Supporting information for

Solution and Solid-state Study of Heteroleptic Hg(II)-thiolates: Crystal Structures of $[Hg_4I_4(SCH_2CH_2NH_2)_4]$ and $[Hg_4I_8(SCH_2CH_2NH_3)_2]_n \cdot nH_2O$

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Experimental Section

General Procedure. The reactions were carried out at room temperature in a mixture of DI water and methanol under nitrogen. The reagents 2-aminoethanethiol hydrochloride (TCI America) and HgI_2 (Alfa Aesar) were used as received. ^{1}H and ^{13}C NMR data were obtained with JEOL-GSX-400 and 270 instruments operating at 199.17 MHz using d_6-DMSO as solvent. The $^{199}Hg\{^{1}H\}$ NMR spectrum of 1 (0.5M) in d_6-DMSO was collected at 25 ºC on a Varian INOV 400 MHz instrument with 4-Nucleus Autoswitchable 5mm Probe and referenced to 1M $HgCl_2$ in DMSO at -1500 ppm[1,2] and checked against external 0.1M $Hg(ClO_4)_2$ in D_2O (-2250 ppm).[3] The IR data was recorded as KBr pellets on a Mattson Galaxy 5200 FT-IR instrument between 400 - 4000 cm^{-1}. Mass Spectral data (MALDI) were obtained on a Kratos Kompact SEQ MALDI-TOFMS at the University of Kentucky Mass Spectrometry Facility. Raman spectra were obtained on a Nicolet FT-Raman 906 Spectrometer ESP between 100 - 800 cm^{-1} in Center for Applied Energy Research at the University of Kentucky Facility. The UV-Vis studies were conducted on an Agilent HP 8453 instrument by using 0.05 mM solutions of 1 and 2 in water:DMSO mixture (80:20 v/v). The TGA analyses were done one DSC 2950 Thermal Analyzer with TGA 2950 Furnace operating at 10 ºC/minute in open atmosphere.

X-ray Crystallography. Crystals of **1** and **2** were obtained by the partial evaporation of the filtrate and by recrystallization in DI water, however, crystals obtained by partial evaporation were used for X-ray. X-ray diffraction data were collected at 90 and 173 ºK on a Nonius Kappa CCD diffractometer unit using Mo-Kα radiation from regular shaped crystals mounted in Paratone-N oil on glass fibers. Initial cell parameters were obtained using DENZO[4] from 1º frames and were refined *via* a least-square scheme using all data-collection frames (SCALEPACK).[4] The structures were solved by direct methods (SHELXL97)[5] and completed by difference Fourier methods (SHELXL97).[5] Refinement was performed against F^2 by weighted full-matrix least-square and empirical absorption correction (SADABS)[5] were applied. Hydrogen atoms were placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography Volume C.[6]

Synthesis of $[Hg_4I_4(SCH_2CH_2NH_2)_4]$ (**1**): To a stirring solution of 2-aminoethanethiol hydrochloride (10 mmol, 1.14 g) and NaOH (10 mmol, 0.4 g) in a mixture of DI water (90 mL) and methanol (10 mL) was added HgI_2 (5 mmol, 2.27 g) and stirred for three days. The precipitate was removed, washed with methanol followed by cold water and vacuum dried. Evaporation of the filtrate at room temperature yielded X-ray quality crystals. Yield: 2.5 g (62%). Mp 175 - 177º. ^{1}H NMR (d_6-DMSO, 200MHz, ppm): δ 2.84 (t, 2H, SCH_2), δ 2.96 (t, 2H, NCH_2), δ 6.06 (br, 2H, NH_2). ^{13}C NMR (d_6-DMSO, 200 MHz, ppm): δ 29.1 (CH_2S), δ 42.7 (CH_2N). $^{199}Hg\{^{1}H\}$ NMR (d_6-DMSO, 400 MHz, ppm):δ -642. IR (KBr, ν/cm^{-1}): 3445, 3164, 2831, 1601, 1555, 1364, 1266, 1153, 1018, 935, 630. MALDI MS (m/z (%)): 356, ($[Hg(SCH_2CH_2NH_2)_2]^+$, 5); 401, ($[HgI(SCH_2CH_2NH_2)]^+$, 5); 146, ($[NH_4I]^+$, 25); 172, ($[CH_2CH_2NH_3I]^+$, 100); 78, ($[SCH_2CH_2NH_2)]^+$, 47). Uv-Vis: λ_{max} = 270 nm. Anal. calcd for

$[Hg_4I_4(SCH_2CH_2NH_2)_4)]$: C, 5.951; H, 1.498; N, 3.470. Found: C, 5.949; H, 1.486; N, 3.481.

Synthesis of $[Hg_4I_8(SCH_2CH_2NH_3)_2]_n \cdot nH_2O$ (2): To a stirring solution of 2-aminoethanethiol hydrochloride (10 mmol, 1.14 g) in a mixture of DI water (90 mL) and methanol (10 mL) was added HgI_2 (5 mmol, 2.27 g) and stirred for three days. The precipitate was removed, washed with methanol followed by cold water and vacuum dried. Evaporation of the filtrate at room temperature yielded X-ray quality crystals. Yield: 4.03 g (80%). Mp 110 - 112º. ^{1}H NMR (d_6-DMSO, 200MHz, ppm): δ 3.04 (m, 4H, SCH_2 and NCH_2), δ 7.68 (br, 3H, NH_3). ^{13}C NMR (d_6-DMSO, 200 MHz, ppm): δ 27.3 (CH_2S), δ 42.5 (CH_2N). IR (KBr, ν/cm^{-1}): 3720, 3448, 3164, 2962, 2831, 1594, 1468, 1407, 1364, 1260, 1086, 804, 675. MALDI MS (m/z (%)): 172, ($[CH_2CH_2NH_3I]^+$ 100); 144, ($[NH_4I]^+$, 7). Uv-Vis: λ_{max} = 270 nm and 360 nm(shoulder). Anal. calcd for $[Hg_4I_8(SCH_2CH_2NH_3)_2]\cdot 2H_2O$: C, 2.392; H, 0.9036; N, 1.395. Found: C, 2.390; H, 0.9032; N, 1.399.

Table S1. Crystal Data for **1** and **2**.

Data	**1**	**2**
Empirical Formula	$C_4H_{12}Hg_2I_2N_2S_2$	$C_2H_9Hg_2I_4NOS$
Formula Weight	807.26	1003.94
Temperature (K)	90.0(2)	90.0(2)
Wavelength Å	0.71073	0.71073
Crystal System	Monoclinic	Orthorhombic
Space Group	P 21/c	P c a 21
Unit Cell Dimensions (Å and º)	a = 9.2107(2) b = 8.1173(2) c = 18.1332(4) α = 90.0 β = 100.5020(10) γ = 90.0	a = 29.6018(3) b = 7.25240(10) c = 13.3459(2) α = 90.000 β = 90.0 γ = 90.00
Volume (Å^3)	1333.04(5)	2865.15(7)
Z	4	8
Density Calculated (mg/m^3)	4.022	4.655
Absorption Coefficient (mm^{-1})	27.911	30.137
F(000)	1392	3392
Crystal Size	0.08 x 0.06 x 0.04 mm	0.15 x 0.10 x 0.10 mm
Reflection Collected	20973	6261
Independent Reflections	3054 (R(int) = 0.0540)	6261 (R(int) = 0.00)
Refinement Method	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Goodness of fit on F^2	1.086	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0248 wR2 = 0.0427	R1 = 0.0345 wR2 = 0.0740
R indices (all data)	R1 = 0.0366	R1 = 0.0429

	wR2 = 0.0455	wR2 = 0.0776
Extinction Coefficient	0.00040(3)	0.00011(2)
Largest diff peak and hole e $Å^{-3}$	1.339 and –1.164	2.342 and –2.345

Table S2. Lowest energy transitions for **1**, **2** and selected Hg(II)-thiolates.

Compounds	λ_{max} (nm)	Reference
1	270	This work
2	270, 360 (sh)	This work
$[Hg_6Cl_8(SCH_2CH_2NH_3)_8)]^{4+}$	270	[7]
$[Hg_9Br_{15}(SCH_2CH_2NH_3)_9]^{3+}$	270, 340 (sh)	[7]
Hg_7-MT	245, 304 (sh)	[7]
Hg-plastocyanin	245, 280 (sh)	[8]
Hg-stellacyanin	240, 278 (sh)	[9]
Hg-MerR	245, 290 (sh)	[9]
$[Hg(SEt)_2$	228, 282 (sh)	[10]
$[Hg(Pr^i)_2]$	228, 262(sh)	[10]
$[Hg(SBu^t)_3]^+$	235, 260(sh)	[10]

sh = shoulder, MT = metallothionein

Table S3. Vibrational frequencies observed for **1** and **2** and corresponding frequencies for several Hg(II)-thiolates.

Compound	ν(Hg-S)	ν(Hg-X)	Reference
1	260 (s), 341 (as)	499(X = N), 127	This work
2	287 (s), 340 (as)	133(t), 106 (br)	This work
$[HgI_2\{SCHNH(CH_3)_2\}_2]$	162 (s), 311 (as)	134 (t)	[11]
$[HgI_2(tzdSH)_2]$	194 (s), 321(as)	126 (t)	[12]
$Hg_2I_6^{2-}$	-	105 (br)	[13]

X = I unless specified, t = terminal, br = bridging, s = symmetric, as = asymmetric stretching, tzdSH = 1,3-thiazolidine-2-thione.

Table S4. Bond distance (Å) and angles (º) for **1**.

Hg(1)-S(1)	2.518(1)	Hg(2)-S(1) #1	2.473(1)
Hg(1)-S(2)	2.476(1)	Hg(2)-S(2)	2.530(1)
Hg(1)-N(1)	2.404(4)	Hg(2)-N(2)	2.371(4)
Hg(1)-I(1)	2.762(4)	Hg(2)-I(2)	2.755(4)
S(2)-Hg(1)-S(1)	123.47(5)	S(2)-Hg(2)-S(1)#1	124.18(5)
N(1)-Hg(1)-S(1)	81.53(1)	N(2)-Hg(2)-S(1)#1	108.94(1)
N(1)-Hg(1)-S(2)	109.45(1)	N(2)-Hg(2)-S(2)	82.00(1)
S(1)-Hg(1)-I(1)	112.34(4)	S(1)#1-Hg(2)-I(2)	112.35(3)
S(2)-Hg(1)-I(1)	115.81(3)	S(2)-Hg(2)-I(2)	112.65(3)
Hg(1)-S(2)-Hg(2)	104.62(5)	Hg(1)-S(1)-Hg(2)#1	100.62(5)

#1= -x+2, -y+1, -z

Table S5. Bond distances (Å) and angles (º) for **2**.

Hg(1)-S(1)	2.464(3)	Hg(2)-S(2)	2.463(3)
Hg(3)-S(1)#1	2.491(3)	Hg(3)-S(2)	2.482(3)
Hg(3)#2-S(1)	2.491(3)	Hg(1)-I(1)	2.936(9)
Hg(2)-I(1)	2.989(1)	Hg(1)-I(2)	3.046(1)
Hg(2)-I(2)	2.932(1)	Hg(1)-I(3)	2.668(1)
Hg(2)-I(4)	2.932(1)	Hg(3)-I(5)	2.965(1)
Hg(4)-I(5)	2.797(1)	Hg(4)-I(6)	3.129(1)
Hg(4)-I(7)	2.704(1)	Hg(4)-I(8)	2.697(1)

S(1)-Hg(1)-I(1)	106.21(8)	S(2)-Hg(2)-I(1)	104.09(3)
S(1)-Hg(1)-I(2)	99.50(8)	S(2)-Hg(2)-I(2)	106.77(8)
S(1)-Hg(1)-I(3)	141.62(8)	S(2)-Hg(2)-I(4)	139.56(8)
I(1)-Hg(1)-I(2)	91.19(3)	I(1)-Hg(2)-I(2)	92.42(3)
I(1)-Hg(1)-I(3)	105.26(3)	I(1)-Hg(2)-I(4)	102.38(3)
I(2)-Hg(1)-I(3)	101.26(3)	I(2)-Hg(2)-I(4)	104.09(3)
S(2)-Hg(3)-S(1)#1	133.59(9)	I(5)-Hg(4)-I(6)	89.96(3)
S(2)-Hg(3)-I(5)	107.56(8)	I(5)-Hg(4)-I(7)	119.61(3)
S(2)-Hg(3)-I(6)	110.62(8)	I(5)-Hg(4)-I(8)	111.07(3)
S(1)#1-Hg(3)-I(5)	98.09(8)	I(6)-Hg(4)-I(7)	95.09(3)
S(1)#1-Hg(3)-I(6)	110.60(8)	I(6)-Hg(4)-I(8)	103.42(3)
I(5)-Hg(3)-I(6)	92.79(3)	I(7)-Hg(4)-I(8)	125.71(3)
Hg(2)-S(2)-Hg(3)	106.65(1)	Hg(1)-S(1)-Hg(3)#2	105.28(1)
Hg(1)-I(1)-Hg(2)	86.21(3)	Hg(1)-I(2)-Hg(2)	85.26(3)
Hg(3)-I(5)-Hg(4)	90.53(3)	Hg(3)-I(6)-Hg(4)	86.70(3)

#1= x, y+1, z, #2 = x,y-1,z

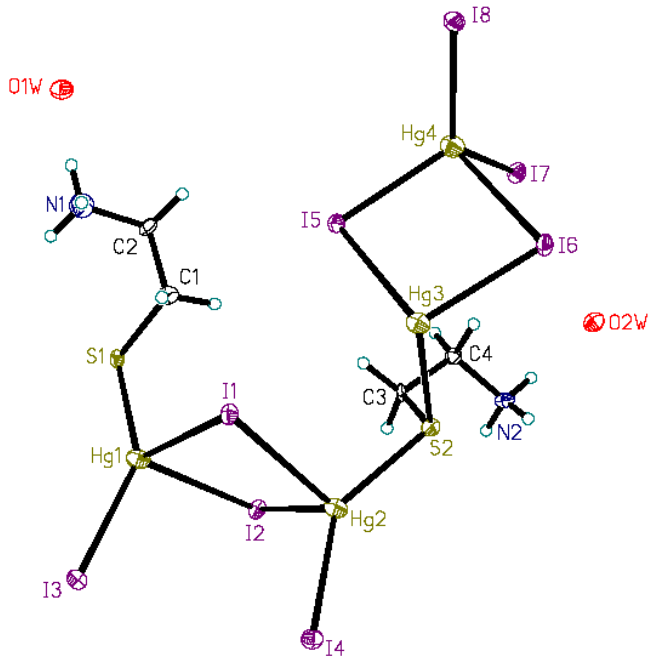


Figure 1. The repeating unit of **2** with 50% thermal ellopsoids

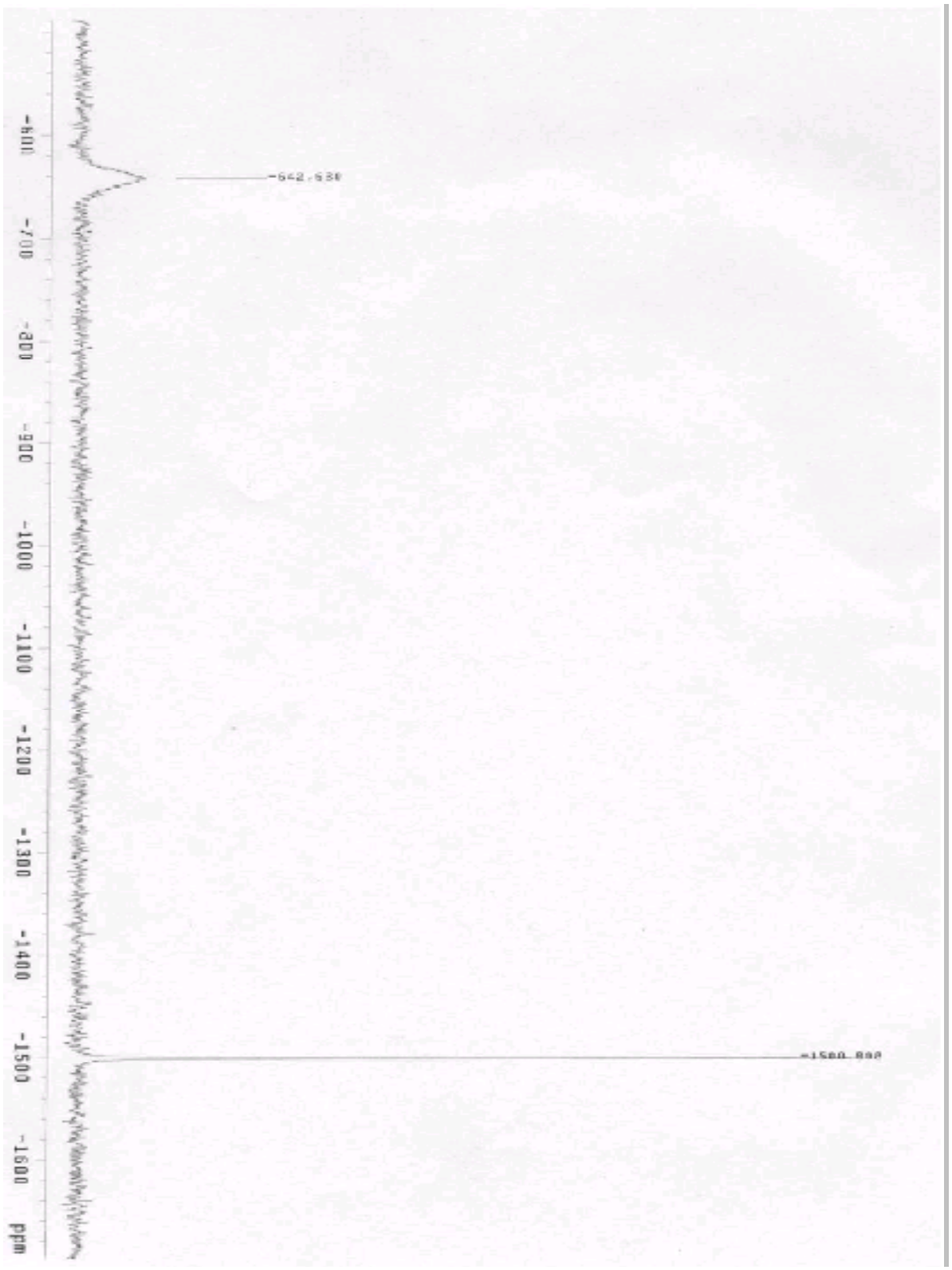
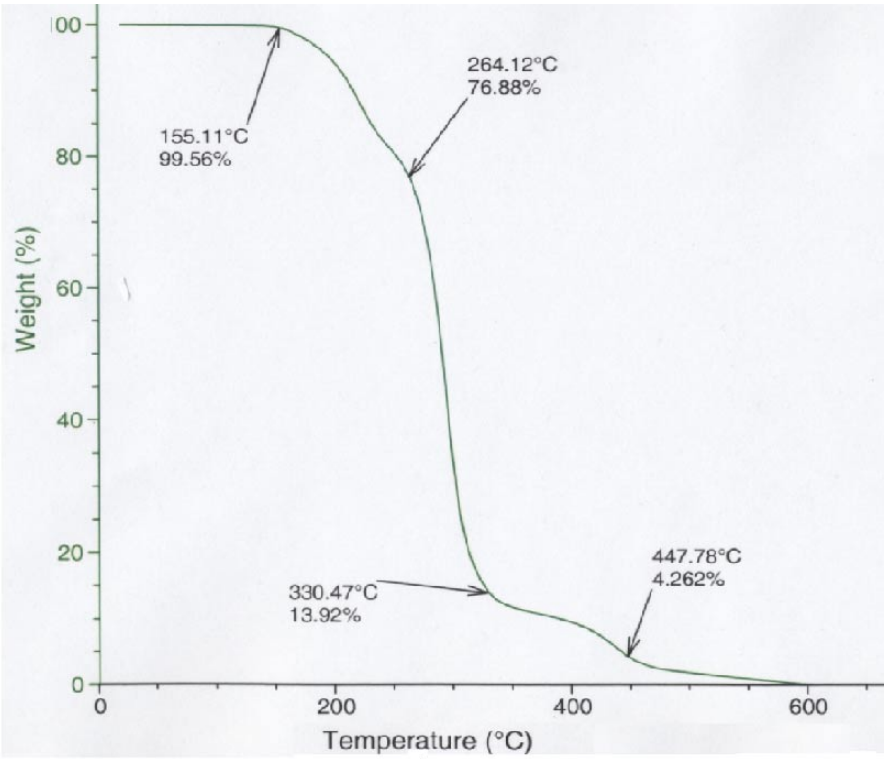
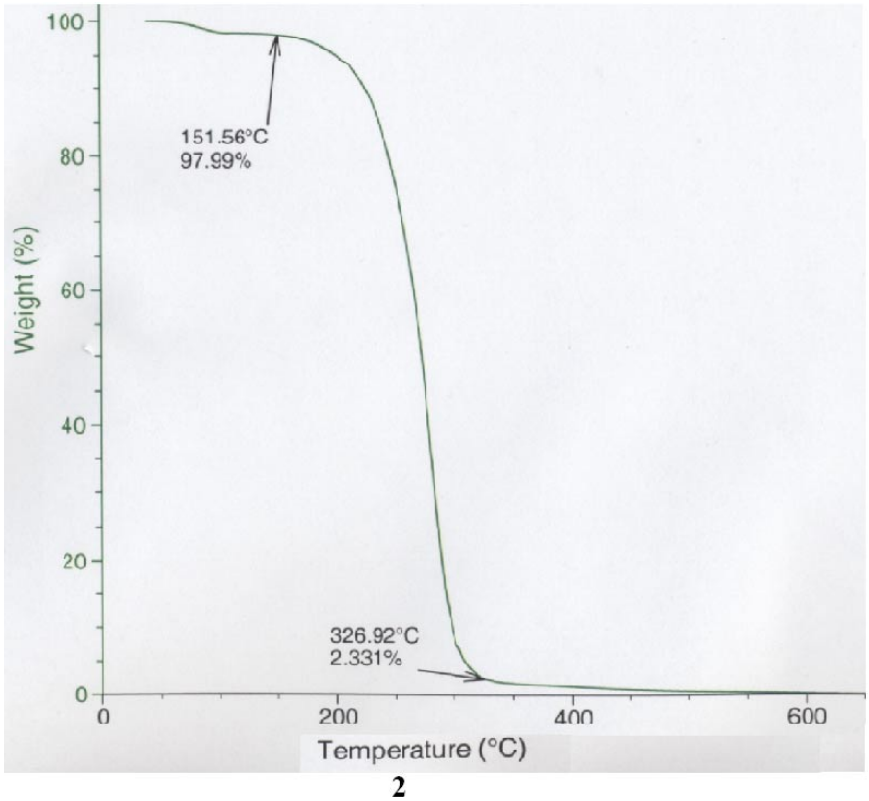


Figure 2. $^{199}Hg[^{1}H]$ NMR of **1** in d_6-DMSO.



1

Figure 3. Thermogram of **1**.



2

Figure 4. Thermogram of **2**.

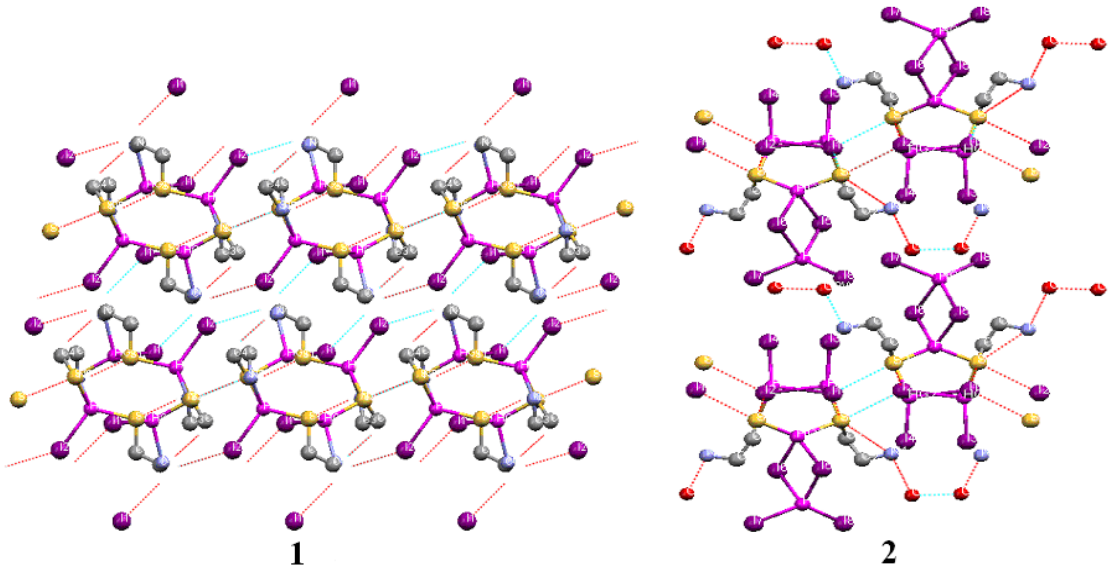


Figure 5. Packing diagrams of **1** and **2** along b-axis emphasizing the hydrogen bonding (shown by dotted lines).

Table S6. Hydrogen bonding geometry in **1** and **2.**

D-H...A	d(D-H)Å	d(H...A)Å	d(D...A)Å	<(DHA)º
		1		
N1 H1A I2	0.92	3.17	3.849(5)	131.9 (2)
N1 H1B I1	0.92	3.20	3.875(4)	131.9 (3)
N1 H1B I2	0.92	3.27	3.698(5)	111.1 (1)
N2 H2C S2	0.92	2.55	3.447(5)	165.9 (2)
N2 H2D S1	0.92	2.61	3.438(5)	150.5 (1)
		2		
N1 H1C I4	0.89	2.98	3.73(2)	142.5 (4)
N1 H1D O1W	0.89	1.97	2.85(3)	166.4
N1 H1E I4	0.89	3.00	3.82(2)	153.6 (4)
N2 H2C I3	0.89	3.05	3.73(2)	134.4 (4)
N2 H2D O2W	0.89	1.82	2.71(3)	174.5
N2 H2E I3	0.89	3.01	3.84(2)	157.4 (4)

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