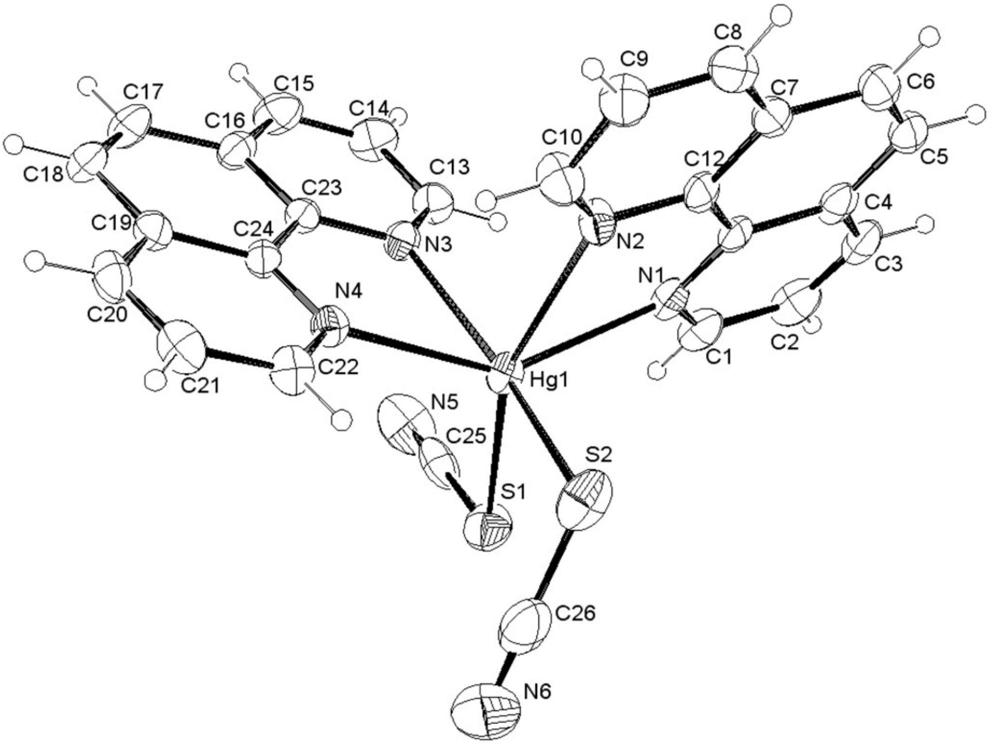

Figure 1. ORTEP diagram of $[Hg(phen)_2(SCN)_2]$ (**1**).

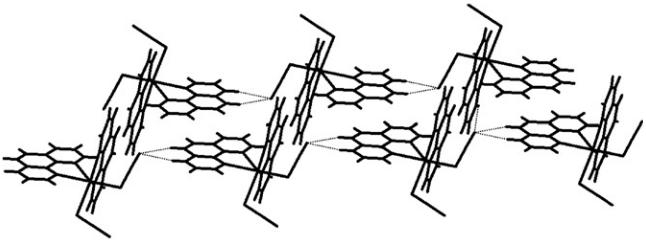

Figure 2. A perspective view of packing down the *a* axis in compound $[Hg(phen)_2(SCN)_2]$ (**1**), showing the N ⋯ HC(phen) interactions.

mostly π to π^*, originating from the pyridyl and phenyl groups of phen and 2,2′-bipy. In the solid state phen, 2,2′-bipy and **1**–**3** have broad fluorescent emission with maximum intensity at ca 467 nm upon excitation at 295 nm (figures 6 and 7); fluorescent intensity of **1** and **3** is weaker and **2** stronger than that of phen and 2,2′-bipy, which can be attributed to the heavy atom effect [15, 16] due to the coordination of the ligand to a heavy Hg(II) center with different counter-ions. The emission maxima of ligands phen,

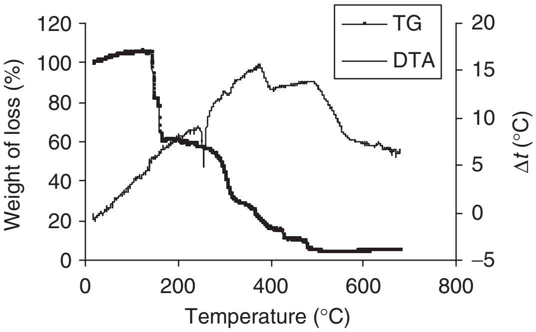

Figure 3. Thermal behavior of [Hg(phen)$_2$(SCN)$_2$] (**1**).

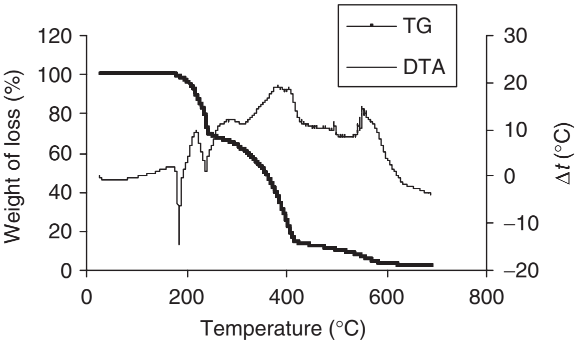

Figure 4. Thermal behavior of [Hg(2,2′-bipy)$_2$(SCN)$_2$] (**2**).

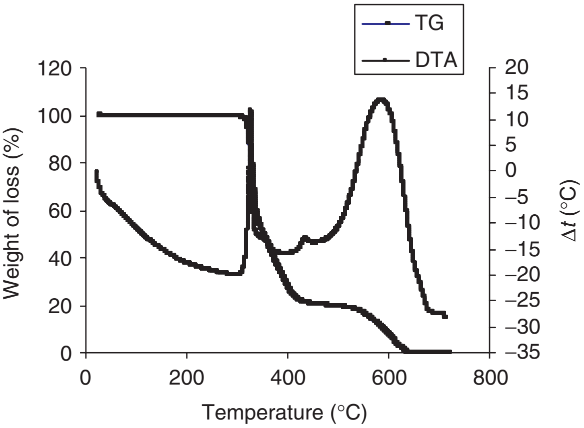

Figure 5. Thermal behavior of [Hg(phen)$_2$(NO$_3$)$_2$] (**3**).

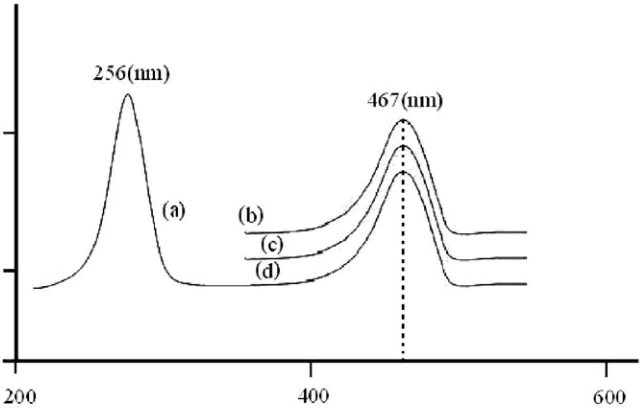

Figure 6. Electronic absorption of phen and compounds **1** and **3** (a), Absorption: $c = 1.36 \times 10^{-4}$ mol L^{-1}, methanol, $d = 1$ cm. Solid state fluorescence spectra for ligand phen (b), compound **1** (c), compound **3** (d). Room temperature, $\lambda_{exc} = 295$ nm.

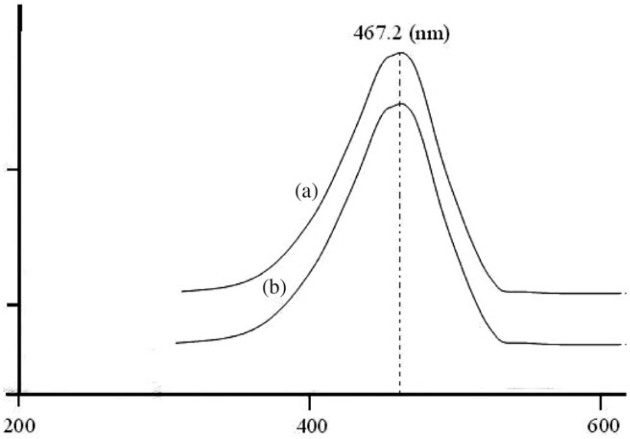

Figure 7. Solid state fluorescence spectra for compound **1** (a), and 2,2′-bipy (b). Room temperature, $\lambda_{exc} = 295$ nm.

2,2′-bipy and **1**–**3** were studied. The UV absorption of phen, 2,2′-bipy and **1**–**3** in the solid state is in the blue region and the emission bands cover much of the blue region, giving the observed blue luminescence. Thus, **1**–**3** have potential applications as luminescent materials in organic light-emitting devices.

Supplementary material

Crystallographic data for the structure reported in the article has been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-623684 for **1**. 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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