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Synthesis, spectral and structural characterization of Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes with 2-mercapto-5-methyl-1,3,4-thiadiazole: A Zn(II) complex acting as a new sensitive and selective fluorescent probe for the detection of Hg²⁺ in H₂O-MeOH medium

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Abstract

Five new complexes, $[Ni(mthd)_2(py)_2]$ (1), $[Cu(en)_2](mthd)_2$ (2), $[H_2en][Hg(mthd)_3]_2 H_2O$ (3), $[Cd(mthd)_2(o-phen)_2]_2 \cdot H_2O(4)$ and $[Zn(mthd)_2(bpy)](5)$ (Hmthd = 2-mercapto-5-methyl-1,3,4thiadiazole), have been synthesized. All the complexes have been fully characterized by various techniques: elemental analyses, IR, electronic and fluorescent spectral data. The ligand is present in the deprotonated thiol form in the complexes $[Cu(en)_2](mthd)_2$ (2) and $[Cd(mthd)_2(o$ phen)₂]₂·H₂O (4). In complex 2, the ligand is ionically bonded, whereas it is covalently bonded through the sulfur in complex 4. In $[Ni(mthd)_2(py)_2]$ (1) the ligand is N,S chelating bidentate bonded through the thiol sulfur and the thiadiazole ring nitrogen adjacent to it, forming a four membered chelate ring. The ligand is covalently bonded through the deprotonated thiadiazole ring nitrogen adjacent to the thiol sulfur in $[Zn(mthd)_2(bpy)]$ (5). The complex anion in $[H_2en][H_2(mthd)_3]_2 \cdot 2H_2O$ (3) has a triangular planar geometry, with bonding through the deprotonated thiolato sulfur atoms from the three ligands. $[Zn(mthd)_2(bpy)]$ (5) is highly fluorescent as compared to the other complexes and has been further used as a metal probe for sensing of Hg^{2+} in H₂O-MeOH solution. Complex 5, upon interaction with Hg^{2+} , shows a hypochromic shift in the absorption spectra whereas the emission spectra exhibited 75%

quenching fluorescence behaviour. The electrochemical studies also suggest the interaction of Hg(II) with the Zn(II) complex, probably *via* the free thione sulfur.

Keywords: Thiadiazole complexes, N,S donor ligand, Fluorescent Zn(II) complex, Electrochemical studies, Intermolecular interactions.

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Introduction

The design and synthesis of fluorescent chemosensors for the selective detection of metal ions is one of the most important research areas in chemistry due to the fundamental and necessary role of these species in biological processes [1]. Search for reagents which can efficiently act as fluorescence sensors for zinc(II) has been an active area of research [2]. An ideal small molecule for a metal ion probe should possess high stability and the capability to quantitatively determine the metal ion concentration with high selectivity and sensitivity toward the specified metal ion when it is present in ion mixtures. If the sensor has a straightforward and high-yielding preparative route, this is an additional practical advantage [3]. Hg^{2+} and Pb^{2+} have attracted the attention of researchers due to their high toxicity and severe effects on living organisms [4]. Despite its high toxicity, mercury is extensively used in many industrial processes and in the manufacture of important products [5]. It is distributed in the environment in various forms, like elemental (Hg^0), inorganic (Hg^{2+}) and organic methyl mercury (CH_3Hg^+). Highly soluble and reactive inorganic mercury (Hg^{2+}) can bind to a variety of ligands and complexes present in organisms, particularly those containing sulfur functionality [6].

One of the most interesting properties of mercapto-substituted thiadiazoles is the existence of thiol-thione tautomerism which influences the reactivity of thiadiazoles in

polymerization processes, substitution reactions at the different moieties and for metal complexation [7,8]. In a previous study, 2,5-dimercapto-1,3,4-thiadiazole and 2-mercapto-5-methyl-1,3,4-thiadiazole have been shown to exhibit tautomeric equilibria, and the structures of the compounds by *ab initio* and DFT computations support the thione form as being the most stable [9]. There exists continuing interest in ambidentate nitrogen-sulfur heterocyclic thiolato ligands on account of their presence in many molecules [10] containing both an endocyclic hard N donor and an exocyclic soft S donor. Some work has been reported on the complexes of 1,3,4-thiadiazole-2-thiones, but very little is known about mixed ligand complexes of these ligands.

In view of this, we have synthesized and characterized Ni(II), Cu(II), Hg(II), Cd(II) and Zn(II) complexes of an ambidentate ligand, 2-mercapto-5-methyl-1,3,4-thiadiazole, containing ethylenediamine/o-phen/bpy/py as a co-ligand. Among the complexes, we report the synthesis and characterization of the fluorescent compound $[Zn(mthd)_2(bpy)]$ (5), which is engaged in selective detection of Hg²⁺ over other metal ions (Pb²⁺, Cu²⁺, Ni²⁺, K⁺, Na⁺, Ag⁺, Zn²⁺ and Cr³⁺) in water:MeOH (50:50 v/v) by additional bonding with the free donor site. This additional bonding approach for metal ion sensing is very effective in that the organic ligand alone shows a poor sensing ability to the metal ion. This fluorescent Zn²⁺ complex shows a highly effective " turn off " sensor for Hg²⁺; the free organic ligand moiety is a less effective sensor than the Zn²⁺ complex.

2. Experimental Section

2.1. Materials and characterization

Commercial reagents were used without further purification and all experiments were carried out in the open atmosphere. 2-Mercapto-5-methyl-1,3,4-thiadiazole (Sigma-Aldrich) was used as

received. All solvents were purchased from Merck Chemicals, India, and were dried and distilled before use by following standard procedures. Carbon, hydrogen, nitrogen and sulfur contents were estimated on a CHN Model CE-440 Analyzer and on an Elementar Vario EL III Carlo Erba 1108. Magnetic susceptibility measurements were performed at room temperature on a Cahn Faraday balance using Hg[Co(NCS)₄] as the calibrant and electronic spectra were recorded on a SIMADZU 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 NMR spectra were recorded in DMSO-d₆ on a JEOL AL300 FT NMR spectrometer using TMS as an internal reference. 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. Syntheses

2.2.1. Synthesis of [Ni(mthd)₂(py)₂] (1)

Ni(OAc)₂·4H₂O (0.248 g, 1 mmol) and Hmthd (0.264 g, 2 mmol) were dissolved separately in 20 ml methanol, mixed together and stirred for 1 h. The blue solid which separated was filtered off, washed successively with an ethanol-water mixture (50:50) and air dried. The precipitate was suspended in methanol to which pyridine (0.4 ml) was added and stirred for 2 h. The resulting clear green solution was filtered and kept for crystallization. Green single crystals of **1** suitable for X-ray analysis were obtained by slow evaporation of the solution over a period of 15 days. Yield: 0.51 g, 48 %; m.p. 210 °C; Anal. Found: C, 40.07; H, 3.31; N, 17.48; S, 26.74 %. Calc. for $C_{16}H_{16}NiN_6S_4$ (479.32): C, 40.06; H, 3.33; N, 17.52; S, 26.70 %. IR (KBr, cm⁻¹):

v(C=N) 1600, v(N-N) 1040, v(C=S) 939, v(Ni-N) 634, v(Ni-S) 432. UV-vis.[λ_{max}, DMSO, cm⁻¹]: 19010, 23810, 32363.

2.2.2. Synthesis of $[Cu(en)_2](mthd)_2(2)$

Cu(OAc)₂·H₂O (0.199 g, 1 mmol) and Hmthd (0.264 g, 2 mmol) were dissolved separately in 15-20 ml methanol, mixed together and stirred for 1 h. The blue solid which separated was filtered, washed with a methanol-water mixture (50:50 v/v) and finally with methanol. A methanol solution (10 ml) of ethylenediamine (0.30 ml, 4 mmol) was added to the methanol suspension of the above compound and stirred for 30 minutes. A clear dark blue solution was obtained which was filtered off and kept for crystallization. Dark blue crystals of **2** suitable for X-ray analysis were obtained by slow evaporation of the above solution over a period of 10 days. Yield: 0.64 g, 52 %; m.p. 130 °C; Anal. Found: C, 26.78; H, 5.41; N, 24.94; S, 28.60 %. Calc. for C₁₀H₂₄CuN₈S₄ (448.20): C, 26.77; H, 5.35; N, 24.98; S, 28.55 %. IR (KBr, cm⁻¹): v(NH) 3252, v(C=N) 1599, v(N-N) 1046, v(C-S) 731, v(Cu-N) 548, v(Cu-S) 431. UV-vis. [λ_{max} , DMSO, cm⁻¹]: 16400, 28410, 33558.

2.2.3. Synthesis of $[H_2en][Hg(mthd)_3]_2 \cdot 2H_2O(3)$

A methanol solution (25 ml) of Hmthd (0.396 g, 3 mmol) was added slowly to a methanol solution of HgCl₂ (0.270 g, 1 mmol) and stirred for 2 h. A white precipitate was obtained which was dissolved in a methanolic solution of en (1.2 ml). This clear solution was filtered off and kept for crystallization. Colorless crystals of **3** suitable for X-ray analysis were obtained by slow evaporation of the above solution over a period of 20 days. Yield: 0.77 g, 48 %; m.p. 160 °C; Anal. Found: C, 18.62; H, 2.63; N, 15.20; S, 29.79 %. Calc. for $C_{20}H_{34}Hg_2N_{14}O_2S_{12}$ (1288.63): C, 18.50; H, 2.70; N, 15.25; S, 29.95 %. IR (KBr, cm⁻¹): v(O-H)

3409, v(NH) 3316, v(C=N) 1558, v(N-N) 1077, v(C-S) 768, v(Hg-S) 427. ¹H NMR (DMSO-d₆, δ, ppm): 2.93 (3H); 3.33 (2H, CH₂); 6.64 (⁺NH₃). UV-Vis. [λ_{max}, DMSO, cm⁻¹]: 33670, 37174.

2.2.4. Synthesis of $[Cd(mthd)_2(o-phen)_2]_2 \cdot H_2O(4)$

A solution of Hmthd (0.264 g, 2 mmol) in MeOH (10 ml) was added to a MeOH solution (10 ml) of Cd(OAc)₂·2H₂O (0.266 g, 1 mmol). This mixture was stirred for 3 h at room temperature. The resulting precipitate was filtered off and washed thoroughly with methanol. A methanol solution of 1,10-phenanthroline (*o*-phen) (0.400 g, 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. Colorless crystals of **4** suitable for X-ray analysis were obtained by slow evaporation of the above solution over a period of 20 days. Yield: 0.44 g, 40 %; m.p. 238 °C; Anal. Found: C, 47.56; H, 3.07; N, 15.15; S, 17.05 %. Calc. for $C_{60}H_{46}Cd_2ON_{16}S_8$ (1488.49): C, 47.83; H, 3.20; N, 14.87; S, 17.03 %. IR (KBr, cm⁻¹): v(OH) 3435, v(C=N) 1621, v(N-N) 1019, v(C-S) 728, v(Cd-S) 427. ¹H NMR (DMSO-d₆, δ , ppm): 3.39 (3H, -CH₃); 7.9-8.9 (8H, aromatic ring). UV-Vis.[λ_{max} , DMSO, cm⁻¹]: 34483.

2.2.5. Synthesis of [Zn(mthd)₂(bpy)] (5)

A solution of Hmthd (0.234 g, 2 mmol) in MeOH (10 ml) was added to a MeOH solution (10 ml) of $Zn(OAc)_2 \cdot 2H_2O$ (0.220 g, 1 mmol). This mixture was magnetically stirred for 2 h at room temperature. The resulting white precipitate was filtered off, washed with methanol. A methanol solution of 2,2'-bipyridyl (bpy) (0.156 g, 1 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 **5** suitable for X-ray analysis were obtained by slow evaporation of the above solution over a period of 15 days. Yield: 0.62 g, 54 %; m.p. 276 °C; Anal. Found: C, 39.64; H, 2.91; N, 17.39; S, 26.42 %. Calc. for $C_{16}H_{14}ZnN_6S_4$ (484.00):

C, 39.66; H, 2.89; N, 17.35; S, 26.44 %. IR (KBr, cm⁻¹): v(C=N) 1600, v(N-N) 1128, v(C=S) 978, v(Zn-N) 415. ¹H NMR (DMSO-d₆, δ, ppm): 3.05 (3H, -CH₃); 7.6-8.9 (8H, aromatic ring). UV-Vis. [λ_{max}, DMSO, cm⁻¹]: 35336, 32155.



Scheme 1. Preparation of complexes 1, 2, 3, 4 and 5.

3. Crystal structure determination

Data for complexes **1**, **2** and **4** were recorded at 296(2) K on a Bruker three-circle diffractometer and those of complexes **3** and **5** at 293(2) K on an Oxford Diffraction Gemini diffractometer equipped with CrysAlis Pro./SMART 6000 CCD software using a graphite monochromated MoK α (λ = 0.71073 Å) radiation source. The structures were solved by direct methods (SHELXL-2008) and refined against all data by full matrix least-squares on F² using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms were included in the refinement at geometrically ideal positions and refined with a riding model [11].

The MERCURY package and ORTEP-3 programs were used for generating the molecular structures [12,13].

4. Results and Discussion

Salts of Ni(II), Cu(II), Cd(II) and Zn(II) react with Hmthd and then with a coligand to yield complexes **1**, **2**, **4** and **5**, respectively, whereas the reaction of HgCl₂ with Hmthd in the presence of ethylenediamine forms $[H_2en][Hg(mthd)_3]_2^2H_2O$ (**3**). Scheme 1 depicts the formation of the complexes which contain 2-mercapto-5-methyl-1,3,4-thiadiazole as a ligand and py/en/*o*-phen/bpy as the coligand. The single crystal X-ray diffraction studies indicate that the ligand (Hmthd) behaves as a uninegative monodentate ligand in complexes **2**, **3**, **4** and **5**, bonding either through the thiadiazole nitrogen adjacent to the thiol sulfur or the thiol sulfur, but as uninegative chelating bidentate ligand in complex **1**, bonding through the thiadiazole ring nitrogen adjacent to the thiol sulfur. In [Ni(mthd))₂(py)₂] (**1**), both the nitrogen and sulfur sites of the ligand are bonded to the nickel ion, forming a four membered chelate ring, having a distorted octahedral geometry around the Ni(II) centre. All the complexes are air stable, non-hygroscopic crystalline solids, which are partially soluble in common organic solvents but soluble in DMF and DMSO, and they can be kept in desiccators over a prolonged period without any sign of decomposition.

4.1. I.R. spectra

The ligand 2-mercapto-5-methyl-1,3,4-thiadiazole shows bands at 2868 and 1554 cm⁻¹ due to v(SH) and v(C=N), respectively. The spectra of all the complexes show the absence of the v(SH) band, indicating bonding through the thiolato sulfur or thiadiazole nitrogen after tautomerization and subsequent bonding through the thiadiazole nitrogen. The disappearance of

the v(SH) band in the spectrum of $[Ni(mthd)_2(py)_2]$ (1) and the presence of bands at 1600 and 939 cm⁻¹ due to v(C=N) (thiadiazole ring) and v(C=S), respectively, indicates that the nickel ion is bonded through the thiadiazole nitrogen adjacent to the thiol sulfur and the thiadiazolato sulfur after loss of a proton from the thiol sulfur. Further new bands appear at 634, 620 and 432 cm⁻¹ due to v(Ni-N) (py), v(Ni-N) (thiadiazole) and v(Ni-S), indicating the formation of a chelate ring and bonding of pyridine to the nickel ion. The IR spectrum of complex 2 shows a band at 3210 cm^{-1} due to the NH stretching vibration of the en ligand. The disappearance of the v(SH) band shows the removal of the proton from the -SH group and the appearance of a new band at 548 cm^{-1} due to v(Cu-N) (en) suggests the formation of a chelate with ethylenediamine [14]. The IR spectrum of $[H_2en][Hg(mthd)_3]_2 H_2O$ (3) shows a band at 3410 cm⁻¹ for v(OH) of the water molecules and a band at 3316 cm^{-1} for v(NH) of the en molecule. The absence of a v(SH) band together with the appearance of a new band for v(Hg-S) at 427 cm⁻¹ suggests bonding of Hg(II) with the thiolato sulfur after loss of a proton. The IR spectrum of complex 4 shows a band at 3456 cm⁻¹ due to the OH stretching vibrations of the water molecule, and the absence of a v(SH)band due to the thiadiazole moiety of the ligand suggests the loss of the SH proton in the complex. The appearance of two new bands at 580 and 427 cm⁻¹ due to v(Cd-N) and v(Cd-S)suggest bonding through the thiolato sulfur and o-phen nitrogen with the metal ion. The IR spectrum of $[Zn(mthd)_2(bpy)]$ (5) shows a band at 1027 cm⁻¹ due to v(C=S), indicating that the ligand is present in the thione form and is bonded through the thiadiazole nitrogen adjacent to the thiol sulfur [15].

4.2. ¹H and ¹³C NMR spectra

The ¹H NMR spectrum of the ligand 2-mercapto-5-methyl-1,3,4-thiadiazole in DMSO d_6 shows signals at 12.05, 3.32 and 2.49 ppm due to the thiadiazole NH, SH and methyl protons,

respectively, indicating the existence of the ligand in the thiol/thione tautomeric forms. The ¹H NMR spectrum of $[H_2en][Hg(mthd)_3]_2 \cdot 2H_2O(3)$ exhibits signals at δ 2.93 and 3.33 ppm for the CH₃ and CH₂ (en) protons and a peak at δ 6.643 ppm for ⁺NH₃ of the protonated ethylenediamine. The disappearance of the SH signal suggests bonding of the soft sulfur atom with the soft Hg(II) in the complex. The ¹H NMR spectrum of $[Cd(mthd)_2(o-phen)_2]_2 \cdot H_2O(4)$ in DMSO-d₆ shows a signal at δ 3.39 ppm due to CH₃ protons. The *o*-phen ring protons appear as a multiplet between 7.9 and 8.9 (m, 8H) ppm. The ¹H NMR spectrum of $[Zn(mthd)_2(bpy)](5)$ in DMSO-d₆ shows a signal at δ 3.05 ppm due to CH₃ protons. The bipyridyl ring protons appear as a multiplet between δ 7.6 and 8.9 (m, 8H) ppm.

4.3. UV-Vis absorption, magnetic moments and photoluminescent studies.

A magnetic moment of 2.91 BM for [Ni(mthd))₂(py)₂] (1) and the presence of two bands at 19010 and 23810 cm⁻¹ ($\varepsilon = 76$ and 100 M⁻¹ cm⁻¹) assigned to the ${}^{3}A_{2}g \rightarrow {}^{3}A_{1}g(F)$ (v₂) and ${}^{3}T_{1}g(P)$ (v₃) transitions, respectively, suggest a distorted octahedral geometry for the complex. A high energy band observed at 32363 cm⁻¹ ($\varepsilon = 1.11 \times 10^{3} \text{ M}^{-1} \text{ cm}^{-1}$) may be assigned to an intraligand/charge transfer transition. [Cu(en)₂](mthd)₂ (2) shows a magnetic moment of 1.72 BM, which indicates the presence of one unpaired electron. The presence of a broad band around 16400 cm⁻¹ ($\varepsilon = 120 \text{ M}^{-1} \text{ cm}^{-1}$) assigned to the envelope of the ${}^{2}B_{1}g \rightarrow {}^{2}A_{1}g$, ${}^{2}B_{2}g$ and ${}^{2}Eg$ transitions suggests a square planar geometry for the complex. Two other high energy bands, observed at 28410 and 33558 cm⁻¹ ($\varepsilon = 4.50 \times 10^{3}$, 1.39 x 10³ M⁻¹ cm⁻¹), may be assigned to intraligand/charge transfer transitions. The [H₂en][Hg(mthd)₃]₂·2H₂O (3), [Cd(mthd)₂(*o*phen)₂]₂·H₂O (4) and [Zn(mthd)₂(bpy)] (5) complexes are diamagnetic and show absorptions in the region of 32150-37100 cm⁻¹ ($\varepsilon = 0.54 \times 10^{3} - 3.2 \times 10^{3} \text{ M}^{-1} \text{ cm}^{-1}$) due to intraligand/charge

transfer transitions [16]. The electronic absorption and emission spectra of complexes **1-5** are depicted in Figures 1(a) and (b).

5. Metal ion sensing behavior of the Zn(II) complex

The sensing behavior of $[Zn(mthd)_2(bpy)]$ (5) with various metal cations $(Pb^{2+}, Cu^{2+}, Ni^{2+}, K^+, Na^+, Hg^{2+}, Ag^+, Zn^{2+} and Cr^{3+})$ as their nitrate salts in H₂O:MeOH (pH 7.4, 100 µM) was investigated by UV-vis and fluorescence spectrophotometry. The absorption spectrum of complex 5 (100 µM) in DMSO shows two bands at 285 and 311 nm ($\varepsilon = 3.2 \times 10^3$, 1.79 x10³ M⁻¹ cm⁻¹), due to intraligand/charge transfer transitions. Upon addition of 1.0 equivalent of Hg²⁺ ions (100 µM), the absorbance decreased (~ 42 %) while λ_{max} showed a slight blue-shift (~12 nm). Under the same conditions, other metal ions, such as Ag⁺, Pb²⁺, Zn²⁺, Cr³⁺, Na²⁺, Ni²⁺, Cu²⁺ and K⁺, showed a decrease in absorption with a red-shift in the UV-vis spectra. The fluorescence spectra of [Zn(mthd)₂(bpy)] (5) on addition of 1.0 and 2.0 equivalents of Hg²⁺ ions (100 µM) showed 50 and 75 % quenching, but the other metal ions did not show such a quenching effect. Fig. 2(a) and 2(b) show the fluorescence spectra and relative fluorescence of complex 5 in the presence of solutions of different metal ions at 343 nm emission wavelength. Scheme 2 shows the proposed mechanism for the interaction of [Zn(mthd)₂(bpy)] (5) with Hg(NO₃)₂.



Scheme 2 Proposed mechanism for the formation of $[Zn(mthd)_2(bpy)]$ (5): $2Hg^{2+}$

5.1. Thermal gravimetric analysis

The thermal properties of [Zn(mthd)₂(bpy)] (5) were studied by TG and DTA in the temperature range 30-800 °C under a nitrogen atmosphere. Thermogravimetric analysis of complex **5** showed that the complex starts decomposing at 230 °C and the thermogram exhibits four distinct decompositions at 230, 290, 360 and 650 °C. The weight loss (32.93 %) at 230 °C could be ascribed to the loss of the bipyridyl molecule with 2 % weight gain and the corresponding endothermic peak at 267 °C was obtained. The second decomposition at 290 °C shows the weight loss (32.04 %) for both ligands (mthd), whilst the third and fourth decompositions at 360 and 650 °C show the degradation of the remaining organic moieties, and after 650 °C the residue of 15.48 % left corresponds to zinc oxide. The corresponding endo and exothermic peaks in the DTA were obtained at 327, 346 and 404 °C (supple. Fig.1).

5.2. Electrochemical behaviour of $[Ni(mthd)_2(py_2)]$ (1)

The cyclic voltammogram of $[Ni(mthd)_2(py_2)]$ (1) (c = 100 µM, DMSO) obtained at a Pyrolytic Graphite Electrode (PGE) in DMSO medium using 0.2 M TBAP as the supporting electrolyte in the potential range -1.0 V to 0.8 V at a scan rate of 50 mV s⁻¹ exhibits an anodic peak at -0.034 V and an associated cathodic peak at -0.786 V with respect to the Ag/AgCl reference (supple. Fig. 2). The separation between the cathodic and anodic peak potentials ($\Delta Ep = Epa - Epc$) of 0.752 V and $E_{1/2}$ [(Epa + Epc)/2] of 0.410 V indicates an irreversible redox process assignable to the Ni(II)/Ni(III) couple [17].

5.3. Electrochemical studies of $[Cu(en)_2](mthd)_2(2)$

The cyclic voltammogram of complex 2 (supple. Fig. 3a) obtained at a Pyrolytic Graphite Electrode (PGE) in DMSO medium using 0.2 M KCl as the supporting electrolyte in the potential range +1.0 V to -1.5 V with a scan rate 50 mV s⁻¹ exhibits only an anodic peak at 0. 515 V with respect to the Ag/AgCl reference. The cyclic voltammogram of the complex

indicates an irreversible redox process assignable to the Cu(II)/Cu(III) couple. However, it is to be noted that the peaks observed at 0.525 and 0.150 V are due to the ligand moiety in the complex [18]. The anodic peak observed at 0.515 V without a corresponding cathodic peak can be assigned to the tri-valent Cu(III), which after being oxidised from the complexing environment could not be re-reduced [19,20].

5.4. ESR spectra

The frozen solution EPR spectrum of $[Cu(en)_2](mthd)_2$ (2) (supple. Fig. 3b) was recorded in methanol at liquid nitrogen temperature. The EPR spectrum of the Cu(II) complex on the high field side is more intense than the low field side, indicating a $d_x^2 g^2$ ground state for the copper(II) ion. Analysis of the spectrum of complex 2 gives $g_{II} = 2.201$ and $g \perp = 2.014$. The trend $g_{II} > g \perp >$ g_e (2.0023) observed for the complex under investigation also suggests a $d_x^2 g^2$ ground state for the Cu(II) ion. Also, the observed g_{II} value of less than 2.30 provides evidence for the appreciable covalent character of the bonding between the Cu(II) ion and the attached ligand in the complex [21].

5.5. Crystal structure description of [Ni(mthd)₂(py)₂] (1)

The ORTEP diagram of the complex $[Ni(mthd)_2(py)_2]$ (1) (Fig. 3) contains a pair of monodeprotonated ligands bonded to the Ni(II) ion *via* the thiadiazole nitrogen adjacent to the thiol sulfur and the thione sulfur, forming two four membered chelate rings with a bite angle of 67.59(4) ° [N(1)-Ni-S(1)]; two pyridine molecules are also coordinated, completing the distorted octahedral structure. The crystallographic data and structural refinement details of complex 1 are given in Table 1 and selected bond lengths and angles are compiled in Table 2. The formation of a four membered C₂N₂Ni chelate ring, with a bite angle of 67.59(4) °, represents a major

deviation from an octahedral geometry. The geometry and bonding parameters agree with those of other pyridine containing complexes $[Ni(NCS)_2(4-methyl pyridine)/(4-ethyl pyridine)_4]$ [22,23]. The distances within the chelate rings are intermediate between single and double bond lengths and the average bond lengths, C6-N1 = 1.315(2) and C6-S1 = 1.708(15) Å, suggest considerable delocalization of charge [24]. In complex 1, the chelate rings and the thiadiazole ring lie nearly in the same plane and make an extended coplanar system with both chelate rings. The values of the dihedral angles suggest that the extended coplanar ring system of the two ligands approach each other orthogonally and shows an unsymmetrical coordination of the two ligands. Thus the two ligands bonded to Ni(II) are the mirror image of each other. Both pyridine rings are symmetrically coordinated to the metal in a *trans* position. The pyridine rings of two nearby molecules are tilted ($\angle ACB = 73.25^{\circ}$) and displaced with respect to each other (supple. Fig. 4). The displacement, as measured by the angle formed between the ring centroids AC and the ring normal BC to the pyridine plane is found to be 0.178 Å with a displacement angle of 19.56°, and the ring centroids contact (Cg...Cg) of 3.901 Å is well within the reported range [25]. In the solid state the complex is stabilized via intermolecular C-H···N and C-H···S interactions (supple. Table 1) between the thiol sulfur and thiadiazole nitrogen adjacent to the thiol sulfur with the same hydrogen atom of the pyridine ring, leading to the formation of a supramolecular linear chain structure.

5.6. Crystal structure description of $[Cu(en)_2](mthd)_2(2)$

Fig. 4 shows molecular structure of $[Cu(en)_2](mthd)_2$ (2) with the atom labeling scheme, showing a weak Cu…S interaction. The crystallographic data and structural refinement details of complex 2 are given in Table 1 and selected bond lengths and angles are listed in Table 3. The crystal structure of complex 2 consists of a complex cation, $[Cu(en)_2]^{2+}$, and the 2-mercapto-5-

methyl-1,3,4-thiadiazole thiolate (mthd) anions. The complex cation consists of two ethylenediamine molecules which chelate Cu(II) in equatorial positions and two ionic bonds with 1,3,4-thiadiazole-2-thiadiazolato anions. The Cu-N distances are found to be in the range 2.016-2.022 Å (Table 4), which is normal for Cu-N (en) coordination. The bite angle for the CuC₂N₄ five membered ring is 84.10(10) °, indicating a substantial distortion in the complex cation. Similar geometrical parameters for the coordination sphere have been reported for other diaqua *bis*-ethylenediamine Cu(II) complexes [26,27]. Each [Cu(en)₂]⁺² cation forms a pair of intermolecular Cu-··S interactions with a distance of 2.975 Å, which is well within the distance of 3.2 Å for the sum of Van der Waals' radii of Cu and S, but greater than a Cu-S covalent bond [28,29]. The Cu(II) in D_{2h} symmetry is bonded to four nitrogen atoms of two en groups, which offer interesting hydrogen bonding packing. In the solid state, the complex is stabilized *via* intermolecular N-H···N interactions (supple. Table 2) between both thiadiazole nitrogens and the NH₂ hydrogen atoms of ethylenediamine, which produce a ladder-like arrangement (supple. Fig. 5).

5.7. Crystal structure description of $[H_2en][Hg(mthd)_3]_2 \cdot 2H_2O(3)$

The crystallographic asymmetric unit of complex **3**, consists of an H_2en^{2+} cation, two complex $[Hg(mthd)_3]^-$ anions and two water molecules. The crystallographic data and structural refinement details of complex **3** are given in Table 1 and selected bond lengths and angles are listed in Table 4. There are two complex anions present in the asymmetric unit of complex **3**, both are structurally identical except for a slight variation in bond lengths and angles. The coordination number of three around each Hg(II) centre in the complex anion is completed by sulfur atoms from three 1,3,4-thiadiazole-2-thiolate anions bonded through Hg-S1, Hg-S3, Hg-S5 and Hg-S7, Hg-S9, Hg-S11 at the distances of 2.443(6), 2.477(7), 2.447(6) and 2.478(7),

2.448(6), 2.462(6) Å, respectively. One H_2en^{2+} cation is present between two units of complex $[Hg(mthd)_3]^-$ anions (Fig. 5). The two thiadiazole rings in each complex unit are almost planar, making a dihedral angle $\angle ACB$ of 71.66° in units containing Hg1 and Hg2. The thiadiazole rings of both complex anion units are almost parallel, but displaced with respect to each other (supple. Fig. 6). The displacement, as measured by the angle formed between the ring centroids AB and the ring normal BC to the thiadiazole plane, is found to be 1.194 Å with a displacement angle of 17.44°, and the ring centroids contact (Cg…Cg) of 3.782 Å is well within the reported range. In the solid state the complex is stabilized *via* intermolecular N-H…O, C-H…N, O-H…N, N-H…S, N-H…N and C-H…S interactions (supple. Table 3) between the thiadiazole nitrogen adjacent to the thiol sulfur and hydrogen atoms of the water molecules. In addition there are Hg…S and S…S interactions between the sulfur of the thiadiazole ring and the thiol group, leading to a stacked linear type arrangement of molecules (supple, Fig. 7).

5.8. Crystal structure description of $[Cd(mthd)_2(o-phen)_2]_2 \cdot H_2O(4)$

The ORTEP diagram of complex **4** shows that in the centrosymmetric unit of [Cd(mthd)₂ (*o*-phen)₂]₂·H₂O the metal ion is six coordinate octahedral, bonded to two thiol sulfur atoms and four nitrogen atoms of the *o*-phen ligands (Fig. 6). The crystallographic data and structural refinement details of complex **4** are given in Table 1 and selected bond lengths and angles are listed in Table 5. The two *o*-phen ligands bond to cadmium *via* Cd1-N1, Cd1-N2, Cd1-N3 and Cd1-N4 at distances of 2.422(2), 2.409(2), 2.447(2) and 2.391(2) Å respectively (Table 5), and these and the Cd-S (2.623 Å) distances are in the normal ranges reported for Cd-N and Cd-S bond lengths [30,31]. The C-N and C-S bond lengths indicate their double bond and single bond character, respectively, thereby suggesting that the ligand is present in the thiol form in complex **4**. The bond lengths and angles of the heterocyclic ligand moiety (mthd) are comparable to those

found in other monodentate thiadiazole ligands. The elements of the structure are joined to each other in the crystal packing by means of an extended system of H-bonds where a hydrogen atom belonging to the o-phen ligand participates in the structure. The complex is stabilized via intermolecular C-H---O and C-H---S interactions (supple. Table 4) occurring between the oxygen atoms of the water molecule and the thiol sulfur and CH hydrogens of a phenyl ring, leading to a scorpion-like architecture. In addition, there are weak O-H…N interactions between the thiadiazole nitrogen atoms and hydrogen of water molecules, forming a single helix-like structure in complex 4. The thiadiazole ring and one *o*-phen ring are almost parallel ($\angle ACB =$ 77.85°), but they are displaced with respect to each other. The displacement, as measured by the angle formed between the ring centroids AB and the ring normal BC to the thiadiazole plane, was found to be 0.057 Å with a displacement angle of 18.99 °, and the ring centroids contact (Cg...Cg) of 3.662 Å is well within the reported range [32]. The crystal structure of complex 4 is stabilized via $\pi \cdots \pi$ interactions between the thiadiazole ring and one o-phen ring. In addition, there are weak intermolecular $\pi \cdot \pi$ interactions between two *o*-phen rings which are almost parallel [$\angle ACB = 90.34^\circ$, displacement = 0.248 Å, displacement angle = 20.94°, Cg...Cg = 3.901 Å]. The values of the $\pi^{...}\pi$ distances suggest stronger interactions between the o-phen and thiadiazole rings as compared to *o*-phen-*o*-phen ring interactions (supple. Fig. 8).

5.9. Crystal structure description of [Zn(mthd)₂(bpy)] (5)

Fig. 7 shows an ORTEP diagram of $[Zn(mthd)_2(bpy)]$ (5) with the atom numbering scheme. The four coordination number of complex 5 is fulfilled by two nitrogen (adjacent to the thiol sulfur) atoms from two thiadiazole ligands and two nitrogen atoms from one bpy ligand. The crystallographic data and structural refinement details of complex 5 are given in Table 1. The average bond lengths C3-S1 = 1.701(16), C6-S3 = 1.692(16), C2-S2 = 1.680(19) and C5-S4 =

1.722 (17) Å, are normal for thiadiazole complexes. The Zn-N bond distances of 1.942(14), 2.010(13), 2.062(14) and 2.074(13) Å, (Table 6) are comparable to the bond lengths reported for other complexes of Zn(II) containing bpy [33,34]. The shorter Zn-N (thiadiazole) bond length, as compared to Zn-N (bpy), indicates that the thiadiazole nitrogen bonds more strongly than the bpy nitrogen. In the solid state, the complex is stabilized *via* intermolecular C-H…S interactions occurring between the thione sulfur and the CH hydrogen of the bpy ring, forming a one dimensional linear arrangement of molecules. A two dimensional rectangular arrangement of metal atoms is obtained by C-H…S and N-H…S interactions between the molecules (supple. Table 5, Fig. 9).

6. Conclusion

The new complexes [Ni(mthd)₂(py)₂] (1), [Cu(en)₂](mthd)₂ (2), [H₂en][Hg(mthd)₃]₂·2H₂O (3), [Cd(mthd)₂(*o*-phen)₂]₂·H₂O (4) and [Zn(mthd)₂(bpy)] (5), derived from 2-mercapto-5-methyl-1,3,4-thiadiazole, have been synthesized and well characterized by various spectroscopic techniques, including their crystal structure determination. In addition to hydrogen bonding, the complexes [Ni(mthd)₂(py)₂] (1), [H₂en][Hg(mthd)₃]₂·2H₂O (3) and [Cd(mthd)₂(*o*-phen)₂]₂·H₂O (4) contain $\pi \cdots \pi$ interactions which stabilize their structures. The free 2-mercapto-5-methyl-1,3,4-thiadiazole is a less effective sensor, but is a "turn-on" sensor upon complexation with Zn(II), showing high sensitivity and being a selective "turn-off" sensor for the Hg²⁺ metal ion. Photoluminescence studies indicate that the [Zn(mthd)₂(bpy)] complex (5) is a fluorescent material with a maximum emission at 375 nm at an excitation wavelength of 311 nm. The UVvis spectra of the Zn(II) complex with the Hg²⁺ metal ion (in a 1:2 ratio) also indicates the "turnoff" sensing behavior of the complex. Thermogravimetric analysis reveals that the complex

 $[Zn(mthd)_2(bpy)]$ (5) has high thermal stability due to the high dimensionality of the molecule, which encourages its fluorescence behaviour.

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8. Supporting Information

CCDC 864050, 864048, 909609, 864047 and 888324 contain the supplementary crystallographic data for $[Ni(mthd)_2(py)_2]$ (1), $[Cu(en)_2](mthd)_2$ (2), $[H_2en][Hg(mthd)_3]_2 H_2O$ (3), $[Cd(mthd)_2(o-phen)_2]_2 H_2O$ (4) and $[Zn(mthd)_2(bpy)]$ (5), respectively. These data can be obtained free of charge *via* <u>http://www.ccdc.cam. ac.uk/ conts/retrieving.html</u>, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or e-mail: <u>deposit@ccdc. cam. ac.uk</u>.

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Acception



Fig. 1 (a) Absorption spectra (b) Photoluminescent spectra of Hmthd and complexes 1-5 (c = 100μ M)



Fig. 2 (a) Photoluminescent spectra of complex 5 ($c = 100 \mu M$); (b) Relative fluorescence of complex 5 (light grey bar) at 343 nm emission intensity in the presence of different metal ion solutions (black bar).



Fig. 3 Ortep diagram of [Ni(mthd)₂(py)₂] (1)



Fig. 5 Ortep diagram of [H₂en][Hg(mthd)₃]₂·2H₂O (3)



Fig. 7 Ortep diagram of [Zn(mthd)₂(bpy)] (**5**)

Compound	1	2	3	4	5
Empirical formula	C ₁₆ H ₁₆ N ₆ NiS ₄	$C_{10}H_{24}CuN_8S_4$	$C_{20}H_{34}Hg_2N_{14}O_2S_{12}$	$C_{60}H_{44}Cd_2N_{16}OS_8$	$C_{16}H_{14}N_6S_4Zn$
Formula weight	479.32	448.20	1288.63	1486.49	483.90
T (K)	296(2)	296(2)	293(2)	296(2)	293(2)
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	P 21/c	P 21/c	P 1	C 2/c	C 2/c
a (Å)	8.696(3)	6.536(4)	8.434(7)	20.383(6)	8.607(2)
b (Å)	9.212(3)	21.046(12)	9.482(7)	25.541(6)	14.114(15)
c (Å)	12.702(4)	7.252(4)	13.363(7)	14.404(3)	33.874(5)
α (°)	90.00	90.00	79.981(5)	90.00	90.00
β (°)	91.8680(10)	110.396(3)	80.979(6)	125.613(10).00	91.13(2)
γ (°)	90.00	90.00	74.875(7)	90.00	90.00
$V(Å^3)$	1017.11(6)	935.15(9)	1009.11(13)	6096.5(3)	4114.2(12)
Ζ	2	2	1	4	8
D_{calc} (Mg m ⁻³)	1.565	1.592	2.121	1.620	1.563
μ (mm ⁻¹)	1.378	1.624	8.262	1.029	1.614
F(000)	492.0	466.0	620.0	2992.0	1968
Crystal size (mm ³)	0.25x0.23x0.21	0.23x0.19x0.17	0.30x0.27x0.25	0.25x0.21x0.19	0.25x0.23x0.21
θ range (°)	2.34 - 25.00	1.94-28.38	2.93-29.08	1.46-28.04	1.5-23.79
Index ranges	$-10 \le h \le 9$	$-8 \le h \le 8$	-11≤h≤11	-26≤ h ≤26	-11≤h≤11
	$-10 \le k \le 10$	$-27 \le k \le 28$	$-12 \le k \le 12$	$-33 \le k \le 33$	$-19 \le k \le 10$
	$-13 \le l \le 15$	$-9 \le 1 \le 9$	$-13 \le l \le 18$	$-17 \le 1 \le 19$	$-43 \le l \le 46$
Reflections	14561	16951	5434	51280	8523
collected					
Independent	1789	2344	4692	7394	5737
reflections					
Data/restraints/	1789/0/125	2344/0/107	5434/9/397	7394/0/395	5737/0/245
parameters					
Goodness-of-fit on F ²	0.831	0.807	1.023	1.001	1.567
Final R indices	0.0205, 0.0859	0.0367, 0.1062	0.0395, 0.0505	0.0340, 0.1123	0.0442, 0.1031
$wR_2 [I > 2\sigma(I)](R_{int})$					
Final R indices (all data)	0.0224, 0.0907	0.0682, 0.1340	0.0852, 0.0926	0.0484, 0.1349	0.0670, 0.1132
Largest diff	0.2170 198	0.3240.322	1.2491.018	1.5140.667	2,300, -2,302
peak/hole (e Å ⁻³)			,	,,	

Table 1. Crystallographic data for $[Ni(mthd)_2(py)_2]$ (1), $[Cu(en)_2](mthd)_2$ (2), $[H_2en][Hg(mthd)_3]_2 H_2O$ (3),
 $[Cd(mthd)_2(o-phen)_2]_2 H_2O$ (4) and $[Zn(mthd)_2(byy)]$ (5)

^{*a*} $R_1 = \Sigma ||F_0| - |Fc||\Sigma|F_0|.$

^b $R_2 = [\Sigma w(|F_0^2| - |F_c^2|)^2 / \Sigma w |F_0^2|^2]^{1/2}.$

Bond lengths (Å)		Bond angles (°)	
Ni(1)-N(1)	2.074(12)	N(1)-Ni(1)-N(1)	180.0(10)
Ni(1)-N(3)	2.083(12)	N(1)-Ni(1)-N(3)	89.0(5)
Ni(1)-S(1)	2.567(4)	N(1)-Ni(1)-S(1)	112.4(4)
S(1)-C(6)	1.708(15)	N(1)-Ni(1)-S(1)	67.5(4)
N(1)-C(6)	1.315(2)	S(1)-Ni(1)-S(1)	180.0(3)
N(3)-C(1)	1.334(2)	C(6)-S(1)-Ni(1)	73.1(5)
N(3)-C(5)	1.337(2)	C(6)-N(1)-Ni(1)	99.8(9)
N(1)-N(2)	1.378(19)	C(1)-N(3)-Ni(1)	121.9(11)

Table 2. Selected bond lengths (Å) and bond angles (°) for [Ni(mthd)₂(py)₂] (1)

Table 3. Selected bond lengths (Å) and bond angles ($^{\circ}$) for [Cu(en)₂](mthd)₂(2)

Bond lengths (Å)		Bond angles (°)	
Cu(1)-N(4)	2.016(3)	N(4)-Cu(1)-N(4)	180.0(1)
Cu(1)-N(3)	2.022(2)	N(4)-Cu(1)-N(3)	84.1(10)
S(1)-C(3)	1.748(3)	N(3)-Cu(1)-N(3)	180.0(1)
N(1)-N(2)	1.388(4)	C(4)-N(3)-Cu(1)	108.4(18)
N(2)-C(3)	1.318(4)	C(5)-N(4)-Cu(1)	108.7(18)
C(3)-S(2)	1.700(3)		

Table 4. Selected bond lengths (Å) and bond angles (°) for $[H_2en][Hg(mthd)_3]_2 2H_2O(3)$

Bond lengths (Å)		Bond angles (°)	
Hg(1)-S(1)	2.443(6)	S(1)-Hg(1)-S(3)	119.3(2)
Hg(1)-S(3)	2.477(7)	S(1)-Hg(1)-S(5)	121.5(2)
Hg(1)-S(5)	2.447(6)	S(3)-Hg(1)-S(5)	118.7(2)
S(1)-C(1)	1.65(2)	C(1)-S(1)-Hg(1)	105.2(9)
S(2)-C(1)	1.79(2)	C(1)-S(2)-C(2)	91.3(10)
N(1)-N(2)	1.42(3)	N(1)-C(1)-S(2)	108.9(16)
C(1)-N(1)	1.33(3)	N(1)-C(1)-S(1)	129.2(17)
C(20)-N(14)	1.54(2)	C(1)-N(1)-N(2)	114.7(17)
N(13)-C(19)	1.42(2)	N(14)-C(20)-C(19)	109.4(10)

Table 5. Selected bond lengths (Å) and bond angles (°) for [Cd(mthd)₂(o-phen)₂]₂·H₂O (4)

Bond lengths (Å)		Bond angles (°)	
Cd(1)-N(1)	2.422(2)	N(4)-Cd(1)-N(2)	90.6(8)
Cd(1)-N(2)	2.409(2)	N(4)-Cd(1)-N(1)	153.9(8)
Cd(1)-S(1)	2.623(9)	N(2)-Cd(1)-N(1)	69.1(8)
S(1)-C(25)	1.721(3)	N(4)-Cd(1)-S(1)	107.3(7)
S(2)-C(25)	1.727(3)	N(2)-Cd(1)-S(1)	156.7(6)
N(1)-C(5)	1.357(3)	N(1)-Cd(1)-S(1)	89.1(6)
N(2)-C(9)	1.363(4)	C(25)-S(1)-Cd(1)	105.8(11)
N(5)-N(6)	1.318(5)	C(5)-N(1)-Cd(1)	115.7(17)

Bond lengths (Å	A)	Bond angles (^c	')
Zn(1)-N(1)	1.942(14)	N(1)-Zn(1)-N(3)	118.4(6)
Zn(1)-N(3)	2.010(13)	N(1)-Zn(1)-N(6)	130.3(6)
Zn(1)-N(6)	2.062(14)	N(3)-Zn(1)-N(6)	101.0(5)
Zn(1)-N(5)	2.074(13)	N(3)-Zn(1)-N(5)	121.9(6)
S(1)-C(3)	1.701(16)	N(1)-Zn(1)-N(5)	101.2(5)
C(16)-N(6)	1.355(17)	N(6)-Zn(1)-N(5)	79.6(5)
N(1)-C(3)	1.42(2)	C(3)-N(1)-N(2)	108.2(14)
N(1)-N(2)	1.407(15)	C(3)-N(1)-Zn(1)	118.3(10)
C(7)-N(5)	1.354(16)	N(2)-N(1)-Zn(1)	133.2(13)
N(5)-C(11)	1.34(2)	C(11)-N(5)-Zn(1)	114.0(10)
N(6)-C(12)	1.35(2)	N(1)-C(3)-S(1)	118.0(12)

 Table 6. Selected bond lengths (Å) and bond angles (°) for [Zn(mthd)₂(bpy)] (5)

Graphical Abstract (Picture)



Graphical Abstract (Synopsis)

The new complexes $[Ni(mthd)_2(py)_2]$ (1), $[Cu(en)_2](mthd)_2$ (2), $[H_2en][Hg(mthd)_3]_2$ $2H_2O(3)$, $[Cd(mthd)_2(phen)_2]_2 \cdot H_2O(4)$ and $[Zn(mthd)_2(bpy)](5)$ (Hmthd = 2-mercapto-5-methyl-1,3,4-thiadiazole) have been synthesized. The ligand is present in the deprotonated thiol form in the $[Cu(en)_2](mthd)_2$ and $[Cd(mthd)_2(phen)_2]_2 \cdot H_2O$ complexes. In complex 2, the ligand is ionically bonded, whereas it is covalently bonded through sulfur in complex 4. In $[Ni(mthd)_2(py)_2]$ (1) the ligand is N,S chelating bidentate bonded through the thiol sulfur and thiadiazole ring nitrogen atoms, forming a four membered chelate ring. The ligand is covalently bonded through the deprotonated thiadiazole ring nitrogen in $[Zn(mthd)(bpy)_2]$ (5). In the complex $[H_2en][Hg(mthd)_3 \frac{1}{2}$ 2H₂O (3) the complex anion has a triangular planar geometry, being bonded to the deprotonated thiolato sulfur atoms from the three ligands. Complex 5 upon interaction with Hg²⁺ illustrates a hypochromic shift in the absorption spectra, whereas the emission spectra exhibites 75% quenching fluorescence behaviour. The electrochemical studies also suggest the interaction of Hg(II) with the Zn(II) complex, probably via free thione sulfur.