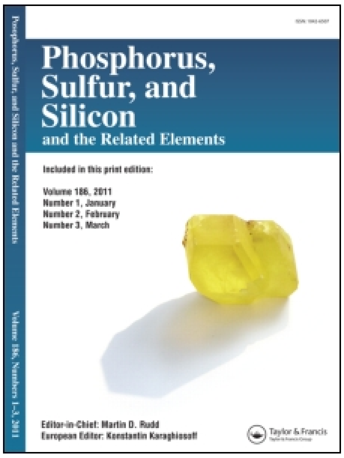

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Spectral, BVS, and Thermal Studies on Bisdithiocarbamates of Divalent Zn, Cd, and Their Adducts: Single Crystal X-Ray Structure Redetermination of (Diiodo) (Tetraethylthiuramdisulfide)mercury(II), [Hg(tetds)I_2]

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The current article describes the TG and DT analyses of divalent Zn, Cd, and Hg dithiocarbamato (dtc) complexes and their adducts (dchdtc = N,N-dicyclohexyldithiocarbamate anion, 4-mpzdtc = 4-methylpiperazinecarbodithioato anion, padtc = N,N′-(iminodiethylene)bisphthalimidedithiocarbamate anion, pipdtc = piperidinecarbodithioate anion, 1,10-phen = 1,10-phenanthroline, and 2,2′-bipy = 2,2′-bipyridine) along with the structural reinvestigation of [Hg(tetds)I_2], where tetds = tetraethylthiuramdisulfide. In the case of Zn(II) and Cd(II) dithiocarbamates and their nitrogenous adducts, thermal decomposition of the nitrogenous bases is followed by the decay of dithiocarbamate leading to the formation of ZnS or CdS as residue. The interaction of iodine with [Hg(dedtc)$_2$] in $CHCl_3$ results in the oxidation of diethyldithiocarbamate leading to the formation of [Hg(tetds)I_2], and the structure was redetermined because the earlier determination was by a Polaroid crystallographic technique with a higher R value. The S-Hg-I bond angles [105.09(3); 105.59(3); 109.26(3), and 100.99(3)°] indicate the near tetrahedral environment around the metal ion. ^1H and ^{13}C NMR spectra of the complex were analyzed. Whether the product formed upon oxidation is a disulfide or an iodo-substituted product, in the present investigation, is clearly decided by the bulkiness of the substituent attached to the nitrogen. Interestingly, the steric influence is a deciding factor only in the case of mercury compounds and the dithiocarbamates involving Zn, Cd forms of the disulfide complexes.

Keywords Dithiocarbamate; mercury; single crystal X-ray structure; thermal studies; thiuramdisulfide

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INTRODUCTION

Among the d^{10} ions, studies on Zn, Cd–sulfur interactions have been extensive in the literature.[1] When dithioacid complexes of Zn(II), Cd(II), or Hg(II) are coordinatively unsaturated, this leads to the formation of compounds of higher coordination number either by the addition of one or two molecules of a Lewis base or by polymerization. This work was undertaken as a continuation of our efforts to understand the chemistry of dithiocarbamates of main group elements.[2–5] Thermoanalytical studies on metal complexes provide valuable information for their applications,[6–9] and recently thermal studies of Cu(II) and Ni(II) dithiocarbamate complexes have been reported.[10,11] In this article we report the TG and DT analyses of complexes involving divalent Zn, Cd, and Hg ions, dithiocarbamates and Lewis bases (where dithiocarbamtes:dchdtc = N,N-dicyclohexyldithiocarbamate anion, 4-mpzdtc = 4-methylpiperazinecarbodithioato anion, padtc = N,N′-(iminodiethylene) bisphthalimidedithiocarbamate anion, pipdtc = piperidinecarbodithioate anion; 1,10-phen = 1,10-phenanthroline and 2,2′-bipy = 2,2′-bipyridine). In addition, the reactivity of I_2 with $Hg(dedtc)_2$ was investigated and the crystalline product obtained was investigated by single crystal diffractometry.

RESULTS AND DISCUSSION

Thermogravimetric Analysis

Ten mixed ligand complexes of divalent Zn, Cd, and Hg (**1–10**) were subjected to thermal studies, and the temperature ranges and percentage mass losses of the decomposition reactions are given in Table I. Representative thermograms of **1** and **2** are given in Figures 1 and 2. The temperature ranges and percentage mass losses of the decomposition reactions are also given in Table I.

Thermal decomposition of $[Zn(4\text{-mpzdtc})_2(1,10\text{-phen})]\cdot H_2O$ (**2**) shows the initial loss of a water molecule, co-crystallized with the complex molecule, which was evidenced from the single crystal structural analysis,[12] followed by the thermal decomposition of 1,10-phen (220°C, 29.5%). The loss of 1,10-phen was followed by the decay of dithiocarbamate up to 540°C, leading to the formation of $Zn(NCS)_2$. Further increase in temperature indicates the decomposition to ZnS.

Zn(II) and Cd(II) dithiocarbamates and their adducts with nitrogenous bases such as 1,10-phen and 2,2′-bipy show similar thermal decomposition patterns. In the case of adducts, after the initial loss of solvent molecules, thermal decomposition of the nitrogenous bases is

TABLE I Thermogravimetric Data for Zn(II), Cd(II), and Hg(II) Complexes

Complex	Mass loss/ Residue (%)	Temp. (°C)	Fragment lost/ End product*
[Zn(4-mpzdtc)$_2$]·H$_2$0 (**1**)	4.3	Up to 120	H_2O
	41.2	300	Zn(NCS)$_2$
	22.0	580	ZnS
[Zn(4-mpzdtc)$_2$(1,10-phen)]·H$_2$0	29.5	220	1,10-phen
(**2**)	28.8	590	ZnS
[Zn(4-mpzdtc)$_2$(2,2′-bipy)]·H$_2$0	3.0	100	H_2O
(**3**)	17.0	380	ZnS
[Cd(4-mpzdtc)$_2$]·C$_2$H$_5$OH·H$_2$O	12.6	140	C_2H_5OH & H_2O
(**4**)	23.0	540	Cd(CN)$_2$
[Cd(4-mpzdtc)$_2$(1,10-phen)]	8.3	Up to 140	C_2H_5OH & H_2O
C$_2$H$_5$OH·H$_2$O (**5**)	—	>380	continuous loss of mass
[Cd(4-mpzdtc)$_2$(2,2′-bipy)] (**6**)	27.0	330	Cd(CN)$_2$
	28.0	680	Cd(CN)(CNO)
[Zn(padtc)$_2$(1,10-phen)]·CHCl$_3$	8.4	Up to 120	$CHCl_3$
(**7**)	21.0	420	Zn(NCS)$_2$& ZnS
[Cd(padtc)$_2$(1,10-phen)]·2H$_2$O	2.8	Up to 110	H_2O
(**8**)	20.0	510	Cd(NCS)$_2$
[Hg(pipdtc)$_2$] (**9**)	69.8	280–300	Piptds
	—	> 300	Mercury
[Hg(pipdtc)I]$_2$ (**10**)	24.5	320	I_2
	31.0	410	Piptds

*Proposed based on final mass of the residue.

simultaneously followed by the decay of dithiocarbamate, leading to the formation of Zn(NCS)$_2$ or Cd(NCS)$_2$/Cd(CN)$_2$ as intermediates. Further increase in temperature results in the decomposition of Zn(NCS)$_2$ to ZnS in the case of Zn(II) adducts, and the observed trend is very similar in Cd(II) adducts also where the final residue corresponds to CdS.

Thermal analysis of **9** shows the decomposition initiated around 280°C; until that temperature is reached, the complex remains stable. Loss of the dithiocarbamate part as a disulfide is complete by 300°C and the reduced mercury evaporates. The observation is almost similar to those reported earlier.[13,14] For [Hg(pipdtc)I]$_2$, loss of I_2 is observed up to 320°C, which is followed by the loss of piperidinethiuramdsulfide up to 410°C. Simultaneously, at 900°C, little residue of insignificant percentage of the initial mass is observed because of the evaporation of reduced metallic mercury. The following reaction (I) is visualized for

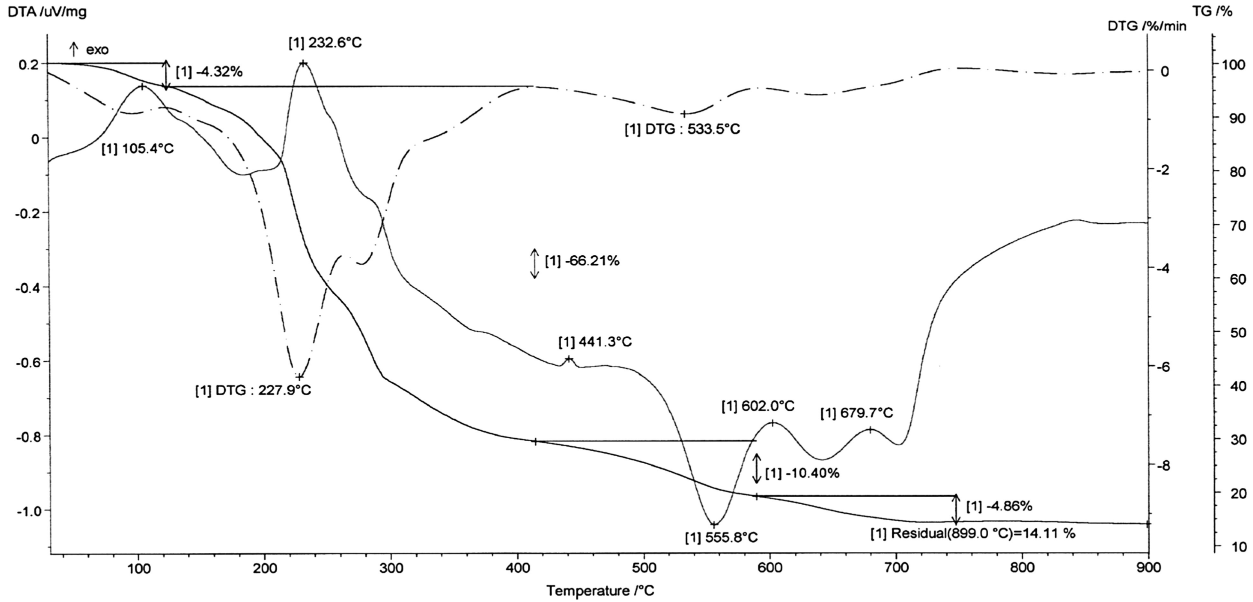

FIGURE 1 Thermogram of [Zn(4-mpzdtc)$_2$]·H$_2$O.

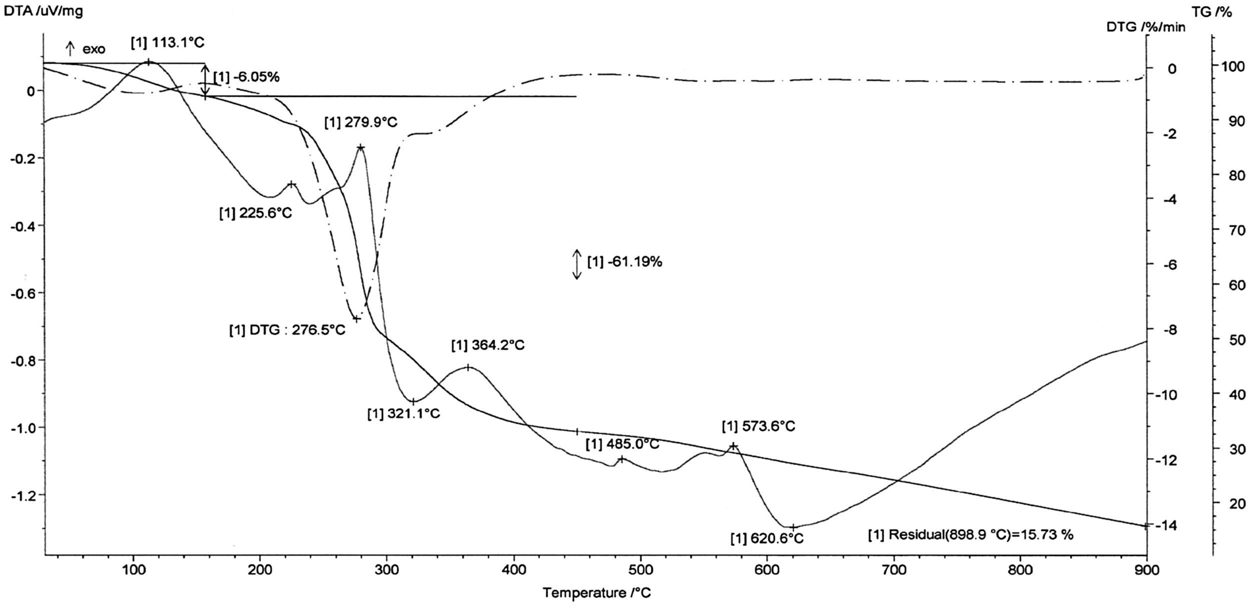

FIGURE 2 Thermogram of $[Zn(4\text{-mpzdtc})_2(1,10\text{-phen})]\cdot H_2O$.

the thermal decomposition:

$$[Hg^{II}(pipdtc)I]_2 \rightarrow 2\ Hg + piptds + I_2 \tag{1}$$

In the case of Cd(II) dithiocarbamates and their adducts, CdS formation occurs at low temperature and the final residue with insignificant mass is obtained as in the case of mercury. Thermal studies of the mixed ligand complexes confirmed the proposed molecular formulae for them. The confirmation of the final residue with powder XRD could not be carried out due to paucity of samples.

Structural Reinvestigation of [Hg(tetds)I_2]

The [Hg(tetds)I_2] complex was reported to be synthesized by mixing tetraethylthiuramdisulfide directly with HgI_2 in ethanol, and the structure was solved by Polaroid crystallographic technique.[15] The interaction of iodine with [Hg(dedtc)$_2$] in $CHCl_3$ results in the oxidation of diethyldithiocarbamate, and thereby the formation of [Hg(tetds)I_2] is reported in the present study; the structure was solved by diffractometric technique with an improved reliability index of R_I (0.039).

From our observation, the interaction of molecular iodine with [M(dtc)$_2$] is of two types:

$$< [M(dtc)_2] + I_2 \longrightarrow [M(tds)I_2](M = Zn \text{ or } Cd \text{ and } tds) \tag{2}$$

$$2[M(dtc)_2] + I_2 \longrightarrow 2\ [M(dtc)I] \quad (M = Hg) \tag{3}$$

Zn(II) and Cd(II) complexes prefer Equation (2), resulting in an oxidation of dtc into tds,[16,17] In the case of [Hg(dtc)$_2$], we have already reported[16] the complete replacement of one of the dtc$^-$ by I$^-$ [Equation (3)] resulting in a dimeric [Hg(dtc)I]$_2$ (where dtc = piperidinedithiocarbamate). However, interestingly, in the present study the trend is reversed for [Hg(tetds)I_2], and the reaction follows Equation (2).

Therefore, formation of thiuramdisulfide is favored unequivocally by Zn(II) and Cd(II) bisdithiocarbamates, and they follow Equation 1. However, in the case of Hg(II) dithiocarbamates, oxidation of diethyldithiocarbamate results in the thiuramdisulfide formation such as Hg(tetds)I_2. In the case of Hg(pipdtc)$_2$ oxidation with iodine, the product formed is not a disulfide, but dimeric [Hg(pipdtc)I]$_2$. A comparison of the important bond parameters of the two compounds is given in Table II. The corresponding BVS values for Hg atoms are also listed in the table. A clear significant reduction in the S-Hg-S angle in Hg(tetds)I_2 indicates the reduced steric influence of the piperidine group comparatively. Therefore, whether the product formed upon oxidation is a disulfide or an iodo-substituted product in the present

TABLE II Comparison of Bond Parameters and BVS Values of [Hg(pipdtc)I] and $[Hg(tetds)I_2]$

Compound	Hg-S	Hg-I	C—S	C—N (Thioureide)	S—C—S	S-Hg-S	S-Hg-I	BVS
[Hg(pipdtc)I]	2.425(2)	2.6422(12)	1.745 (8)	1.316(11)	119.4(5)	108.95(8)	141.18(7)	2.0718 (Hg)
	2.615(2)		1.733 (8)				109.83(6)	3.2480 (N-6)
$[Hg(tetds)I_2]$	2.6549(13)	2.6779(5)	1.689(5)[a]	1.314(6)	122.3(3)	100.76(4)	105.09(3)[b]	2.3744 (Hg)
	2.6567(13)	2.6812(5)	1.691(5)	1.315(6)	121.1(3)		105.59(3)	3.2352 (N-10)
								3.2004 (N-15)

[a] The other two C—S distances 1.793(5) and 1.796(5) Å (where the sulfur atoms involved in the disulfide bond) are omitted.

[b] The remaining S-Hg-I bond angles are 100.99(3) and 109.26(3)°.

TABLE III IR Spectral Data and NMR Chemical Shifts of [Hg(tetds)I_2]

IR (cm^{-1})		NMR (ppm)[a]			
$\nu_{C-N(thioureide)}$	ν_{C-S}		α-CH_2-	β-CH_3	N $^{13}CS_2$ (Thioureide)
1512 (s)	1067 (s)	^1H	4.24 (q); 4.02 (q)	1.66 (t); 1.34 (t)	
		^{13}C	12.09; 14.82	49.50; 55.27	195.28

[a] Chemical shifts in $CDCl_3$.

investigation is clearly decided by the bulkiness of the substituent attached to the nitrogen. Interestingly, the steric influence is a deciding factor only in the case of mercury compounds, and the dithiocarbamates involving Zn, Cd form the disulfide complex.

IR Spectral Studies

Important infrared spectral bands are shown in Table III. IR spectrum of [Hg(tetds)I_2] shows a thioureide $\nu_{(C-N)}$band at 1512 cm^{-1}. The Hg(dedtc)$_2$ complex shows that the band at 1496 cm^{-1} is due to the mesomeric drift of electron density from the dithiocarbamate towards the metal center. The $\nu_{(C-S)}$ band appears at 1067 cm^{-1}.

NMR Spectral Studies

^{1}H NMR

NMR spectral chemical shifts are in Table III. As expected, two sets of signals were observed for methyl and methylene protons for [Hg(tetds)I_2]. The methylene protons were observed at 4.24 ppm and 4.02 ppm as quartets. The two triplets at 1.66 ppm and 1.34 ppm are due to the methyl protons. In the case of parent Hg(dedtc)$_2$ complex, only one set of signals was obtained for methylene [3.90 ppm (q)] and methyl protons [1.3 ppm (t)]. The residual solvent signals at 1.50 ppm and 2.17 ppm for H_2O and acetone in $CDCl_3$ were ignored.[18]

^{13}C NMR

For [Hg(tetds)I_2], the thioureide carbon resonates at 195.28 ppm, which is significantly shielded compared to the chemical shifts observed for similar dithiocarbamate complexes.[19] The methyl carbons were observed at 12.09 and 14.82 ppm. The slightly deshielded methylene carbons resonate at 49.50 and 55.27 ppm, respectively.

BVS Calculations

BVS calculations were performed on the [Hg(tetds)I_2] compound by established procedures.[20,21] The mercury atom shows a valence of 2.3744, indicating the predominance of covalent interactions,[22] which is in line with its soft nature. BVS of the two nitrogen atoms N(10) and N(15) are 3.2352 and 3.2004, respectively, which again indicates the existence of a partially double-bonded thioureide bond supported by NMR and IR spectral studies. A comparison of the BVS values for dimeric $[\mathrm{Hg(pipdtc)I}]_2^{16}$ is presented in Table II. The central mercury atom in the dimeric structure shows a BVS value of 2.0718, which is significantly lower than the value obtained for Hg in [Hg(tetds)I_2]. In the dimer, mercury is bonded to one iodine and three sulfurs, and the induced softness is relatively less. The interaction therefore is relatively less covalent in nature. However, thioureide nitrogen shows its partially double-bonded nature. In both complexes, the higher BVS values observed for mercury indicate its soft nature.

Structural Analysis

The ORTEP diagram of [Hg(tetds)I_2] is shown in Figure 3. The complex is monomeric and discrete. Eight units of [Hg(tetds)I_2] are present in the unit cell. The thiuramdisulfide of diethyldithiocarbamate and two iodide ions are involved in complex formation with the metal ion. The Hg-S distances [2.6549(13) and 2.6567(13) Å] are almost similar and are significantly different from those of the values observed in the

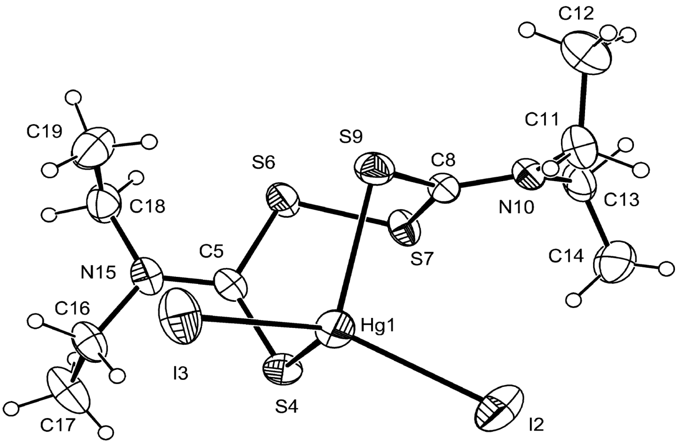

FIGURE 3 ORTEP of [Hg(tetds)I_2].

parent complex.[23] The Hg-S distances are significantly long compared to the distances observed in similar dithiocarbamate complexes. Two sets of C—S bond distances [1.689(5); 1.691(5) and 1.793(5); 1.796(5) Å] corresponding to single and double-bonded distances were observed. The C=S bonds of the disulfide in the present complex are on the same side as a requirement for coordination with metal. The Hg-I bond distances [2.6779(5) and 2.6812(5) Å] are almost symmetric. The S-Hg-I bond angles [105.09(3); 105.59(3); 109.26(3) and 100.99(3)°] indicate the near tetrahedral environment around the metal ion. The larger I-Hg-I bond angle 131.14(2)° suggests that the mercury ion is in a highly distorted tetrahedral environment. The disulfide S—S distance 2.0035(19) Å is larger than the distances observed in the free disulfides.[24] The significant increase observed in the disulfide S—S bond distance is due to the larger strain involved in forcing the two C=S bonds to assume a *cis* form in order to coordinate to the Hg ion. The thioureide C—N bond distances [1.314(6) and 1.315(6) Å] are almost similar to the values observed for the parent [Hg(dedtc)$_2$]. The thioureide distances are characteristic of partial double-bond nature.

EXPERIMENTAL

Synthesis and Characterization

Preparation of the Complexes

In general, the parent complexes, [M(dtc)$_2$] [M = Zn or Cd or Hg], were prepared by mixing the corresponding amine (1 mmol) and carbondisulfide (76 mg, 1 mmol) in ethanol under ice cold conditions (0°C). To the yellow dithiocarbamic acid solutions, aqueous solutions of the metal salts [$ZnSO_4$ or $Cd(NO_3)_2$ or $HgCl_2$] were added with constant stirring. Pale yellow solids separated from the solution, which were filtered, washed with water and alcohol, and were then dried in air.

Adducts were prepared by adding a hot solution of 1,10-phen (200 mg, 1 mmol) or 2,2′-bipy (155 mg, 1 mmol) in benzene to a hot suspension of the parent dithiocarbamate (1 mmol) in a benzene:chloroform (1:1) mixture. The resulting pale yellow solution was filtered and cooled. The separated yellow adduct was filtered and recrystallized from a benzene:chloroform (1:1) solvent mixture. Details of the masses of the individual substances used in the preparation are given in Table IV.

[Hg(tetds)I$_2$]: Iodine (250 mg, 1 mmol) in chloroform (100 cm^3) was added to a solution of [Hg(dedtc)$_2$] (500 mg, 1 mmol) in chloroform. Initially, the color of the iodine disappeared on addition, and after about 90 min of continuous stirring following dropwise addition of iodine, a slight excess of iodine was evident. The addition of iodine was stopped,

TABLE IV Details of the Masses of the Individual Substances Used in the Preparation

Complex	Amine	Weight (1 mmol)/mg
[Zn(4-mpzdtc)$_2$]	1-Methylpiperazine	100
[Cd(4-mpzdtc)$_2$]	1-Methylpiperazine	100
[Zn(padtc)$_2$]	N,N′-(iminodiethylene)bisphthalimide	365
[Cd(padtc)$_2$]	N,N′-(iminodiethylene)bisphthalimide	365
[Hg(pipdtc)$_2$]	Piperidine	85
[Hg(dedtc)$_2$]	Diethylamine	75
Adducts	Parent complex	
[Zn(4-mpzdtc)$_2$(1,10-phen)]	[Zn(4-mpzdtc)$_2$]	415
[Zn(4-mpzdtc)$_2$(2,2′-bipy)]	[Zn(4-mpzdtc)$_2$]	415
[Cd(4-mpzdtc)$_2$(1,10-phen)]	[Cd(4-mpzdtc)$_2$]	465
[Cd(4-mpzdtc)$_2$(2,2′-bipy)]	[Cd(4-mpzdtc)$_2$]	465
[Zn(padtc)$_2$(1,10-phen)]	[Zn(padtc)$_2$]	975
[Cd(padtc)$_2$(1,10-phen)]	[Cd(padtc)$_2$]	1025
[Hg(pipdtc)I]$_2$	[Hg(pipdtc)$_2$][a]	520

[a] + Iodine (250 mg, 1 mmol).

the suspension was filtered, and the clear filtrate was left undisturbed for evaporation at room temperature. After 2 days, pale yellow crystals separated from the solution. The crystals were filtered, washed with chloroform, and dried in air. Yield: 60% (450 mg), mp: 116–118°C. Anal. Calcd. for $C_{10}H_{20}HgI_2N_2S_4$: C, 15.99; H, 2.68; N, 3.73. Found: C, 15.72; H, 2.54; N. 3.52%.

Thermogravimetry

A STA 409 PC thermal sciences instrument was used for the thermal analysis of the samples. Experiments were carried out in atmospheric air using alumina as reference. The heating rate of the furnace was fixed at 10°C per minute, and the samples were heated up to 900°C by taking 5 mg of sample in a platinum crucible.

General Procedures

All the reagents and solvents employed were commercially available analytical grade materials used as supplied, without further purification. IR spectrum of [Hg(dedtc)$_2$] was recorded on ABB Bomem MB 104 spectrophotometer (range 4000–400 cm^{-1}) as a KBr pellet. NMR spectra were recorded on Bruker AMX 400 spectrometer at room temperature, using $CDCl_3$ as solvent. ^{13}C NMR spectrum was recorded in proton decoupled mode.

X-Ray Crystallography

Details of the crystal data, data collection, and refinement parameters for [Hg(dedtc)$_2$] are summarized in Table V. The intensity data were collected at ambient temperature (295 K) on Bruker AXS Smart diffractometer with CCD (Area detector) using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The structure was solved by direct

TABLE V Crystal Data, Data Collection, and Refinement Parameters for [Hg(tetds)I$_2$]

Complex	[Hg(tetds)I$_2$]
Empirical formula	$C_{10}H_{20}Hg\,I_2N_2S_4$
FW	750.9
Crystal dimensions (mm)	0.19 × 0.31 × 0.35
Color	Pale yellow
Habit	Column, irregular
Crystal system	Orthorhombic
Space group	P_{bca}
a/Å	13.062(2)
b/Å	23.187(3)
c/Å	14.061(2)
α/°	90.0
β/°	90.0
γ/°	90.0
U/Å^3	4258.6(10)
Z	8
Dc/gcm^{-3}	2.342
μ/cm^{-1}	10.511
F(000)	2752
λ/Å	Mo Kα (0.71069)
θ Range/°	1.76–28.24
Scan type	ω-2θ
Index ranges	$-17 \leq h \leq 16$, $-29 \leq k \leq 30$, $-18 \leq l \leq 18$
Reflections collected	4885
Observed reflections [$F_o > 4\sigma(F_o)$]	3264
Weighting scheme	$W = 1/[\sigma^2(F_o^2) + (0.319\,P)^2 + 0.000P]$, Where $P = (F_o^2 + 2\,F_c^2)/3$
Number of parameters refined	173
Final R, R_w (observed, data)	0.0338, 0.0619
Goodness of fit	1.018

TABLE VI Selected Bond Distances and Bond Angles for [Hg(tetds)I_2]

Bond distances	
Hg(1)–S(4)	2.6549(13)
Hg(1)–S(9)	2.6567(13)
Hg(1)–I(2)	2.6779(5)
Hg(1)–I(2)	2.6812(5)
S(4)–C(5)	1.689(5)
C(5)–N(15)	1.315(6)
C(5)–S(6)	1.796(5)
S(6)–S(7)	2.0035(19)
S(7)–C(8)	1.793(5)
C(8)–N(10)	1.314(6)
C(8)–S(9)	1.691(5)
N(10)–C(11)	1.464(6)
N(10)–C(13)	1.478(6)
Bond angles	
S(4)–Hg(1)–S(9)	100.76(4)
S(4)–Hg(1)–I(2)	105.09(3)
S(9)–Hg(1)–I(2)	105.59(3)
S(4)–Hg(1)–I(3)	109.26(3)
S(9)–Hg(1)–I(3)	100.99(3)
I(2)–Hg(1)–I(3)	131.14(2)
C(5)–S(4)–Hg(1)	95.06(15)
N(15)–C(5)–S(4)	124.6(4)
N(15)–C(5)–S(6)	113.2(4)
S(4)–C(5)–S(6)	122.3(3)

methods using SHELXS-97[25] and was refined by SHELXL-97.[26] All the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were refined isotropically. Selected bond lengths and bond angles are given in Table VI.

Supplementary Material

CCDC 216778 contains the supplementary crystallographic data for [Hg(tetds)I_2]. 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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