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# Hg(II) complexes of 4-phenyl-5-(3-pyridyl)-1,2,4-triazole-3-thione and 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione and a Ni(II) complex of 5-(thiophen-2-yl)-1,3,4-oxadiazole-2-thione: Synthesis and X-ray structural studies

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ABSTRACT

Three new mixed ligand complexes, $[Hg(en)(4\text{-pptt})_2]$ (**2**) {4-pptt = 4-phenyl-5(3-pyridyl)-1,2,4-triazole-3-thione}, $[Hg(en)(4\text{-pot})_2]$ (**3**) {4-pot = 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione} and $[Ni(en)_2(5\text{-thot})_2]$ (**4**) {5-thot = 5-(thiophen-2-yl)-1,3,4-oxadiazole-2-thione}, have been prepared containing en as a co-ligand. It is observed that 5-(pyridine-4-carbonyl) hydrazine carbodithioic acid methyl ester undergoes cyclization during complexation with Hg(II) in the presence of ethylenediamine and formed complex **3** containing 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione. The metal complexes have been characterized with the aid of elemental analyses, IR, magnetic susceptibility and single crystal X-ray studies. The ligand 4-pptt (**1**) and complexes **2**, **3** and **4** crystallize in the monoclinic system, space group *P*21/*n*, *P*21/*c*, *P*121/*c*1 and *P*21/*n* respectively. The ligand is present in the deprotonated thiol form in complexes **2** and **3**, and is bonded covalently through sulfur, while in complex **4** the ligand 5-(thiophen-2-yl)-1,3,4-oxadiazole-2-thione is present as the thione form and is bonded to Ni(II) through the oxadiazole nitrogen. Complex **4** shows quasi-reversible redox behavior assignable to a $Ni^{2+}/Ni^{3+}$ one electron transfer. The photoluminescence properties indicate that the complexes are fluorescent materials with maximum emissions at 433, 376 and 465 nm for complexes **2**, **3** and **4** at excitation wavelengths of 293, 273 and 327 nm, respectively. All the complexes contain extended hydrogen bonding that provides a supramolecular framework.

## 1. Introduction

The coordination chemistry of nitrogen–sulfur containing heterocyclic ligands, such as 1,2,4-triazoles, 1,3,4-oxadiazoles and 1,3,4-thiadiazoles, is an emerging and rapidly developing area of research [1–3]. These compounds have received much attention on account of their important pharmacological activities, such as antiviral, analgesic, antimicrobial, antidepressant and antifungal effects [4]. Triazole derivatives have been used as starting materials to synthesize a variety of compounds and also as ligands to obtain metal complexes with specific properties [5]. It has been reported that the thione form of 1,2,4-triazole-3-thiones and 1,3,4-oxadiazole-2-thiones are important for their antifungal activity [6,7]. 1,2,4-Triazoles and their derivatives have received much interest because of the fact that (1) a number of functionalized triazoles are readily accessible, (2) they have heterocyclic π-conjugated systems with good coordination abilities to metal centers and own the capability to exhibit luminescence or other properties, (3) they show a variety of bridging modes with extra potential donor sites provided by the functional groups substituted on the triazole rings and (4) they contain nitrogen atoms as hydrogen bond acceptors and aromatic systems which contribute to π–π stacking, leading to secondary non-covalent interactions in metal–triazole complexes [8]. 1,2,4-Triazole-3-thiones are known to act as bridging ligands in complexes of Cu(II), Fe(II), Pt(II) and Ru(II) through their nitrogen and sulfur sites, forming coordination compounds that are interesting from both magnetic and chemical aspects [9]. 1,3,4-Oxadiazole derivatives, which belong to an important group of heterocyclic compounds, have been the subject of extensive study in recent years [10]. The oxadiazole molecules act as spacers *via* coordination and hydrogen bonding, and show intermolecular cooperative interactions [11]. Although some work has been reported on the binary complexes of 1,3,4-oxadiazole-2-thiones and 1,2,4-triazole-3-thiones [9(b,g),12], little is known about the mixed ligand complexes of these ligands. In view of this, we have synthesized and characterized Hg(II) complexes of the versatile ligands 4-phenyl-5-(3-pyridyl)-1,2,4-triazole-3-thione (Hpptt) and 5-(4-pyridyl)-1,3,4-oxadiazole-2-thiol (Hpot) and a

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Ni(II) complex of 5-(thiophen-2-yl)-1,3,4-oxadiazole-thione (Hthot), containing ethylenediamine as a co-ligand.

## 2. Experimental

### 2.1. Materials and methods

Commercial reagents were used without further purification and all experiments were carried out in the open atmosphere. Ethyl nicotinate, ethyl 2-thiophene carboxylate, isonicotinic acid hydrazide, phenyl isothiocyanate (Sigma–Aldrich), $CS_2$ (SD Fine Chemicals, India) and KOH (Qualigens) were used as received. $[Ni(en)_2(SCN)_2]$ was prepared by the reported method [13]. All the solvents were purchased from Merck and used after purification. The yield calculation is based on the weight of the ligand or the initial starting material where intermediates were not isolated. Carbon, hydrogen and nitrogen contents were estimated on a Carlo Erba 1108 model microanalyser. Magnetic susceptibility measurement was performed at room temperature on a Cahn Faraday balance using $Hg[Co(NCS)_4]$ as the calibrant. Electronic spectra were recorded on a Shimadzu 1700 UV–Vis spectrophotometer in DMSO. IR spectra were recorded in the 4000–400 $cm^{-1}$ region as KBr pellets on a Varian Excalibur 3100-FT IR spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were recorded in DMSO-$d_6$ and $CDCl_3$ on a JEOL AL 300 FT NMR spectrometer using TMS as an internal reference. The fluorescence spectra were measured at room temperature with a Varian CARYECLIPSE spectrophotometer in DMSO. The electrochemical experiments were performed with a BAS CV-50W voltammetric analyzer (Bioanalytical System, West Lafayette, USA), using a three-electrode system with a Pyrolytic Glass electrode as the working electrode, a platinum wire as the counter electrode and Ag/AgCl was used as the reference electrode.

### 2.2. Synthesis

#### 2.2.1. Synthesis of 4-phenyl-5-(pyridin-3-yl)-2H-1,2,4-triazole-3-thione (Hpptt) (**1**)

To a suspension of finely powdered nicotinic acid hydrazide (2.74 g, 20 mmol) in benzene was added phenyl isothiocyanate dropwise (2.4 mL, 20 mmol) and the mixture was then refluxed for 8 h at 80 °C. The solid 1-nicotinoyl-4-phenyl thiosemicarbazide obtained upon cooling was filtered off, washed with water and diethyl ether, and dried. 1-Nicotinoyl-4-phenyl thiosemicarbazide (2.72 g, 10 mmol) was added to the ethanol solution of NaOH (0.5 g, 12 mmol) and refluxed for 6 h. After cooling, the resulting clear solution was acidified with dil. HCl and the obtained precipitate was filtered off, washed with water and air dried. The solid was dissolved in ethanol and suitable crystals of **1** were obtained from this solution after 12 days [14]. Yield (1.12 g, 60%). M.p. 190 °C; *Anal.* Calc. for $C_{13}H_{10}N_4S$ (254.31): C, 61.40; H, 3.96; N, 22.03; S, 12.60. Found: C, 61.43; H, 4.01; N, 21.98; S, 12.58%. IR (KBr, $\nu$, $cm^{-1}$): 3219 $\nu$(NH), 1613 $\nu$(C=N), 950 $\nu$(C=S), 740 (pyridine ring), 686 (phenyl ring). $^1H$ NMR (DMSO-$d_6$, $\delta$, ppm): 7.25 (2H), 7.15 (1H), 7.13 (2H) (phenyl ring); 8.35 (1H), 8.34 (1H), 7.47 (1H) (pyridine ring); 8.37 (1H, NH). $^{13}C$ NMR (DMSO-$d_6$, $\delta$, ppm): 150.56, 150.45 (C5, C7), 121.04, 118.63 (C4, C6), 140.27 (C3) (pyridine ring); 138.40 (C8), 117.28 (C11), 121.55 (C9, C13), 122.18 (C10, C12) (phenyl ring); 201.05 (C1), 160.46 (C2) (triazole ring). UV–Vis. [DMSO, $\lambda_{max}$, nm]: 287.

#### 2.2.2. Synthesis of N′-(pyridine-4-carbonyl) hydrazine carbodithioic acid methyl ester (4-pchcdme)

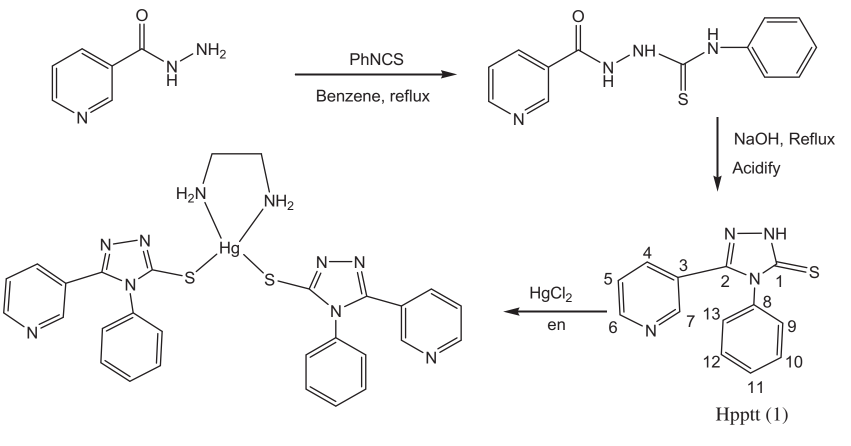
The preparation and characterization of *N*′-(pyridine-4-carbonyl) hydrazine carbodithioic acid methyl ester (4-pchcdme) is described elsewhere [15].

#### 2.2.3. Synthesis of potassium N′-(thiophene-2-carbonyl) hydrazine carbodithioate [K($H_2$tchcd)]

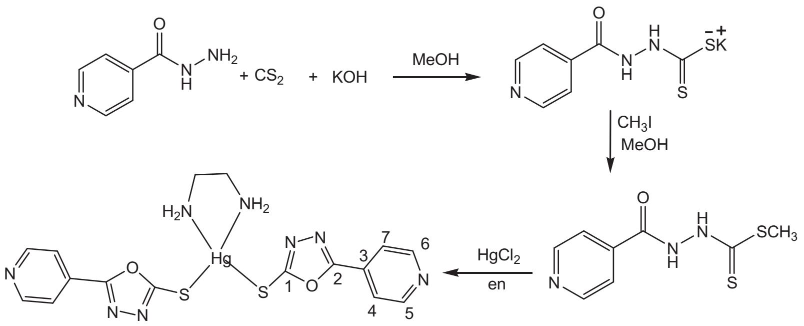
Potassium *N*′-(thiophene-2-carbonyl) hydrazine carbodithioate [K($H_2$tchcd)] was prepared by the dropwise addition of $CS_2$ (1.2 mL, 20 mmol) to a solution of thiophene 2-carboxylic acid hydrazide (2.84 g, 20 mmol) in methanol (30 mL) in the presence of KOH (1.2 g, 20 mmol), stirring the reaction mixture for 30 min. The solid which separated was filtered off, washed with 10% (v/v) mixture of ethanol–ether and dried. Yield (1.54 g, 85%). M.p. 220 °C; *Anal.* Calc. for $C_7H_6N_3OS_2K$ (257.00): C, 28.01; H, 1.94; N, 10.89; S, 37.35. Found: C, 28.02; H, 1.95; N, 10.90; S, 37.34%. IR (KBr, $\nu$, $cm^{-1}$): 3213s, 3140s $\nu$(NH), 1666s $\nu$(C=O), 1062s $\nu$(N–N), 985s $\nu$(C=S). $^1H$ NMR (DMSO-$d_6$, $\delta$, ppm): 11.74, 10.42 (s, 2H, NH), 7.92-7.14 (m, 3H, aromatic ring). $^{13}C$ NMR (DMSO-$d_6$, $\delta$, ppm): 178.50 (>C=S), 157.19 (>C=O), 128.40 (C3), 127.68 (C4), 125.97 (C5), 129.18 (C6).

#### 2.2.4. Synthesis of [Hg(en)(pptt)$_2$] (**2**)

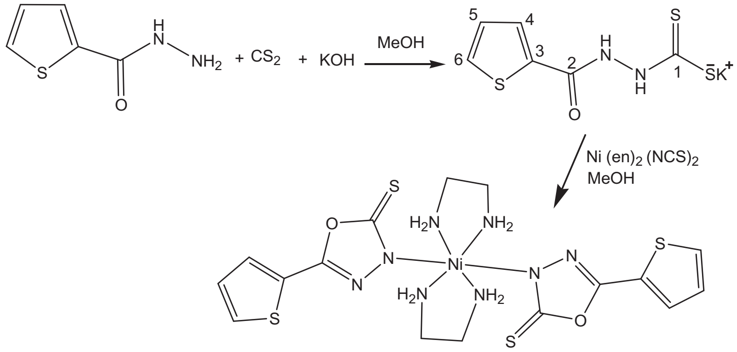
A methanol solution (20 mL) of $HgCl_2$ (0.235 g, 1 mmol) was stirred with a methanol solution (20 mL) of Hpptt (0.5 g, 2 mmol). The resulting white precipitate was filtered off, washed with methanol and then suspended in methanol, to which an excess (0.30 mL, 5 mmol) of ethylenediamine was added and stirred until total dissolution of the precipitate was observed. The resulting solution was filtered off and kept for crystallization. White crystals of **2** suitable for X-ray analysis were obtained by slow evaporation of the solution over a period of 10 days. Yield (0.78 g, 52%). M.p. 280 °C; *Anal.* Calc. for $C_{28}H_{30}HgN_{10}S_2$ (771.35): C, 43.55; H, 3.88;



**Scheme 1.** Preparation of the ligand Hpptt (**1**) and its complex [Hg(en)(4-pptt)$_2$] (**2**).



**Scheme 2.** Preparation of $[Hg(en)(4\text{-pot})_2]$ (**3**).



**Scheme 3.** Preparation of $[Ni(en)_2(5\text{-thot})_2]$ (**4**).

N, 18.15; S, 8.29. Found: C, 43.53; H, 3.86; N, 18.14; S, 8.28%. IR (KBr, $\nu$, $cm^{-1}$): 3229 $\nu$(NH) (en), 1600 $\nu$(C=N); 835 $\nu$(C–S); 772 (py. ring), 698 (phenyl ring). $^1H$ NMR (DMSO-$d_6$, $\delta$, ppm): 6.59–7.51 (m, 5H) (phenyl ring); 8.45 (1H), 7.61 (1H), 7.58 (1H) (pyridine ring); 2.72 (4H, $NH_2$) 2.40 (4H, $CH_2$). $^{13}C$ NMR (DMSO-$d_6$, $\delta$, ppm): 150.56, 150.45 (C5, C7), 121.04, 118.63 (C4, C6), 140.27 (C3) (pyridine); 135.35 (C8), 117.28 (C11), 128.12 (C9, C13), 129.57 (C10, C12) (phenyl); 56.41 ($CH_2$); 154.76 (C=N); 183.77 (C=S) (triazole ring). UV–Vis. [DMSO, $\lambda_{max}$, nm; $\varepsilon_{max}$, $M^{-1}$ $cm^{-1}$]: 293 (9000) (Scheme 1).

### *2.2.5. Synthesis of [Hg(en)(4-pot)₂] (3)*

$HgCl_2$ (0.270 g, 1 mmol) and freshly prepared *N′*-(pyridine-4-carbonyl) hydrazine carbodithioic acid methyl ester (0.454 g, 2 mmol) were dissolved separately in 15–20 mL methanol, mixed together and stirred for 20 min. The yellow precipitate was separated by filtration, washed successively with methanol–water mixture (50:50) and finally with methanol. A methanol solution (10 mL) of ethylenediamine (0.15 mL, 2 mmol) was added to the methanol suspension of the above compound and stirred for 1 h. A clear solution was obtained which was filtered and kept for crystallization. White crystals of **3** suitable for an X-ray analyses were obtained by slow evaporation of the above solution over a period of 10 days. Yield: (0.74 g, 55%). M.p. 260 °C; *Anal.* Calc. for $C_{16}H_{16}N_8HgO_2S_2$ (617.08): C, 31.10; H, 2.59; N, 18.14; S, 10.37. Found: C, 31.11; H, 2.58; N, 18.15; S, 10.36%. IR (KBr, $\nu$, $cm^{-1}$): 3232s $\nu$(NH), 1606s $\nu$(C=N), 1214s $\nu$(C–O–C), 1080s $\nu$(N–N), 824 $\nu$(C–S), 485 $\nu$(Hg–S). $^1H$ NMR (DMSO-$d_6$, $\delta$, ppm): 8.74 (d, 2H), 7.79 (d, 2H) pyridine ring, 2.72 (s, 4H, $NH_2$), 2.33 (s, 4H, $CH_2$). $^{13}C$ NMR (DMSO-$d_6$, $\delta$, ppm): $\delta$ 178.50 (C=S), 156.05 (C=N), 128.40 (C3), 127.68 (C5, C6), 119.31 (C4, C7), 47.64 (C1, C2). UV–Vis. [DMSO, $\lambda_{max}$, nm ($\varepsilon_{max}$, $M^{-1}$ $cm^{-1}$)]: 273 (34000) (Scheme 2).

### *2.2.6. Synthesis of [Ni(5-thot)₂(en)₂] (4)*

A methanolic solution (10 mL) of $[Ni(en)_2(NCS)_2]$ (0.237 g, 1 mmol) was mixed with an aqueous–methanol solution (50:50 v/v) (10 mL) of potassium *N′*-(thiophene-2-carbonyl) hydrazine carbodithioate $[K^+(H_2tchcd)^-]$ (0.514 g, 2 mmol) and the reaction mixture was filtered. The filtrate was kept for crystallization, whereupon red crystals of complex **4** were obtained after 10 days. Yield (0.63 g, 60%). M.p. 250 °C; *Anal.* Calc. for $C_{16}H_{22}N_8O_2S_4Ni$ (545.37): C, 35.20; H, 4.04; N, 20.54; S, 23.47. Found: C, 35.21; H, 4.03; N, 20.53; S, 23.46%. IR (KBr, $\nu$, $cm^{-1}$): 3231s $\nu$(NH), 1593s $\nu$(C=N), 1088s $\nu$(N–N), 962 $\nu$(C=S), 518s $\nu$(Ni–N). UV–Vis. [DMSO, $\lambda_{max}$, nm ($\varepsilon_{max}$, $M^{-1}$ $cm^{-1}$)]: 327 (40000), 361 (36000), 526 (102), 793 (55) (Scheme 3).

## 3. X-ray crystallography

Data for compounds **1** and **2** were recorded at 296(2) K and those of **3** and **4** were obtained at 295(2) K on a Bruker three-circle diffractometer/Oxford Diffraction Gemini diffractometer equipped with SMART 6000/CCD CrysAlis Pro software using a graphite monochromated Mo Kα ($\lambda$ = 0.71073 Å) radiation source. The structures were solved by direct methods and refined (SHELX-08) against all data by full matrix least-square on $F^2$ using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were included in the refinement at geometrically ideal positions and refined with a riding model [16]. The MERCURY package was used for the molecular graphics [17]. Molecular structure diagrams were generated using the ORTEP-3 for Windows program [18].

## 4. Results and discussion

It has been observed that 5-(3-pyridyl)-1,2,4-triazole-3-thione and 5-(pyridine-4-carbonyl) hydrazine carbodithioic acid methyl ester react with $HgCl_2$ and then with ethylenediamine to form four coordinate tetrahedral Hg(II) complexes (**2** and **3**) containing en as a co-ligand. The potassium N-(thiophene-2-carbonyl) hydrazine carbodithioate reacts with $[Ni(en)_2(NCS)_2]$ to form the six coordinate octahedral Ni(II) complex **4**. The elemental analyses and physical measurements of complexes **3** and **4** indicate that both hydrazinic hydrogens from the acylhydrazine carbodithioate $[–C(O)NHNHC(S)S^{-}–]$ moiety and one sulfur atom were missing from the resulting complexes. Complexes **2** and **3** were obtained by shaking $[Hg(L)_2]$ (L = 5-(3-pyridyl)-1,2,4-triazole-3-thione/5-(4-pyridyl)-1,3,4-oxadiazole-2-thione) with a methanol solution of ethylenediamine taken in a 1:2 molar ratio, whereas complex **4** was obtained by the reaction of potassium *N′*-(thiophene-2-carbonyl)] hydrazine carbodithioate $[K^{+}(H_2tchcd)^{-}]$ with $[Ni(en)_2(NCS)_2]$. Schemes 1–3 depict the synthesis of the ligands and their Hg(II) and Ni(II) complexes. The complexes are stable towards air and moisture for several days. Complexes **2**, **3** and **4** are insoluble in ethanol, methanol and chloroform, but are soluble in DMSO, and melt at 280, 260 and 250 °C, respectively. The complexes were fully characterized by magnetic susceptibility measurements, IR, UV–Vis and X-ray spectroscopies. The analytical data of the complexes corroborate well with their respective formulations.

### 4.1. IR spectra

The IR spectrum of the free ligand 5-(3-pyridyl)-1,2,4-triazole-3-thione (Hpptt) in the thione form is expected to give rise to characteristic bands due to $\nu$(NH), $\nu$(C=N) and $\nu$(C=S), which occur at 3219, 1613 and 950 $cm^{-1}$, respectively. The bands at 740 and 686 $cm^{-1}$ are due to the pyridine and phenyl rings, respectively. The IR spectrum of the ligand potassium *N′*-(thiophene-2-carbonyl) hydrazine carbodithioate $[K(H_2tchcd)]$ shows absorptions due to the stretching modes of NH (3213 (m) and 3140 (m) $cm^{-1}$), C=O (1666 $cm^{-1}$), N–N (1062 $cm^{-1}$) and C=S (985 $cm^{-1}$). The IR spectra of complexes **2** and **3** show no bands due to $\nu$(NH), indicating conversion of the thione form to the thiol form of triazole/oxadiazole upon complexation. A negative shift of about 110 $cm^{-1}$ in $\nu$(C–S) shows that the thiol sulfur is participating in bonding in complexes **2** and **3**. The IR spectra of complexes **2**, **3** and **4** show bands around 3230 $cm^{-1}$ due to the N–H stretching vibrations of ethylenediamine. In $[Ni(en)_2(5\text{-thot})_2]$, $\nu$(C=S) shows a small negative shift indicating that the thione sulfur does not participate in bonding, but this shift can be attributed to the involvement of sulfur in hydrogen bonding with the $NH_2$ hydrogens of ethylenediamine [19].

### 4.2. $^{1}H$ and $^{13}C$ NMR spectra

The $^{1}H$ NMR spectrum of Hpptt shows a signal at 8.37 ppm due to the triazole NH proton. The protons of the phenyl ring appear as multiplets between 7.86 and 7.36 ppm, and of the pyridine ring between 8.35 and 7.47 ppm. The signals at 201.05 and 160.46 ppm in the $^{13}C$ NMR spectrum are attributed to the >C=S and >C=N carbons, respectively. The $^{1}H$ NMR spectrum of $[Hg(en)(4\text{-pptt})_2]$ (**2**) exhibits two signals at $\delta$ 2.72 and 2.40 ppm for the $CH_2$ and $NH_2$ protons of ethylenediamine along with a slight downfield shift for the aromatic protons. The disappearance of the triazole NH proton at 8.37 ppm shows conversion of the thione form of the ligand to the thiol form, and subsequent bonding of the thiol sulfur with Hg(II) in complex **2**. The $^{13}C$ NMR spectrum of **2** shows various signals for the carbon atoms, of which the signals at $\delta$ 183.77 and 154.8 ppm are due to the >C–S and >C–N carbons, respectively. The $^{1}H$ NMR spectrum of 5-(pyridine-4-carbonyl) hydrazine carbodithioic acid methyl ester exhibits two signals at $\delta$ 11.75 and 11.55 ppm for the amide and thioamide protons, respectively, and one signal at 2.0 ppm due to the methyl protons. The $^{13}C$ NMR spectrum of the ester shows six signals for six carbon atoms, of which the signals at $\delta$ 204.11 and 164.04 ppm are due to the >C=S and >C=O, carbons, respectively. The signal for the $CH_3$ carbon is observed at $\delta$ 16.92 ppm in the ester, which is absent in complex **3** showing the absence of the methyl group in complex **3**. The absence of both the hydrazinic protons and the methyl group for complex **3** suggests cyclization of the S-methyl hydrazine carbodithioate moiety to 5-(4-pyridyl)-1,3,4-oxadiazole-2-thiol during formation of the complex. Complexes **2** and **3** show NCS carbon signals at 183.77 and 178.50 ppm respectively, indicating metal sulfur bonding. The $^{1}H$ NMR spectrum of *N′*-(thiophene-2-carbonyl) hydrazine carbodithioate $K(H_2tchcd)$ exhibits two signals at $\delta$ 11.74 and 11.42 ppm for the amide and thioamide protons. The three protons of the thiophene ring appear as a multiplet between $\delta$ 7.92 and 7.14 ppm. The $^{13}C$ NMR spectra of $[K(H_2tchcd)$ shows six signals for six carbon atoms, of which the signals at $\delta$ 178.50 and 157.50 ppm are due to the >C=S and >C=O carbons, respectively. The thiophene ring carbons appear at C3:128.40, C4:127.68, C5:125.97 and C6:129.18 ppm.

## 5. Magnetic moment and electronic absorption

The $[Hg(en)(4\text{-pptt})_2]$ and $[Hg(en)(4\text{-pot})_2]$ complexes are diamagnetic and show absorptions in the high energy region due to intraligand/charge transfer transitions. $[Ni(en)_2(5\text{-thot})_2]$ shows a

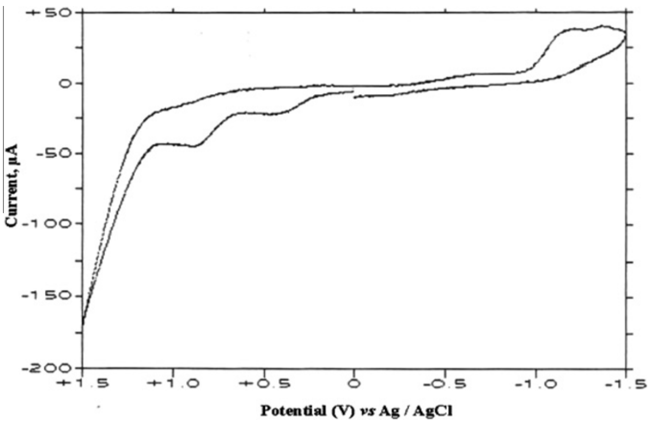


**Fig. 1.** Cyclic voltammogram of $[Ni(en)_2(5\text{-thot})_2]$ in DMSO at PGE using 0.2 M KCl as the supporting electrolyte.

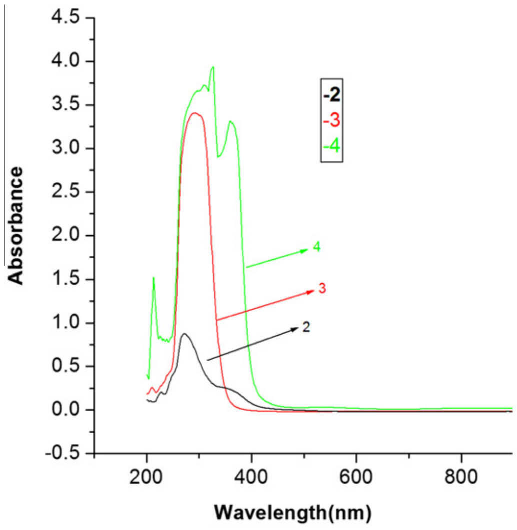


**Fig. 2.** UV–Vis excitation spectra of **2**, **3** and **4**.

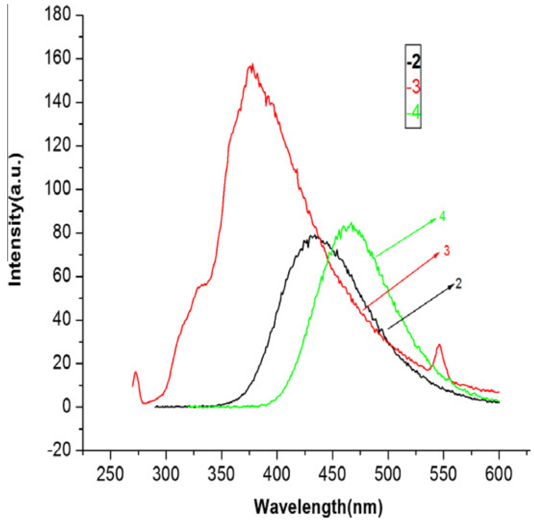


**Fig. 3.** Photoluminescence emission spectra of **2**, **3** and **4**.

magnetic moment of 2.83 BM and exhibits two d–d bands at 793 and 526 nm assigned to the $^3A_2g \rightarrow {}^3T_2g(F)$ ($\nu_1$) and $^3T_1g(F)$ ($\nu_2$) transitions, respectively, in the distorted octahedral geometry of complex **4**. The other two high energy bands may be assigned to intraligand/charge transfer transition [20].

## 6. Electrochemical studies

The cyclic voltammogram of complex **4** (Fig. 1) obtained at a Pyrolytic Graphite Electrode (PGE) in DMSO medium using 0.2 M KCl as the supporting electrolyte in the potential range +1.5 V to −1.5 V with a scan rate 50 mV s$^{-1}$ exhibits a cathodic peak at $E_{pc}$ = 0.891 V and the associated anodic peak at $E_{pa}$ = 1.192 V with respect to the Ag/AgCl reference. The separation between the cathodic and anodic peak potentials ($\Delta E_p = E_{pa} - E_{pc}$) of 0.301 V and the $E_{1/2}$ value [$(E_{pa} + E_{pc})/2$] of 1.041 V indicate a quasi-reversible redox process assignable to Ni(II)/Ni(III). However, it is to be noted that the peak separation ($\Delta E_p = E_{pa} - E_{pc}$) is quite large as compared to that expected for a one electron process and hence it can be concluded that this quasi-reversible redox process is a coupled chemical reaction to the electrochemical change. The voltammogram also exhibits an additional ill defined oxidation peak at 1.375 V and a well defined reduction peak at 0.414 V.

### *6.1. Photoluminescent properties*

The photoluminescent properties of complexes **2**, **3**, **4** and the Hpptt ligand were examined in the solution state at room temperature (30 °C). The ligand (Hpptt) displays a photoluminescent emission at 433 nm upon excitation at 287 nm. The main chromosphere of the ligand is the aromatic five-membered triazole ring and its conjugation degree is further enhanced by the electron-donating thiol group and the phenyl ring. The photoluminescence of the Hpptt ligand has been assigned as originating from intraligand (IL) $\pi$–$\pi^*$ transitions. The complexes **2**, **3** and **4** exhibit weak luminescence properties. In complexes **2** and **4** excitation at 293 and 327 nm at room temperature result in emissions at 435 and 465 nm, respectively (Figs. 2 and 3). Complex **3** exhibits a fluorescent property, the emission maximum being observed at 376 nm upon excitation at 273 nm due to a ligand transition. The photoluminescent quantum yields for complexes **2**, **3** and **4** measured in DMSO versus anthracene were found to be 0.60%, 0.34% and 0.33%, respectively. The origin of the emission bands for complexes **2** and **4** may be mainly ascribed to an intraligand emission state [21]. The violet-blue emission of complex **2** and blue emission of complex **4** in the solution state imply that these complexes may be potentially applicable as materials for light emitting diode devices.

### *6.2. Crystal structure descriptions*

The molecular structures of compounds **1**, **2**, **3** and **4** were determined by single crystal X-ray diffraction. The details of data

**Table 1**
Crystallographic data and structure refinement for **1**, **2**, **3** and **4**.

| Compound | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Empirical formula | $C_{13}H_{10}NS$ | $C_{28}H_{26}HgN_{10}S_2$ | $C_{16}H_{16}HgN_8O_2S_2$ | $C_{16}H_{22}N_8NiO_2S_4$ |
| Formula weight | 254.32 | 767.32 | 617.08 | 545.37 |
| *T* (K) | 296(2) | 293(2) | 295(2) | 295(2) |
| $\Lambda$ (Mo Kα) (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | *P*21/*n* | *P*21/*c* | *P*121/*c*1 | *P*21/*n* |
| *a* (Å) | 6.0573(4) | 13.638(9) | 12.9479(11) | 11.9679(4) |
| *b* (Å) | 18.3976(13) | 9.066(6) | 14.1593(9) | 8.8841(3) |
| *c* (Å) | 11.4326(8) | 23.664(17) | 11.5205(9) | 12.0806(4) |
| $\beta$ (°) | 105.021(4) | 96.624(6) | 110.924(10) | 113.588(4) |
| *V* (Å$^3$) | 1230.51(15) | 2906(3) | 1972.8(3) | 1177.14(7) |
| *Z* | 4 | 4 | 4 | 2 |
| $D_{calc}$ (mg m$^{-3}$) | 1.373 | 1.754 | 1.487 | 1.539 |
| $\mu$ (mm$^{-1}$) | 0.249 | 5.477 | 8.045 | 1.209 |
| *F*(000) | 528.0 | 1504 | 1184 | 564 |
| $\theta$ range (°) | 2.15–28.80 | 3.29–29.19 | 5.12–25.50 | 5.00–32.68 |
| Index ranges | $-8 \leqslant h \leqslant 8$ | $-17 \leqslant h \leqslant 18$ | $-15 \leqslant h \leqslant 15$ | $-14 \leqslant h \leqslant 17$ |
| | $-24 \leqslant k \leqslant 24$ | $-10 \leqslant k \leqslant 12$ | $-17 \leqslant k \leqslant 17$ | $-13 \leqslant k \leqslant 12$ |
| | $-15 \leqslant l \leqslant 15$ | $-32 \leqslant l \leqslant 18$ | $-13 \leqslant l \leqslant 13$ | $-16 \leqslant l \leqslant 17$ |
| Reflections collected | 2509 | 7884 | 5743 | 3912 |
| Independent reflections | 1426 | 4812 | 4098 | 2930 |
| Data/restraints/parameters | 2509/0/163 | 7884/0/371 | 5743/0/263 | 3912/10/158 |
| Goodness-of-fit on $F^2$ | 0.795 | 0.911 | 1.067 | 1.034 |
| Final *R* indices $wR_2$[b][$I > 2\sigma(I)$]($R_{int}$) | 0.0463, 0.1216 | 0.0731, 0.0929 | 0.0708, 0.1877 | 0.0379, 0.0774 |
| Final $R$[a] indices (all data) | 0.0997, 0.1554 | 0.0422, 0.0783 | 0.1047, 0.2084 | 0.0587, 0.0881 |
| Largest difference in peak/hole (e Å$^{-3}$) | 0.155, −0.159 | 0.116, −0.760 | 1.487, −1.755 | 0.288, −0.277 |

[a] $R_1 = \Sigma||F_o| - |F_c||\Sigma|F_o|$.
[b] $R_2 = [\Sigma w(|F_o{}^2| - |F_c{}^2|)^2/\Sigma w|F_o{}^2|^2]^{1/2}$.

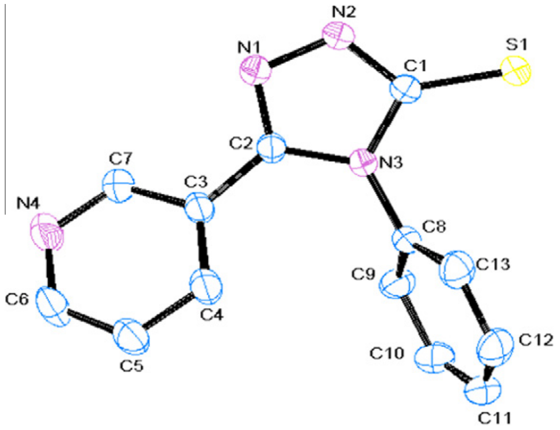


**Fig. 4.** ORTEP diagram of the ligand Hpptt (**1**).

**Table 2**
Selected molecular dimensions (Å and °) in Hpptt (**1**).

| Bond lengths (Å) | | Bond angles (°) | |
|---|---|---|---|
| S(1)–C(1) | 1.677(2) | C(2)–N(1)–N(2) | 104.47(18) |
| N(1)–C(2) | 1.301(3) | C(1)–N(2)–N(1) | 113.83(18) |
| N(1)–N(2) | 1.366(3) | C(1)–N(3)–C(2) | 107.57(17) |
| N(2)–C(1) | 1.341(3) | C(1)–N(3)–C(8) | 125.12(17) |
| N(3)–C(1) | 1.377(3) | C(2)–N(3)–C(8) | 127.29(17) |
| N(3)–C(2) | 1.391(3) | N(2)–C(1)–N(3) | 103.43(18) |
| N(3)–C(8) | 1.440(3) | N(2)–C(1)–S(1) | 128.28(17) |

**Table 3**
Selected molecular dimensions (Å and °) in [Hg(en)(pptt)$_2$] (**2**).

| Bond lengths (Å) | | Bond angles (°) | |
|---|---|---|---|
| Hg(1)–N(10) | 2.323(5) | N(10)–Hg(1)–N(9) | 75.45(17) |
| Hg(1)–N(9) | 2.354(4) | N(10)–Hg(1)–S(1) | 116.44(12) |
| Hg(1)–S(1) | 2.451(13) | N(9)–Hg(1)–S(1) | 118.32(12) |
| Hg(1)–S(2) | 2.484(14) | N(10)–Hg(1)–S(2) | 111.26(12) |
| S(1)–C(1) | 1.725(5) | N(9)–Hg(1)–S(2) | 105.38(12) |
| S(2)–C(14) | 1.732(6) | S(1)–Hg(1)–S(2) | 120.98(5) |
| N(2)–C(2) | 1.306(6) | C(1)–S(1)–Hg(1) | 97.43(16) |
| N(2)–N(1) | 1.378(6) | C(14)–S(2)–Hg(1) | 99.13(17) |
| N(1)–C(1) | 1.322(6) | C(28)–N(10)–Hg(1) | 110.0(4) |
| N(5)–N(6) | 1.395(6) | C(27)–N(9)–Hg(1) | 108.0(4) |
| N(5)–C(14) | 1.304(6) | N(1)–C(1)–S(1) | 127.1(4) |

**Table 4**
Selected molecular dimensions (Å and °) in [Hg(en)(4-pot)$_2$] (**3**).

| Bond length (Å) | | Bond angle (°) | |
|---|---|---|---|
| Hg(1)–N(2) | 2.274(15) | N(2)–Hg(1)–N(1) | 75.9(5) |
| Hg(1)–N(1) | 2.368(12) | N(2)–Hg(1)–S(1B) | 114.8(3) |
| Hg(1)–S(1B) | 2.428(5) | N(1)–Hg(1)–S(1B) | 116.9(4) |
| Hg(1)–S(1A) | 2.449(4) | N(2)–Hg(1)–S(1A) | 119.8(3) |
| S(1A)–C(1A) | 1.687(16) | N(1)–Hg(1)–S(1A) | 104.8(3) |
| S(1B)–C(1B) | 1.749(16) | S(1B)–Hg(1)–S(1A) | 117.06(14) |
| N(1)–C(1) | 1.45(2) | C(1A)–S(1A)–Hg(1) | 101.3(5) |
| C(2)–N(2) | 1.45(2) | C(1B)–S(1B)–Hg(1) | 103.6(5) |
| C(2)–C(1) | 1.49(3) | C(1)–N(1)–Hg(1) | 108.6(10) |
| O(1A)–C(1A) | 1.359(17) | C(2)–N(2)–Hg(1) | 109.3(11) |

**Table 5**
Selected bond lengths (Å) and bond angles (°) in [Ni(en)$_2$(5-thot)$_2$] (**4**).

| Bond length (Å) | | Bond angles (°) | |
|---|---|---|---|
| Ni–N(12) | 2.098(14) | N(12)–Ni(1)–N(11) | 82.62(6) |
| Ni–N(11) | 2.103(16) | N(12)–Ni(1)–N(11) | 97.38(6) |
| Ni–N(1) | 2.137(14) | N(12)–Ni(1)–N(1) | 87.81(6) |
| S(1)–C(1) | 1.678(18) | N(12)–Ni(1)–N(1) | 92.19(6) |
| O–C(2) | 1.359(2) | N(11)–Ni(1)–N(1) | 90.42(6) |
| O–C(1) | 1.389(2) | N(11)–Ni(1)–N(1) | 89.58(6) |
| N(1)–C(1) | 1.320(2) | N(1)–Ni(1)–N(1) | 180.0 |
| N(1)–N(2) | 1.406(2) | C(2)–O–C(1) | 104.27(27) |
| N(2)–C(2) | 1.284(2) | C(1)–N(1)–N(2) | 108.30(13) |

collection, structure solution and refinement are listed in Table 1. ORTEP diagrams of compounds **1**, **2**, **3** and **4** with atom numbering schemes are shown in Figs. 4, 6, 8 and 10 respectively. Selected bond lengths and angles are included in Tables 2–5. Hydrogen bond parameters for complexes **3** and **4** are given in Tables 6 and 7.

### 6.2.1. Crystal structure description of Hpptt (1)

Fig. 4 shows the molecular structure of Hpptt (**1**), which is stabilized by $\pi\cdots\pi$ interactions and intermolecular C–H···N and N–H···S hydrogen bonding, producing a supramolecular structure (Fig. 5). The N–H···S hydrogen bonds are formed between the triazole nitrogen and thione sulfur. In addition to this, there is a C–H···S weak interaction between the thione sulfur and phenyl ring hydrogen. The dihedral angle between the triazole and pyridine rings is found to be 27.55°, indicating that both rings are tilted with respect to each other, whereas the dihedral angle between the triazole and phenyl rings is 70.73°, suggesting that the phenyl ring is almost perpendicular to the triazole ring. The bond lengths and angles for the pyridine, phenyl and triazole rings are normal. The S(1)–C(1) bond length [1.677(2) Å] is found to be in the range for carbon sulfur double-bonds [S=C (1.56 Å)] [22] and indicates that the ligand is present in the thione form. This is further supported by the adjacent N(1)–C(2) bond length of [1.301(3) Å], which comes in the range for a C–N single bond [1.310 Å] [23]. The two triazole rings are tilted ($\angle ACB = 69.23°$) and displaced with respect to each other (Fig. 5). The displacement, as measured by the angle formed between the ring centroids AB and the ring normal BC to the triazole plane, is found to be 0.364 Å with a displacement angle of 16.38°, and the ring centroids contact (Cg···Cg) of 3.973 Å is well within the reported range [24].

### 6.2.2. Crystal structure description of [Hg(en)(4-pptt)$_2$] (2)

The molecular structure of complex **2** shows that in the complex unit of [Hg(en)(4-pptt)$_2$] (**2**), the metal ion is four coordinate tetrahedral, bonding through two nitrogens of en ligands and two thiolato sulfur atoms of the triazole ligand. The exocyclic C(1)–S(1) bond distance of 1.726(8) Å is longer as compared to Hpptt (**1**) (1.677 Å), indicating the conversion of the thione form of the ligand to the thiol form and subsequent bonding of the thiolato sulfur to Hg(II). The exocyclic C(1)–S(1) bond distance of 1.726(8) Å is smaller as compared to an earlier reported value of 1.82 Å, showing strong Hg–S bonding [25]. The Hg–S distances are in the range 2.454–2.472 Å (Table 3) which is normal, as reported for Hg–S bonding [26]. The bonding parameters within the en molecule agree with those of other en complexes of Hg(II) [27]. The mercury, in a tetrahedral geometry, is bonded to two nitrogen atoms of an en ligand which is involved in hydrogen bonding. The elements of the structure are linked together in the crystal packing *via* intramolecular N–H···N interactions between the pyridine nitrogen atom and NH$_2$ of en. C–H···S intramolecular interactions occur between the phenyl ring carbon and thiolato sulfur, leading to the formation of a supramolecular network (Fig. 7).

### 6.2.3. Crystal structure description of [Hg(en)(4-pot)$_2$] (3)

In complex **3**, the ligand 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione is situated on an inversion center and Hg is on a two-fold axis. The C=S bond distance in the complex is larger (1.695 Å) than that

**Table 6**
Hydrogen bonds for [Hg(en)(4-pot)$_2$] (Å and °) (**3**).

| D–H···A | D–H (Å) | H···A (Å) | D···A (Å) | ∠D–H···A (°) | Symmetry equivalent operators |
|---|---|---|---|---|---|
| N(1)–H(1C)...N(3A) #1 | 0.90 | 2.14 | 3.02(2) | 165.5 | #1 $x-1, -y+3/2, z-1/2$ |
| N(1)–H(1D)...N(3B) #2 | 0.90 | 2.37 | 3.221(19) | 158.6 | #2 $x+1, -y+3/2, z+1/2$ |

**Table 7**
Hydrogen bonds for [Ni(en)$_2$(5-thot)$_2$] (Å and °) (**4**).

| D–H···A | D–H (Å) | H···A (Å) | D···A (Å) | ∠D–H···A (°) | Symmetry equivalent operators |
|---|---|---|---|---|---|
| N(11)–H(11A)...S(1) #2 | 0.90 | 2.80 | 3.611(16) | 149.9 | #1 $-x+1, -y+1, -z+2$ |
| N(11)–H(11B)...O #3 | 0.90 | 2.51 | 3.311(19) | 149.2 | #2 $-x+1/2, y-1/2, -z+3/2$ |
| N(12)–H(12A)...N(2) #1 | 0.90 | 2.40 | 3.024(2) | 126.7 | #3 $x+1/2, -y+1/2, z+1/2$ |
| N(12)–H(12B)...S(1) | 0.90 | 2.53 | 3.290(16) | 142.7 | |

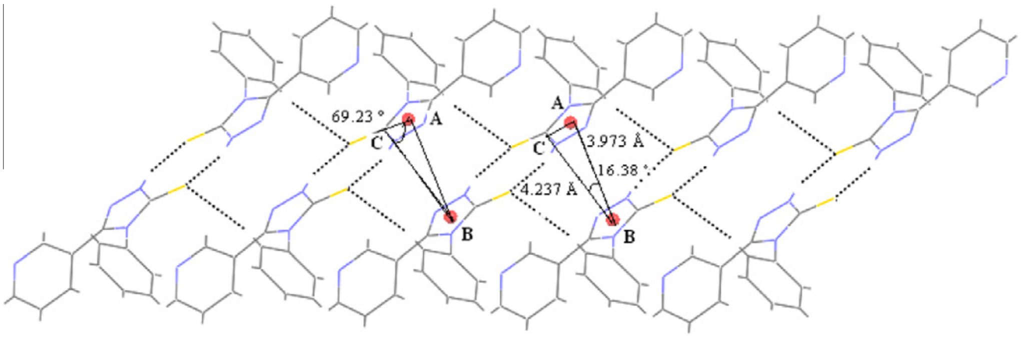


**Fig. 5.** Showing π···π stacking and the relative shift between two triazole ring centroids and C–H···N and N–H···S hydrogen bonding leading to the supramolecular structure.

of the ligand (1.661 Å) (Table 2) because of weakening of the C=S bond due to its involvement in intramolecular hydrogen bonding between thione sulfur and the $NH_2$ hydrogen of en. This is in accordance with a decrease in $\nu$(C=S) in the IR spectrum of the complex, as discussed earlier. The deviation in bond angle as compared to the expected value for a regular tetrahedron represents a minor deviation from the tetrahedral geometry (Table 4). The separation between the two planes formed by the oxadiazole rings in the same complex is found to be 1.779 Å. In complex **3** the chelate and phenyl rings lie nearly in the same plane. The phenyl ring thus makes an extended coplanar system with the chelate ring. The dihedral angle of 2.28° formed between the oxadiazole and phenyl rings suggests that the extended coplanar ring system of the two ligands around Hg(II) approaches symmetrically and coordinates to the metal. In the solid state the complex is stabilized *via* intermolecular N–H···N interactions between oxadiazole nitrogen atoms and $NH_2$ hydrogen atoms of the en molecule, leading to the formation of a symmetrical linear arrangement (Fig. 9). The pyridine and oxadiazole rings are almost parallel (∠ACB = 82.69°), but area displaced with respect to each other (Fig. 10). The displacement, as measured by the angle formed between the ring centroids AB and the ring normal BC to the oxadiazole plane, is found to be 0.103 Å, with a displacement angle of 22.88° and the ring centroids contact (Cg···Cg) of 3.553 Å is well within the reported

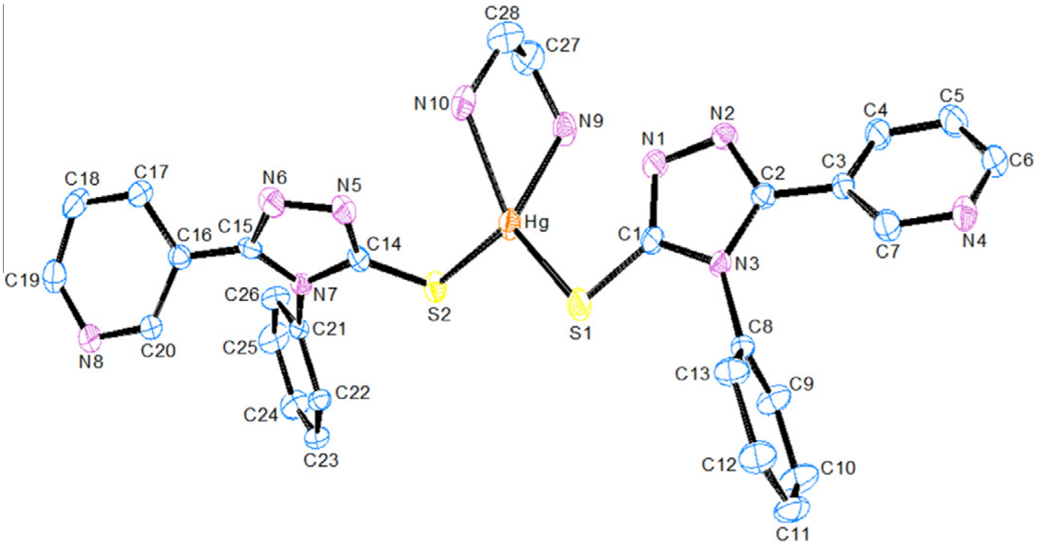


**Fig. 6.** ORTEP diagram of [Hg(en)(pptt)$_2$] (**2**).

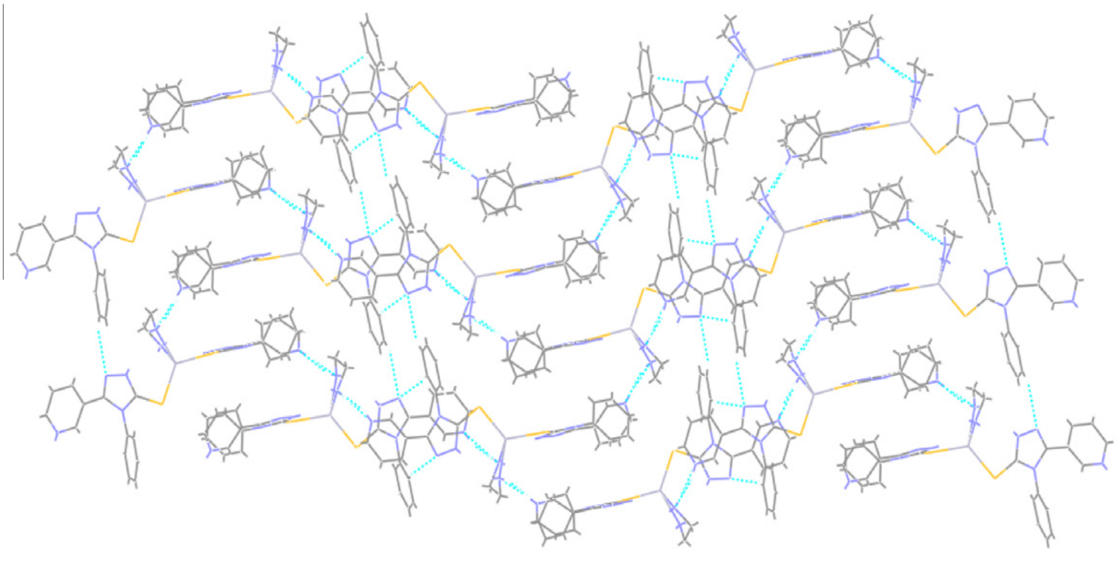


**Fig. 7.** N–H···N interaction between the pyridine nitrogen and $NH_2$ of an en molecule.

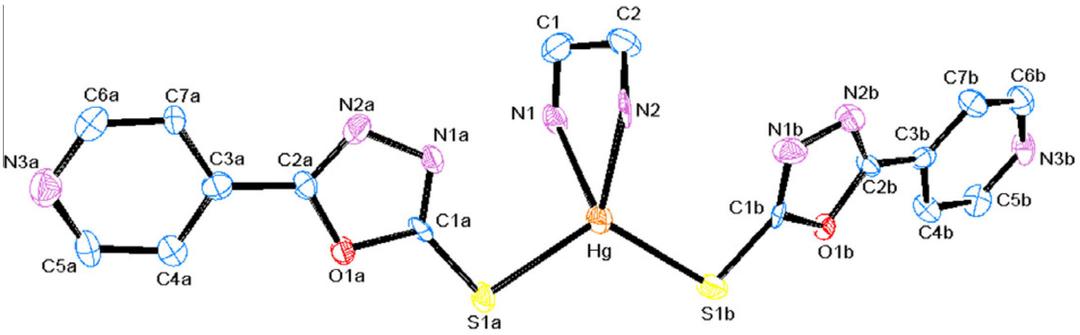


**Fig. 8.** ORTEP diagram of [Hg(en)(4-pot)$_2$] (**3**).

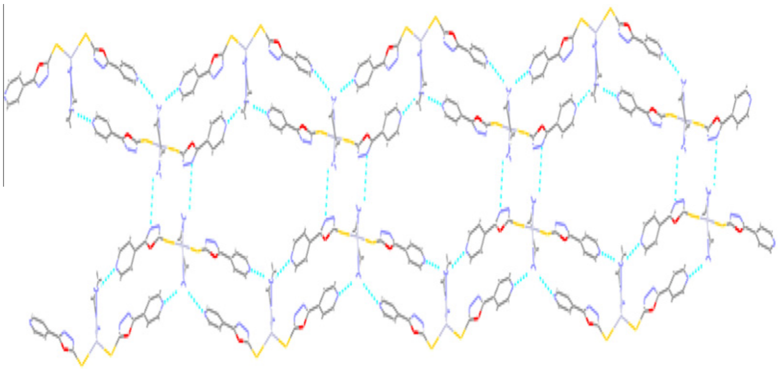


**Fig. 9.** Linear arrangement of molecules *via* N–H···N interactions.

range [24]. Similarly the two pyridine rings are also almost parallel (∠DFE = 97.72°) but displaced by 0.433 Å with respect to each other, as measured by the angle formed between the ring centroids DE and the ring normal EF to the pyridine plane, with a displacement angle of 20.45°. The ring centroids contact (Cg···Cg) of 3.917 Å is found within the limits of π···π interactions. The values of the π···π interactions suggest stronger interactions between the pyridine and oxadiazole rings as compared to the pyridine–pyridine rings.

### 6.2.4. Crystal structure description of [Ni(en)$_2$(5-thot)$_2$] (4)

The molecular structure of **4** shows that in the centro symmetric unit of [Ni(en)$_2$(5-thot)$_2$] (**4**) the metal ion is six coordinated, four equatorial nitrogens of two en and two axial nitrogens of 5-(thiophen-2-yl)-1,3,4-oxadiazole-2-thiolato anions (Fig. 11). The elements of the structure are linked together in the crystal packing *via* intramolecular N–H···S interactions between the thione sulfur and $NH_2$ hydrogen atoms of the en ligand (Fig. 12). The arrangement of the monomeric [Ni(en)$_2$(5-thot)$_2$] units in the two

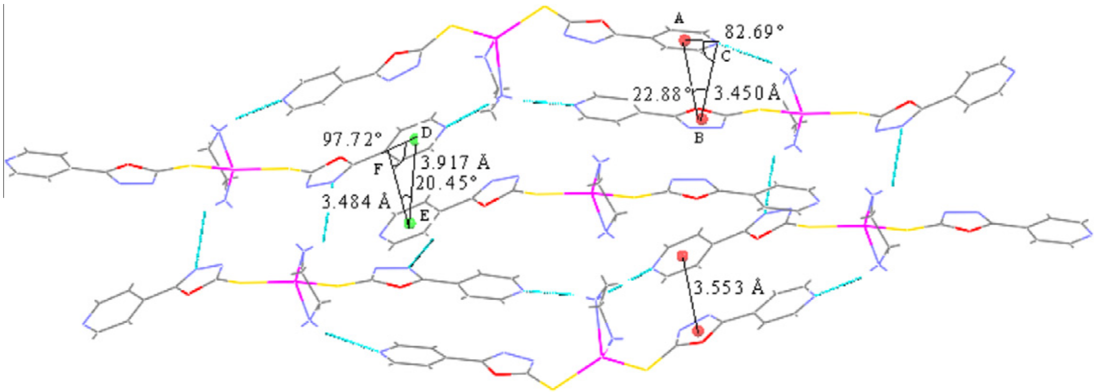


**Fig. 10.** Showing π···π stacking and the relative shift between two pyridine–pyridine and pyridine–oxadiazole ring centroids.

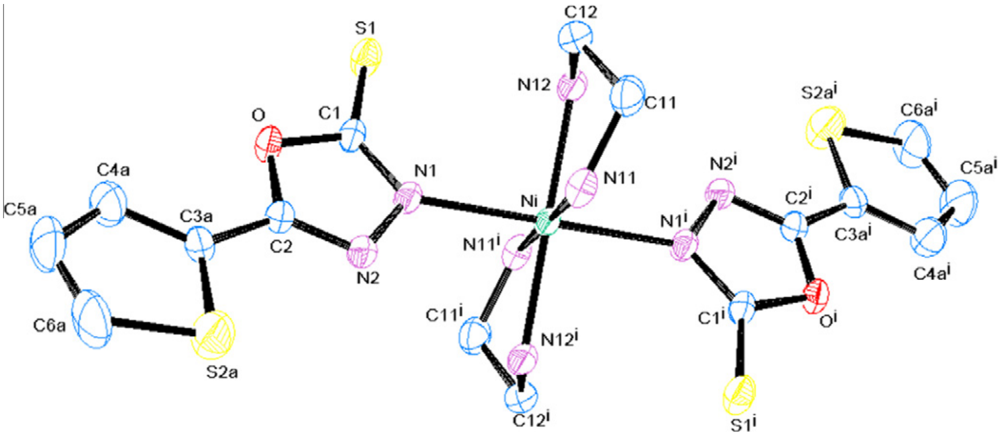


**Fig. 11.** ORTEP diagram of the [Ni(en)$_2$(5-thot)$_2$] complex (**4**).

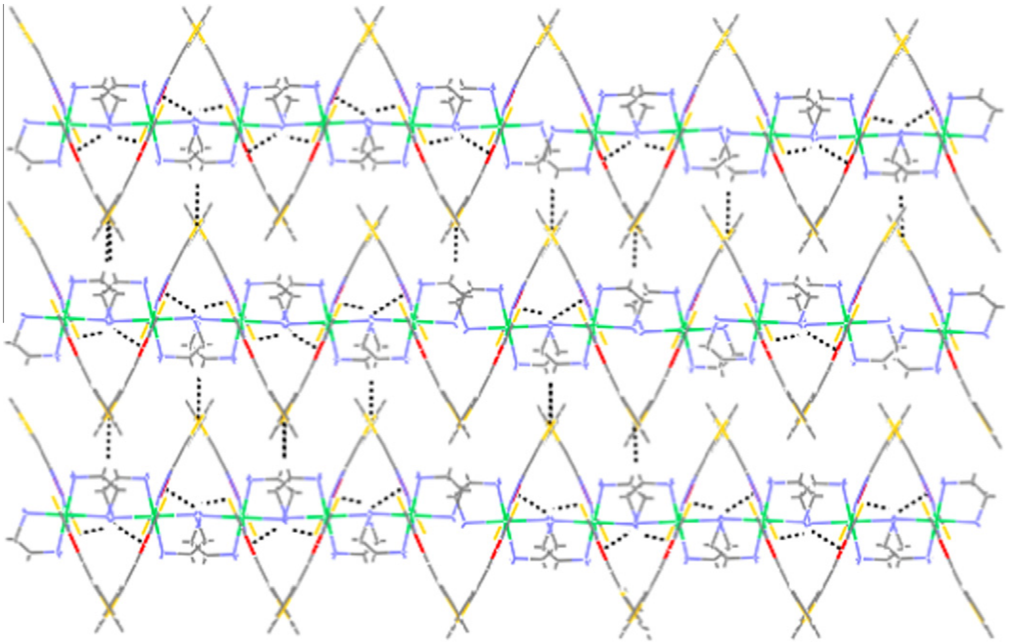


**Fig. 12.** Wave-like arrangement formed by N–H···O and N–H···S interactions in [Ni(en)$_2$(5-thot)$_2$] (**4**).

dimensional architecture along the *a* axis provide a supramolecular network (Fig. 12). The dihedral angle between the plane formed by the oxadiazole and the thiophen ring is 7.35°, indicating that both rings are almost coplanar. Within the chelate rings formed by two en ligands, the Ni–N(11) bond distance is 2.1031(16) Å and that of Ni–N(12) is 2.0981(14) Å (Table 2). The complex involves two five membered chelate rings, $C_2N_2Ni$, with a bite angle of 82.62(6)°, which represent a minor deviation from the octahedral geometry. The geometry and bonding parameters within the en molecule agree with those of other en complexes [28]. The nickel centre, in $D_{4h}$ symmetry, is bonded to four nitrogen atoms of two en ligands which offer interesting hydrogen bonding. Weak intermolecular N–H···O and N–H···S interactions occurring between the oxadiazole oxygen/thione sulfur and $NH_2$ hydrogen atoms of en stabilize the structure of complex **4**. The two N···S distances of 3.611(16) and 3.290(16) Å are close to the mean N···S distance reported for NH···S hydrogen bonds by Shrinivasan and Chacko [29].

## 7. Conclusion

This paper reports on the syntheses and crystal structures of Hpptt (**1**) and three new Hg(II) and Ni(II) complexes of 5-(3-pyridyl)-1,2,4-triazole-3-thione, 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione and 5-(thiophene-2-yl)-1,3,4-oxadiazole-2-thione, containing ethylene diamine as a co-ligand. In $[Hg(en)(4\text{-pptt})_2]$ (**2**) and $[Hg(en)(4\text{-pot})_2]$ (**3**), the Hg(II) centre has a four coordinate tetrahedral arrangement involving two nitrogen atoms of en ligands and two covalently bonded sulfur atoms from triazole-3-thiolato/oxadiazole-2-thiolato anions. In $[Ni(en)_2(5\text{-thot})_2]$ (**4**), the Ni(II) centre has a six coordinated octahedral arrangement involving four nitrogen atoms of en ligands and two nitrogen atoms of oxadiazole-2-thione anions. The crystal structures of the complexes are stabilized by various intermolecular and intramolecular hydrogen bondings. $[Ni(en)_2(5\text{-thot})_2]$ (**4**) shows quasi-reversible redox behavior assignable to a $Ni^{2+}/Ni^{3+}$ one electron transfer. The photoluminescence properties indicate that the complexes are fluorescent materials with maximum emissions at 433, 376 and 465 nm for complexes **2**, **3** and **4** at an excitation wavelength of 293, 273 and 327 nm, respectively. All the complexes contain extended hydrogen bonding, providing supramolecular frameworks.

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## Appendix A. Supplementary data

CCDC 875784, 864052, 841681 and 841506 contains the supplementary crystallographic data for Hpptt (**1**), $[Hg(en)(4\text{-pptt})_2]$ (**2**), $[Hg(en)(4\text{-pot})_2]$ (**3**) and $[Ni(en)_2(5\text{-thot})_2]$ (**4**), respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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