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Predominant ionic interactions in CdS_4N_2 and HgS_4 coordination environments

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Synthesis and spectral investigation of [Cd(cpzdtc)$_2$] (**1**), [Cd(cpzdtc)$_2$(1,10-phen)] (**2**), [Cd(cpzdtc)$_2$(2,2′-bipy)]·0.4H$_2$O (**3**), [Hg(cpzdtc)$_2$] (**4**), [Hg(cpzdtc)$_2$(1,10-phen)] (**5**), [Hg (cpzdtc)$_2$(2,2′-bipy)] (**6**) (where cpzdtc = cinnamylpiperazinedithiocarbamate, 1,10-phen = 1,10-phenanthroline and 2,2′-bipy = 2,2′-bipyridine) and single-crystal X-ray structures of **3** and **4** are reported. ^{1}H NMR spectra show deshielding of the protons attached to C4 and C4′ and ^{13}C NMR signal of the thioureide carbons are observed at 203.4, 206.6, 206.5, 203.3, 206.7 and 206.6 ppm for **1**–**6**. X-ray photoelectron spectroscopy (XPS) chemical shifts clearly indicate localization of positive charge on the central metal ions and for adducts involving mercury, very little change is observed in the binding energies of $Hg_{4f7/2}$, N_{1s} and S_{2s} electrons, indicating predominant ionic interaction. Single-crystal X-ray structural analysis of **3** showed cadmium is in a distorted octahedral environment with CdS_4N_2 chromophore, whereas in **4**, mercury is in a distorted tertrahedral coordination environment. BVS values were 1.993 for **3** and 2.166 for **4**, supporting predominantly ionic interaction consistent with XPS data.

Keywords: Cadmium; Mercury; Ionic interaction; X-ray crystal structures; Thioureide

1. Introduction

Metal-dithiolate compounds have varied applications in chemical, agriculture, and pharmaceutical industries [1]. Dithiocarbamates are versatile ligands which bind to a number of transition and main group elements, including cadmium and mercury, supporting a wide range of oxidation states [2]. In medicine, tetraethylthiuram disulfide is used as an aldehyde dehydrogenase inhibitor and hence in treating chronic alcoholism. Tetraethylthiuram disulfide exhibits anticancer and anti-HIV properties [3,4]. Gold dithiocarbamates are potential antitumor agents [5]. Metal compounds of dithiocarbamates serve as highly efficient precursors for nano-metal sulfides and some materials synthesized from metal dithiocarbamates are molecular rectifiers [6–8]. Group 12 metals interact with dithiocarbamates and nitrogenous bases extensively [9–11]. Interaction of cadmium has been described as being ionic, whereas mercury has been described as being covalent due to its soft nature. Bond valence sum (BVS) model is obeyed by those molecules which have

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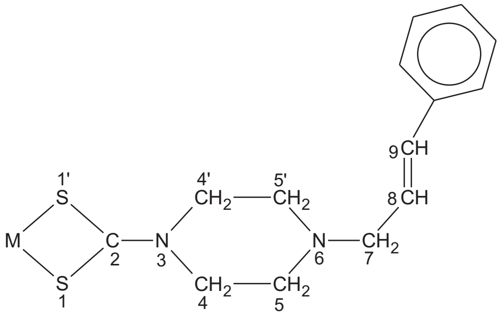
predominant ionic interactions and hence provide a means of identifying the nature of interaction in compounds [12]. BVS is calculated from the bond distances determined from single-crystal X-ray diffraction. According to BVS model, the oxidation state Vi of a bonded atom is equivalent to the sum of the individual bond valences s_{ij}: $Vi = \Sigma\ s_{ij}$, where i denotes an atom bonded to j and $s_{ij} = \exp\{r_0 - r_{ij}/b\}$. The b parameter is commonly taken to be a "universal constant" equal to 0.37, r_{ij} is the bond distance from the X-ray structure determination, and the r_0 parameters have been directly calculated or extrapolated [13,14] for a large number of ion (atom) pairs. Atom i is usually chosen as an electropositive atom (cation) and atom j as an electronegative atom (anion) [13]. In continuation of our interest in understanding the structure and properties of group 12 dithiocarbamates and their adducts, this article reports the synthesis and characterization of simple and mixed ligand complexes involving cinnamylpiperazine dithiocarbamate (A), 1,10-phenanthroline, 2,2′-bipyridine, Cd(II) and Hg(II) and analyzes the nature of interaction prevailing in two of the compounds whose crystal structures have been determined.



(A)

2. Experimental

All reagents and solvents were commercially available analytical grade materials (E Merck) and were used as supplied. IR spectra were recorded on an Avatar Nicolet FT-IR spectrophotometer (4000–500 cm^{-1}) as KBr pellets. NMR spectra were recorded as saturated $CDCl_3$ solutions at room temperature on Bruker AMX-400 and Bruker AV400 spectrometers. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Shimadzu ESCA 3400 X-ray photoelectron spectrometer and MgKα X-ray was the excitation source; the C1s signal (contamination) was used as the reference for correction [15].

2.1. *X-ray crystallography*

Intensity data were collected at ambient temperature (295 K) using graphite monochromated MoKα radiation (Kα = 0.71073 Å) on a Bruker Charge-coupled device (CCD) diffractometer for **3** and **4**. Data were corrected for absorption using SADABS and ω-scan technique was used for data collection [16,17]. Structure was solved with SHELX97-S and was refined by SHELX97-L [18]. All non-hydrogen atoms were refined anisotropically and all hydrogens were fixed geometrically. ORTEP-3 was used for drawing the molecular plots [19]. Mercury program was used for plotting the non-covalent interactions in the molecules [20].

2.2. *Preparation of [Cd(cpzdtc)$_2$] (1)*

Cinnamylpiperazine (2 mmol) and carbon disulphide (2 mmol) in ethanol (10 mL) were mixed under ice-cold conditions (5 °C) to form a yellow solution of dithiocarbamic acid. An aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ (1 mmol) was then added with continuous stirring. A pale yellow precipitate was obtained, which was washed with ethanol and then dried in air. (Yield: 72%; dec.: 209–211 °C.) Anal. Calcd for $C_{28}H_{34}CdN_4S_4$ (666.79): C, 50.40; H, 5.14; N, 8.40. Found: C, 50.37; H, 5.10; N, 8.36%.

2.3. *Preparation of [Cd(cpzdtc)$_2$(1,10-phen)] (2)*

A mixture of Cd(cpzdtc)$_2$ (0.25 mmol, 0.167 g) and 1,10-phen (0.25 mmol, 0.049 g) in chloroform–toluene (1:2 v/v; 20 mL) was refluxed for 2 h followed by concentration to 10 mL. After two days, a pale yellow solid separated from the solution. The solid was filtered and dried over anhydrous calcium chloride. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of chloroform and toluene (1:1 v/v) solution of the compound. (Yield: 62%; dec.: 237–239 °C.) Anal. Calcd for $C_{40}H_{42}CdN_6S_4$ (846.89): C, 65.36; H, 5.76; N, 11.43. Found: C, 65. 32; H, 5.71; N, 11.37%.

2.4. *Preparation of [Cd(cpzdtc)$_2$(2,2′-bipy)]·0.4 H_2O (3)*

A mixture of Cd(cpzdtc)$_2$ (0.25 mmol, 0.167 g) and 2,2′-bipy (0.25 mmol, 0.039 g) in chloroform-toluene (1:2 v/v; 20 mL) was refluxed for 2 h followed by concentration to 10 mL. After two days, a colorless solid separated from the solution. The solid was filtered and dried over anhydrous calcium chloride. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of chloroform and toluene (1:1 v/v) solution of the compound. (Yield: 61%; dec.: 184–187 °C.) Anal. Calcd for $C_{38}H_{42.80}CdN_6O_{0.40}S_4$ (830.62): C, 54.95; H, 5.19; N, 10.12. Found: C, 54.91; H, 5.16; N, 10.06 %.

2.5. *Preparation of [Hg(cpzdtc)$_2$] (4)*

Cinnamylpiperazine (2 mmol) and carbon disulfide (2 mmol) in ethanol (10 mL) were mixed under ice-cold condition (5 °C) to form a yellow solution of dithiocarbamic acid. An aqueous solution of $HgCl_2$ (1 mmol, 0.271 g, 25 mL of H_2O) was then added with continuous stirring. A colorless precipitate was obtained, which was washed with ethanol and then dried in air. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of acetonitrile and chloroform (1:1 v/v) solution of the compound. (Yield: 59%; dec.: 170–174 °C.) Anal. Calcd for $C_{28}H_{34}HgN_4S_4$ (755.40): C, 44.52; H, 4.54; N, 7.42. Found: C, 44.49; H, 4.51; N, 7.39 %.

2.6. *Preparation of [Hg(cpzdtc)$_2$(1,10-phen)] (5)*

A mixture of Hg(cpzdtc)$_2$ (0.25 mmol, 0.189 g) and 1,10-phen (0.25 mmol, 0.049 g) in acetonitrile–chloroform (2:1 v/v; 20 mL) was refluxed for 2 h followed by concentration to 10 mL. After two days, a pale yellow solid separated from the solution. The solid was filtered and dried over anhydrous calcium chloride. (Yield: 68%; dec.: 178–181 °C.) Anal. Calcd for $C_{40}H_{42}HgN_6S_4$ (935.07): C, 51.35; H, 4.52; N, 8.98. Found: C, 51.31; H, 4.49; N, 8.95%.

2.7. *Preparation of [Hg(cpzdtc)$_2$(2,2′-bipy)] (6)*

A mixture of Hg(cpzdtc)$_2$ (0.25 mmol, 0.189 g) and 2,2′-bipy (0.25 mmol, 0.039 g) in acetonitrile–chloroform (2:1 v/v; 20 mL) was refluxed for 2 h followed by concentration to 10 mL. After two days, a pale yellow solid separated from the solution was filtered and dried over anhydrous calcium chloride. (Yield: 63%; dec.: 182–184 °C.) Anal. Calcd for $C_{38}H_{42}HgN_6S_4$ (911.07): C, 50.07; H, 4.64; N, 9.22. Found: C, 50.04; H, 4.61; N, 9.19%.

3. Results and discussion

3.1. *Infrared spectral studies*

Selected infrared spectral data are given in table 1. The $\nu_{C–N}$(thioureide) appears at 1468–1508 cm^{-1}. Thioureide bands of adducts of cadmium show a lowering of wavenumber compared with the parent but the trend is reversed for mercury. Bands of $\nu_{C–S}$ are observed at 1015–1032 cm^{-1} (**1–6**) without a split supporting bidentate coordination of the dithiocarbamate. The phenyl ring $\nu_{C–H}$ is at 2915–2760 cm^{-1} in the complexes. Characteristic bands due to 1,10-phen and 2,2′-bipy are at 1638–1590 cm^{-1} (1,10-phen) and 1647–1579 cm^{-1} (2,2′-bipy). Other bands due to 1,10-phen and 2,2′-bipy are masked by those of dithiocarbamate.

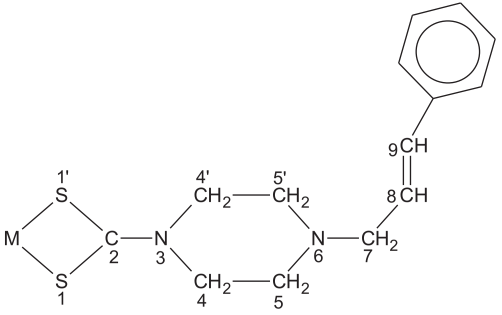
3.2. *NMR spectral studies*

NMR (^{1}H and ^{13}C) spectral data of the compounds are given in table 2. A triplet at 2.54–2.65 ppm is due to methylene protons at C5 and C5′ and another triplet at 4.06–4.25 ppm is assigned to protons (methylene) attached to C4 and C4′. The observed deshielding of the –CH$_2$ protons is attributed to shift of electron density towards nitrogen of NR$_2$, forcing high electron density on the sulfur (or the metal) through the thioureide pi-system. However, the C(7)H$_2$, C(8)H and C(9)H of the cinnamyl group resonate at 3.15–3.21 (d), 6.19–6.28 (m) and 6.48–6.576(d) ppm, respectively. Signals at 7.21–9.04 ppm are due to phenyl ring protons and merge with signals of the ring protons of 1,10-phen and 2,2′-bipy.

Table 1. Infrared spectral data (cm^{-1}).

Complex	$\nu_{C–N}$ (thioureide)	$\nu_{C–S}$	$\nu_{C–H}$	1,10-Phen/2,2′-bipy/ 4,4′-bipy ring frequencies
[Cd(cpzdtc)$_2$] (**1**)	1476	1015	2915, 2814, 2859, 2767	–
[Cd(cpzdtc)$_2$(1,10-phen)] (**2**)	1468	1018	2919, 2808, 2851, 2767	1638, 1593
[Cd(cpzdtc)$_2$(2,2′-bipy)]·0.4 H$_2$O (**3**)	1468	1020	2919, 2851, 2808, 2761	1593, 1643
[Hg(cpzdtc)$_2$] (**4**)	1477	1019	2920, 2861, 2806, 2761	
[Hg(cpzdtc)$_2$(1,10-phen)] (**5**)	1508	1021	2922, 2849, 2802, 2760	1590, 1621
[Hg(cpzdtc)$_2$(2,2′-bipy)] (**6**)	1484	1032	2921, 2852, 2812, 2767	1579, 1647

Table 2. ^{1}H and ^{13}C NMR spectral data (ppm).



Complex	NMR	$N^{13}CS_2$ (thioureide)	CH_2(C4, C4′)	CH_2(C5, C5′)	CH_2(C7)	CH(C8)	CH(C9)	Aromatic ring protons/carbons
[Cd(cpzdtc)$_2$] (**1**)	^{1}H	–	4.22–4.25 (t)	2.63–2.65 (t)	3.19–3.21 (d)	6.20–6.27 (m)	6.52–6.56 (d)	7.24–7.38[a]
	^{13}C	203.4	52.4	52.9	60.4	125.5	126.4	127.8–136.6[a]
[Cd(cpzdtc)$_2$(1,10-phen)] (**2**)	^{1}H	–	4.22–4.24 (t)	2.54–2.56 (t)	3.15–3.17 (d)	6.21–6.25 (m)	6.49–6.53 (d)	7.22–9.04[b]
	^{13}C	206.6	52.3	52.7	60.7	125.7	126.0	121.3–149.8[b]
[Cd(cpzdtc)$_2$(2,2′-bipy)].0.4H$_2$O (**3**)	^{1}H	–	4.22–4.24 (t)	2.54–2.57 (t)	3.16–3.17 (d)	6.20–6.27 (m)	6.48–6.54 (d)	7.21–9.02[b]
	^{13}C	206.5	52.1	52.5	60.5	125.8	126.3	121.2–150.6[b]
[Hg(cpzdtc)$_2$] (**4**)	^{1}H	–	4.06–4.09 (t)	2.61–2.63 (t)	3.19–3.21 (d)	6.19–6.26 (m)	6.52–6.56 (d)	7.24–7.39[a]
	^{13}C	203.3	52.3	53.2	60.4	125.5	126.4	127.8–136.6[a]
[Hg(cpzdtc)$_2$(1,10-phen)] (**5**)	^{1}H	–	4.23–4.25 (t)	2.54–2.57 (t)	3.16–3.17 (d)	6.22–6.26 (m)	6.50–6.54 (d)	7.23–9.05[b]
	^{13}C	206.7	52.3	52.7	60.7	125.8	126.1	121.4–149.9[b]
[Hg(cpzdtc)$_2$(2,2′-bipy)] (**6**)	^{1}H	–	4.22–4.25 (t)	2.55–2.58 (t)	3.16–3.18 (d)	6.21–6.28 (m)	6.49–6.56 (d)	7.21–9.02[b]
	^{13}C	206.6	52.2	52.6	60.6	125.9	126.4	121.3–150.7[b]

^{13}C NMR signals of the thioureide carbons are at 203.4, 206.6, 206.5, 203.3, 206.7 and 206.6 ppm for **1–6**, respectively. The methylene carbons (C4, C4′), (C5, C5′) and (C7) appear at 52.1–60.7 ppm. The olefinic carbons, C8 and C9 are at 125.5–126.4 ppm and are not greatly affected on complexation. Aromatic carbon signals are observed at 121.3–150.7 ppm; signals of 1,10-phen and 2,2′-bipy merge with the ring carbon signals of cinnamylpiperazine. Generally, the deshielding of ^{13}C(S2) in main group metal dithiocarbamates is greater than those of normal valence state transition metal dithiocarbamates, which is in line with the observed thioureide carbon chemical shifts of the synthesized compounds [21].

3.3. *X-ray photoelectron spectral studies*

X-ray photoelectron spectral data for the complexes are given in table 3. Representative XPS binding energies corresponding to Cd_{3d}, Hg_{4f}, N_{1s} and S_{2s} electrons of [Cd(cpzdtc)$_2$] (**1**) and [Hg(cpzdtc)$_2$] (**4**) are shown in Supplementary material. For **1**, $Cd_{3d5/2}$-binding energy was 404.7(2.0) eV and the corresponding free element value is 403.7 eV [22]. A well marked increase indicates increased positive charge on cadmium corresponding to its divalent state. S_{2s}-binding energy was 226.1 (1.4) eV, which showed little change compared with the bare element (226.6 eV). For adducts, all three binding energies measured for $3d_{5/2}$, N_{1s}, and S_{2s} electrons showed a further decrease compared with the parent, indicating increased electron density. The $Hg_{4f7/2}$-binding energy measured for **4**, 101.3(1.1) eV, clearly indicates localization of positive charge on it when compared with the corresponding free element value 99.8 eV. Binding energy of N_{1s} electron showed very little decrease compared with the free element. However, the S_{2s}-binding energy showed a significant decrease in magnitude. On adduct formation with 1,10-phen, binding energies of mercury did not change significantly. In the adduct, though, the binding energy of S_{2s} electron showed a small increase, N_{1s}-binding energy remained the same. Shifts observed for the parent and adducts clearly indicate localization of positive charge on the metal ions. Particularly in the case of adducts involving cadmium, increasing ease of electron removal is observed. For mercury complexes, very little change is observed in the binding energies of $Hg_{4f7/2}$, N_{1s}, and S_{2s} electrons compared with free element values, due to predominant ionic interactions.

3.4. *Structural analysis*

Crystal data collection and refinement parameters for **3** and **4** are summarized in table 4. Selected bond distances and angles are given in table 5.

Table 3. X-ray photoelectron spectral data.

	Binding energy (eV)			
Complex	$Cd_{3d5/2}$	$Hg_{4f7/2}$	N_{1s}	S_{2s}
[Cd(cpzdtc)$_2$] (**1**)	404.7 (2.0)	–	399.3 (2.0)	226.1 (1.4)
[Cd(cpzdtc)$_2$(1,10-phen)] (**2**)	404.2 (1.3)	–	399.1 (1.2)	225.4 (1.1)
[Cd(cpzdtc)$_2$(2,2′-bipy)].0.4 H_2O (**3**)	404.2 (1.2)	–	399.0 (1.1)	225.1 (2.0)
[Hg(cpzdtc)$_2$] (**4**)	–	101.3 (1.1)	399.3 (1.3)	225.7 (1.3)
[Hg(cpzdtc)$_2$(1,10-phen)] (**5**)	–	101.1 (1.4)	399.3 (1.2)	225.3 (2.0)

FWHM values are given in parentheses.

Table 4. Data collection and refinement parameters for **3** and **4.**

Complex	**3**	**4**
Empirical formula	$C_{38}H_{42.80}CdN_6S_4O_{0.40}S_4$	$C_{28}H_{34}HgN_4S_4$
Formula weight	830.6	755.4
Crystal dimensions (mm)	0.06 × 0.08 × 0.21	0.18 × 0.15 × 0.07
Crystal system	Triclinic	Monoclinic
Space group	P–1	P21/c
a (Å)	9.068(3)	8.4927(4)
b (Å)	14.363(5)	33.5979(16)
c (Å)	16.482(6)	10.7380(5)
α (°)	104.299(4)	90
β (°)	101.570(4)	94.7951(9)
γ (°)	91.924(4)	90
U (Å^3)	2030.1(12)	3053.2(2)
Z	2	4
D_c (g cm^{-3})	1.359	1.643
μ (cm^{-1})	0.779	5.339
Diffractometer	Bruker APEX–II CCD	Bruker APEX–II CCD
Scan type	ω scans	ω scans
Index ranges	$-10 \leqslant h \leqslant 10$; $-17 \leqslant k \leqslant 17$; $-19 \leqslant l \leqslant 19$	$-10 \leqslant h \leqslant 10$; $-40 \leqslant k \leqslant 40$; $-13 \leqslant l \leqslant 13$
Reflections collected	16,469	34,546
Unique reflections	7358	5676
Observed reflections $F_o > 4\sigma(F_o)$	2819	3643
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0229P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2 + 6.0696P]$, where $P = (F_o^2 + 2F_c^2)/3$
Final R, R_w	0.0757, 0.1065	0.0508, 0.1157
Goodness-of-fit	0.995	1.069

Table 5. Selected bond distances (Å) and angles (°) for **3** and **4**.

3				**4**			
Cd1–N5	2.379(6)	N5–Cd1–N6	67.4(2)	Hg1–S2	2.3955(18)	S2–Hg1–S3	151.74(8)
Cd1–N6	2.402(7)	N5–Cd1–S2	131.96(17)	Hg1–S3	2.4498(18)	S2–Hg1–S4	135.47(7)
Cd1–S2	2.619(2)	N6–Cd1–S1	124.08(18)	Hg1–S4	2.6944(17)	S3–Hg1–S4	70.21(5)
Cd1–S1	2.695(2)	S2–Cd1–S1	67.81(7)	Hg1–S1	2.787(2)	S2–Hg1–S1	68.93(6)
Cd1–S4	2.695(2)	N5–Cd1–S4	93.41(18)	S1–C1	1.698(6)	S3–Hg1–S1	120.45(7)
Cd1–S3	2.706(3)	N6–Cd1–S4	133.94(17)	S2–C1	1.744(7)	S4–Hg1–S1	107.49(6)
S1–C1	1.742(8)	S2–Cd1–S4	127.66(8)	S3–C15	1.720(6)	C1–S1–Hg1	80.7(2)
S2–C1	1.713(8)	S1–Cd1–S4	94.66(7)	S4–C15	1.723(6)	C1–S2–Hg1	92.4(2)
S3–C15	1.713(8)	N5–Cd1–S3	115.62(17)	N1–C1	1.314(7)	C15–S3–Hg1	89.3(2)
S4–C15	1.703(9)	N6–Cd1–S3	84.58(18)	N1–C5	1.458(8)	C15–S4–Hg1	81.51(2)
N1–C1	1.318(9)	S2–Cd1–S3	104.59(8)	N1–C2	1.463(8)	C1–N1–C5	123.7(5)
N1–C5	1.468(9)	S1–Cd1–S3	149.65(8)	N2–C3	1.444(8)	C1–N1–C2	124.6(6)
N1–C2	1.482(9)	S4–Cd1–S3	66.01(7)	N2–C4	1.454(7)	C5–N1–C2	111.6(5)
N2–C3	1.480(9)	C1–S1–Cd1	85.5(3)	N2–C6	1.459(8)	C3–N2–C4	108.8(5)
N2–C4	1.485(9)	C1–S2–Cd1	88.5(3)	N3–C15	1.322(7)	C3–N2–C6	111.0(5)
N2–C6	1.500(10)	C15–S3–Cd1	87.2(3)	N3–C19	1.456(8)	N1–C1–S1	123.1(5)
N3–C15	1.337(9)	C15–S4–Cd1	87.8(3)	N3–C16	1.469(8)	N1–C1–S2	118.9(5)
N3–C16	1.461(9)	C1–N1–C5	126.6(7)	N4–C18	1.446(8)	S1–C1–S2	118.0(4)
N3–C19	1.492(9)	C1–N1–C2	121.9(7)	N4–C20	1.451(8)	N1–C2–C3	111.3(5)

The ORTEP diagram of [Cd(cpzdtc)$_2$(2,2′-bipy)]·0.4H$_2$O (**3**) is shown in figure 1. Two molecules of **3** are present in the unit cell. The cadmium is in a distorted octahedral environment of CdS$_4$N$_2$ with four sulfurs from two chelating dithiocarbamates and two

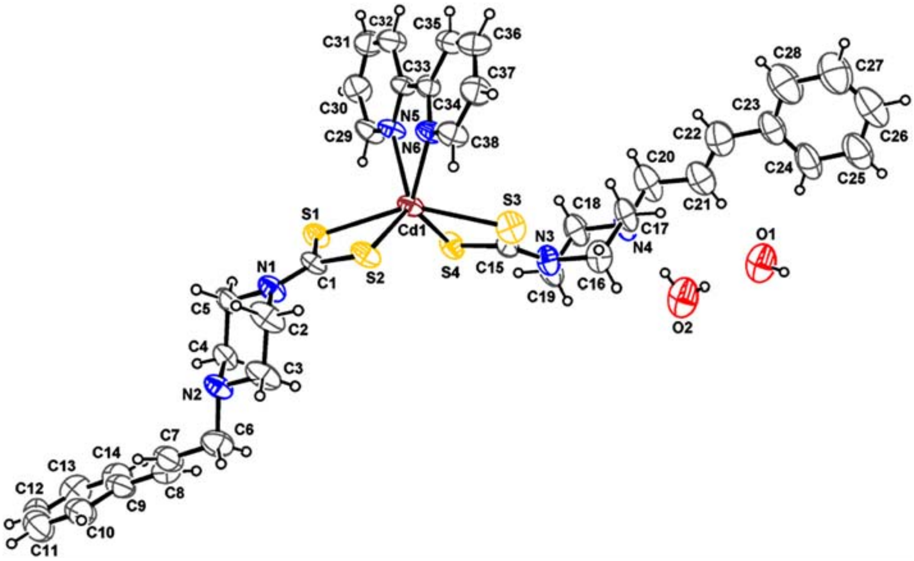


Figure 1. ORTEP of [Cd(cpzdtc)$_2$(2,2′-bipy)]·0.4H$_2$O.

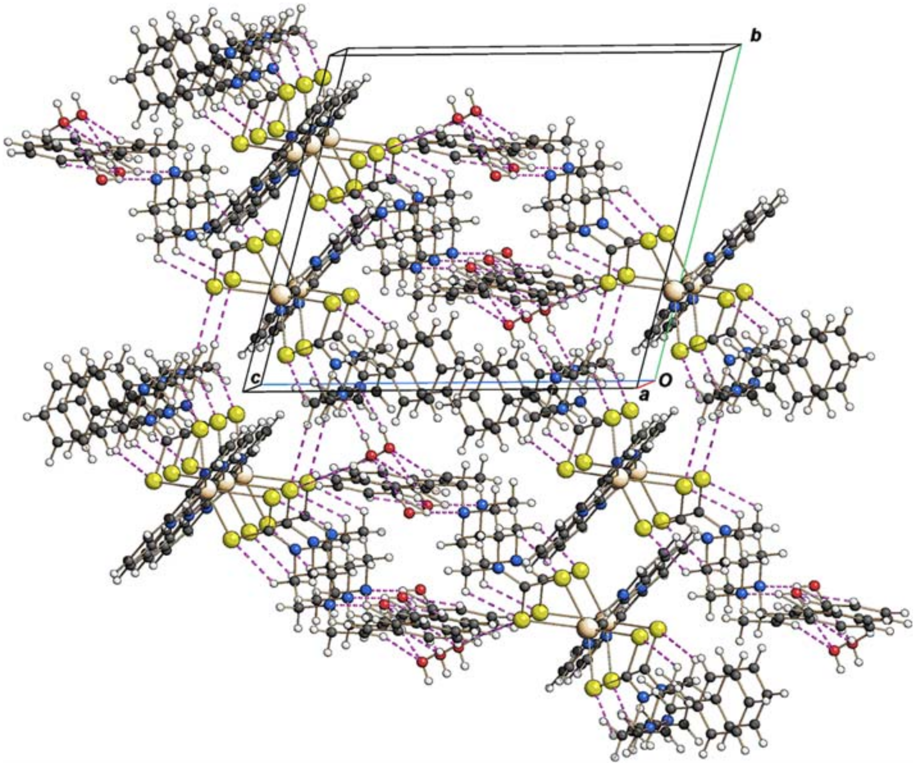


Figure 2. Stacked molecules of **3**.

nitrogens from 2,2′-bipy. Pyridine rings of 2,2′-bipy are not coplanar, slightly tilted by an angle of 10.88° with respect to each other. The MS_2C ring is almost planar as observed in other dithiocarbamato complexes. In **3**, there is a significant difference between Cd–S distances (2.695(2), 2.619(2), 2.706(3), 2.695(2) Å). Of the two pairs of C–S distances (1.742(8), 1.713(8), 1.713(8), 1.703(9) Å), there is a significant asymmetry in one of the pairs considering the esds associated with the distances. The short thioureide (C–N) distances (1.318(9) and 1.377(9) Å) indicate delocalization of π-electron density on S_2CN and the contribution of thioureide bond to the structure. The S–Cd–S bite angles (67.81(7) and 66.01(7)°) are significantly lower than the angles associated with similar bisdithiocarbamates, due to increase in coordination number and steric influence of 2,2′-bipy. The Cd–N distances are asymmetric (2.379(6) and 2.402(7) Å) and the N(5)–Cd(1)–N(6) angle is 67.4(2)°, less than the normal octahedral bond angle due to chelation. The bond parameters associated with the dithiocarbamate and 2,2′-bipy rings show normal values. figure 2 shows the perfect stacking observed in the molecule. The unit cell contains a non-integer number of atoms of a given type because of partially occupied (solvent) sites and substitutional disorder. This disorder is also responsible for large Hirshfield displacements.

An ORTEP perspective of [Hg(cpzdtc)$_2$] (**4**) is shown in the figure 3. [Hg(cpzdtc)$_2$] (**4**) contains four molecules per unit cell. The central mercury is in a distorted tetrahedral environment of four sulfurs from two chelating cinnamylpiperazinedithiocarbamate groups (MS_4 coordination). Short thioureide C–N distances (1.314(7) and 1.322(7) Å) indicate that the π-electron density is delocalized over the S_2CN, and the bond has strong double-bond character. The observation is also supported by the fact that S–C–N angles (123.1(5) and 118.9(5)°) are greater than those of S–C–S angles (118.0(4)°). Very small bite angles (68.93(6) and 70.21(5)°) of dithiocarbamate leads to a distorted tetrahedral geometry. The significant asymmetry in pairs of Hg–S bonds (2.787(2), 2.3955(18), 2.4498(18), and

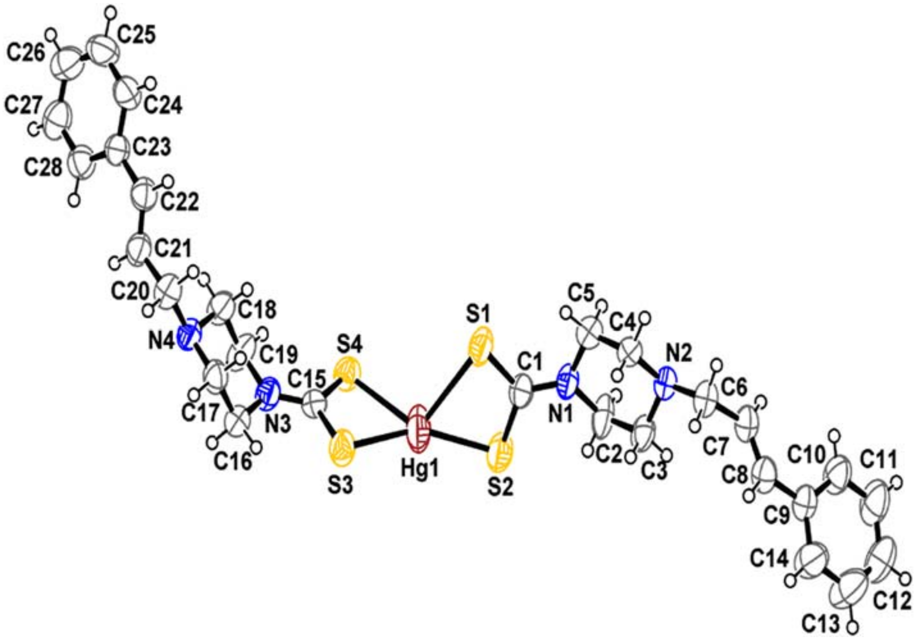


Figure 3. ORTEP of [Hg(cpzdtc)$_2$].

2.6944(17) Å) indicates that the negative charge is localized on one sulfur of the dithiocarbamate, clearly indicating ionic binding. The phenyl and alkyl groups attached to the cinnamylpiperazinedithiocarbamate show normal bond parameters. Large Hirshfield displacement and Ueq values for some bonds are due to the presence of heavy mercury in the molecule.

3.5. *Weak non-covalent interactions*

Figure 4 shows the non-covalent interactions in [Cd(cpzdtc)$_2$(2,2′-bipy)]·0.4 H_2O, where non-covalent S···H interactions contribute significantly to the stabilization of the molecule. Four such interactions S2···H36(bipy-bipy): 2.937 Å; S2···H3B (equatorial proton of

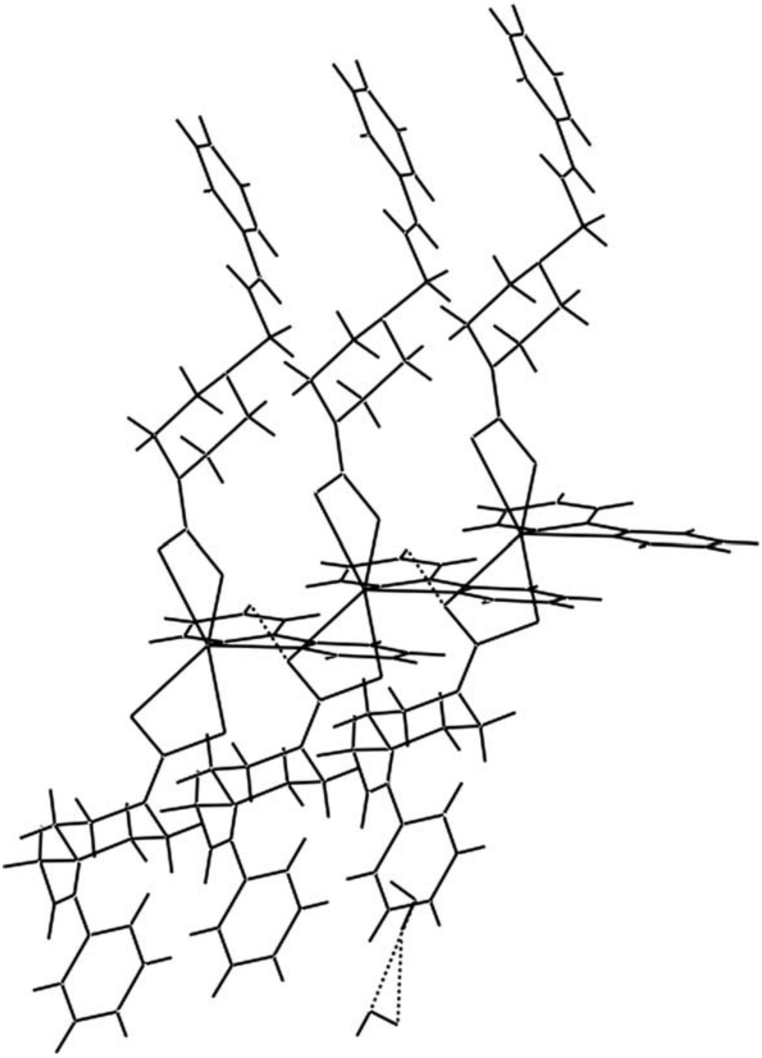


Figure 4. Weak non-covalent interactions in **3**.

piperazine): 2.816 Å; S3···H1W (water): 2.782 Å; S4···H29 (bipy) prevail per molecule. In the crystal structure of $\{Zn[S_2CN(CH_2CH_2OH)Et]_2\}_2$ [23], dinuclear molecules are connected into straight chains mediated by O–H···O interactions. The 1D polymers thus formed are connected into a layer *via* O–H···S interactions. Additional stability to the layers is afforded by C–H···O and C–H···S contacts and S···H interactions in bis(diallyldithiocarbamato)zinc(II) [24]. Similarly, 01W and 02W of water show short contacts with hydrogen, carbon and nitrogen. However, the positions of oxygens are clouded by the associated disorder. The molecules are packed along the *a*-axis.

Weak non-covalent interactions observed in $[Hg(cpzdtc)_2]$ are shown in figure 5. In **4**, S3···S3 non-bonded interaction observed at 3.231 Å is responsible for the stabilization of the molecule in the solid state. For $MeHg(S_2CNEt_2)$ [25], $PhHg(S_2CN(CH_2)_4)$ [26], and $PhHg(S_2CN(nPr)_2$ [27], molecules in the crystalline state are held together by similar S···S weak non-covalent interactions. In addition, non-covalent interactions such as S2···C19 (3.485 Å) and S2···N3 (3.330 Å) prevail in the complex. A short H2A···H26 (2.3893 Å) is due to packing requirements in the solid structure.

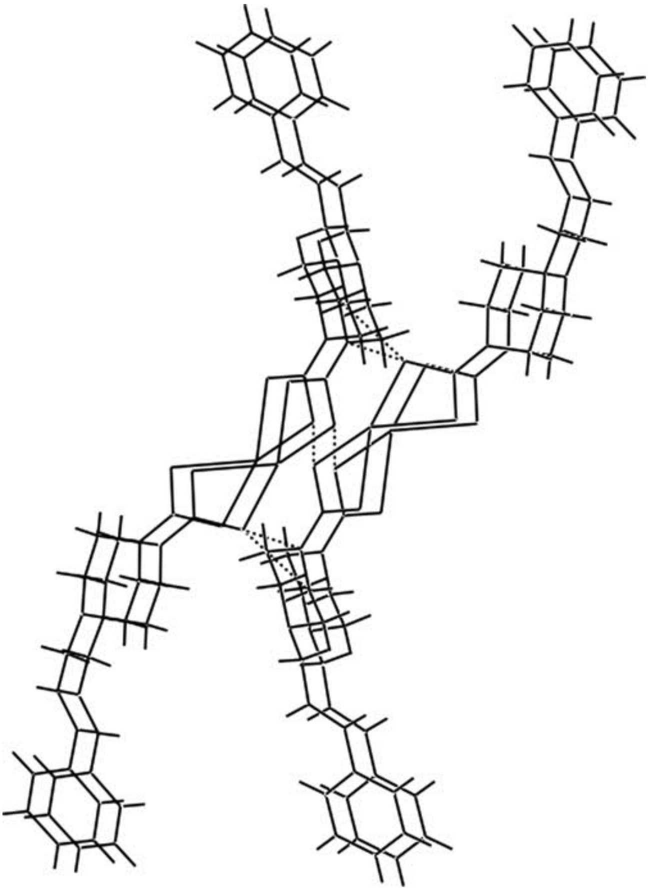


Figure 5. Weak non-covalent interactions in **4**.

Table 6. BVS* calculation for 3.

S. No.	Bond	Bond distance (Å)	v_{ij} = exp $((R_{ij} - d_{ij})/0.37)$
1	Cd–S	2.695	0.326
2	Cd–S	2.619	0.400
3	Cd–S	2.706	0.316
4	Cd–S	2.695	0.326
5	Cd–N	2.379	0.322
6	Cd–N	2.402	0.303
		$BVS = V_{ij} = \sum_{v_{ij}} =$	1.993

*R_{ij} (Cd–S) = 2.28.
*R_{ij} (Cd–N) = 1.96.
V_{ij} corresponds to the individual bond valence contribution and the sum is BVS equivalent to V_{ij}.
*Ref. [13].

3.6. *BVS analysis*

BVS analysis can be used to estimate bond lengths and give information about the valence of the central metal ion. Calculation of BVS value for **3** is explained in table 6. The Rij values employed in the calculations are 2.28, 1.96 and 2.22 for Cd-S, Cd-N and Hg-S bonds. For [Cd(cpzdtc)$_2$(2,2′-bipy)]·0.4 H_2O (**3**) and four coordinated [Hg(cpzdtc)$_2$] (**4**), the BVS was 1.993 and 2.166 (OK/B), respectively, which are very close to the formal oxidation state of +2 [28,29]. The agreement observed here shows predominant ionic interaction in the compounds. BVS of cadmium was found to be 1.98 for a sterically demanding dithiocarbamate analog reported earlier [11].

4. Conclusions

Of the six compounds synthesized in this study, only two crystallized suitable for single-crystal X-ray structure determination. IR spectra show the presence of the characteristic thioureide stretching band. NMR spectra indicate a larger deshielding of protons proximate to the metal center and the thioureide carbon showed a significant chemical shift in adducts compared with the bisdithiocarbamate. The bisdithiocarbamate of mercury showed ionic bonding with localized C=S and C–S bonds. However, the cadmium adduct showed optimization of the steric forces enabling neat stacking of the bipyridyl rings. BVS analysis of the two structures unambiguously showed the interactions to be simply ionic. In the case of mercury compound, BVS obtained in the present study, 2.166, clearly establish an ionic interaction in spite of the soft nature of mercury. The observation is also supported by XPS investigation. Both structures indicate the existence of weak non-covalent interactions.

Supplementary material

CCDC 804968 and 804967 contain the supplementary crystallographic data for **3** and **4**. 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.

References

[1] J. Nieuwenhuizen, A.W. Ehless, J.G. Haashoot, S.R. Janse, J. Reedijk, J. Baerends. *J. Am. Chem. Soc.*, **121**, 163 (1999).
[2] G. Hogarth. *Prog. Inorg. Chem.*, **53**, 71 (2005).
[3] B. Cvek, Z. Dvorak. *Curr. Pharm. Des.*, **13**, 3155 (2007).
[4] R. Malcolm, M.F. Olive, W. Lechner. *Exp. Opin. Drug Saf.*, **7**, 459 (2008).
[5] V. Milacic, D. Fregona, Q.P. Dou. *Histol. Histopathol.*, **23**, 101 (2008).
[6] D.C. Onwudiwe, P.A. Ajibade. *Int. J. Mol. Sci.*, **12**, 5538 (2011).
[7] N. Alam, M.S. Hill, G. Kociok-Koehn, M. Zeller, M. Mazhar, K.C. Molloy. *Chem. Mater.*, **20**, 6157 (2008).
[8] D. Gao, F. Scholz, H.-G. Nothofer, W.E. Ford, U. Scherf, J.M. Wessels, A.F. Von Wrochem. *J. Am. Chem. Soc.*, **133**, 5921 (2011).
[9] P.A. Ajibade, D.C. Onwudiwe. *J. Coord. Chem.*, **64**, 2963 (2011).
[10] M. Altaf, H. Stoeckli-Evans, S.S. Batool, A.A. Isab, S. Ahmad, M. Saleem, S.A. Awan, M.A. Shaheen. *J. Coord. Chem.*, **63**, 1176 (2010).
[11] K. Ramalingam, S. Uma, C. Rizzoli, G. Marimuthu. *J. Coord. Chem.*, **63**, 4123 (2010).
[12] V.I. Sidey, P.M. Milyan, O.O. Semrad, A.M. Solomon. *J. Alloy Compd.*, **457**, 480 (2008).
[13] I.D. Brown, D. Altermatt. *Acta Crystallogr. Part B*, **41**, 244 (1985).
[14] G.J. Palenik. *Can. J. Chem.*, **84**, 99 (2006).
[15] G. Polzonetti, C. Preti, G. Tosi. *Polyhedron*, **5**, 1969 (1986).
[16] A.C.T. North, D.C. Phillips, F.S. Mathews. *Acta Crystallogr. Sect. A*, **24**, 351 (1968).
[17] Bruker, SADABS (Version 2007/4), Bruker AXS Inc., Madison, WI, (2008).
[18] G.M. Sheldrick. *Acta Crysallogr., Part A*, **64**, 112 (2008).
[19] L.J. Faruggia. *ORTEP-3 for Windows*. University of Glasgow (1999).
[20] C.F. Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. VandeStreek. *J. Appl. Crystallogr.*, **39**, 453 (2006).
[21] H.L.M. Van Gaal, J.W. Diesveld, F.W. Pijpers, J.G.M. Van der Linden. *Inorg. Chem.*, **18**, 3251 (1979).
[22] Bare atom values quoted in the VG ESCA III (1980) operation manual.
[23] R.E. Benson, C.A. Ellis, C.E. Lewis, E.R.T. Tiekink. *Cryst. Eng. Comm.*, **9**, 930 (2007).
[24] B.F. Ali, K.A. Al-Souod, R. Al-Far, Z. Judeh. *Struct. Chem.*, **17**, 423 (2006).
[25] C. Chieh, L.P.C. Leung. *Can. J. Chem.*, **54**, 3077 (1976).
[26] C.S. Lai, E.R.T. Tiekink. *Acta Crystallogr. Sect. E*, **58**, 674 (2002).
[27] C.S. Lai, E.R.T. Tiekink. *Appl. Organomet. Chem.*, **17**, 194 (2003).
[28] N.E. Brese, M.Ó. Keeffe. *Acta Crystallogr. Sect. B*, **47**, 192 (1991).
[29] M.Ó. Keeffe, N.E. Brese. *J. Am. Chem. Soc.*, **113**, 3226 (1991).