Two dimensional polydodecameric water-chloride cluster enfolding $(Hg\text{-}Cl\text{-}Hg)^+$ concealed cascade cryptate accomplished through reductive-encapsulation using Hg(II) and a homoditopic octaaza cryptand

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SUPPORTING INFORMATION

All the ligands have been synthesized by using known methods. Other starting materials were of commercially available reagent quality unless otherwise stated. Melting points were recorded by using Tempo melting point apparatus in capillary tube and are uncorrected. FT-IR spectra were recorded in KBr pellets on a JASCO FT-IR-4100 spectrophotometer. NMR has been recorded by using Bruker Avance-500 and 400MHz spectrometer and using commercially available duterated solvents. Single crystal X-ray diffraction data collection was performed with a Bruker AXS Kappa Apex II CCD diffractometer. Thermogravimetric analysis (TGA) data were collected on a Q500 Hi-Res TGA instrument under Nitrogen atmosphere in the temperature range 30-900 °C with a heating rate of 20 °C/min.

Synthesis of Dimercury (I) cryptate $[Hg_2Cl(L1)]Cl.12H_2O$ (1):

To a magnetically stirred solution of **L1** (53mg, 0.088mmol) in MeOH: H_2O (1:1, 5mL), a solution of $HgCl_2$ (47.52mg, 0.176mmol) in MeOH: H_2O (1:1, 5mL) was added slowly. A white precipitate came out soon after the addition of the $HgCl_2$ to the solution of **L1** in MeOH: H_2O which became soluble after few minutes. Then the reaction mixture was stirred for 12h at room temperature. Then it was centrifuged and the clear solution thus obtained was kept for slow evaporation of the solvent. Nice crystalline solid for complex **1** (111mg, 98%) was obtained after 4days.

Physical appearance: Colorless crystalline solid

Yield: (111mg, 98%), **m.p:** > 300 ^oC, Anal. calcd for ($C_{36}H_{78}Cl_2Hg_2N_8O_{12} - 1.5\ H_2O$): C, 34.31; H, 6.00; N, 8.89. Found: C, 34.13; H, 6.11; N, 9.01%.

IR (neat): 3398, 3312, 3231, 3197, 2956, 2921, 2861, 1668, 1637, 1518, 1457, 1355, 1281, 1215, 1162, 1078, 1059, 1027, 996, 940, 877, 811, 713, 619 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d6): δ 7.49 (bs, 12H, Ar-H), 4.26 (bs, 12H, Bn-H), 3.30 (bs, 12H, $NH\text{-}CH_2$), 3.21 (bs, 12H, $N\text{-}CH_2$).

Synthesis of the metal complex [Hg(L2)Cl]Cl (2):

To a magnetically stirred solution of **L2** (41.66mg, 0.1mmol) in MeOH: H_2O (1:1, 5mL), a solution of $HgCl_2$ (27.15mg, 0.1mmol) in MeOH: H_2O (1:1, 5mL) was added slowly. A dark grey precipitate came out soon after the addition of the $HgCl_2$ to the solution of **L2** in MeOH: H_2O which became soluble after few minutes. Then the reaction mixture was stirred for 12h at room temperature. Then it was centrifuged and the clear solution thus obtained was kept for slow evaporation of the solvent. Nice crystalline solid for complex **2** (67 mg, 97.3%) was obtained after 5days.

Physical appearance: Colorless crystalline solid

Yield: (67mg, 97.3%), **m.p:** 195-200 ^oC, Anal. calcd for $C_{27}H_{36}Cl_2HgN_4$: C, 47.13; H, 5.27; N, 8.14. Found: C, 47.49; H, 5.93; N, 8.45%.

IR (neat): 3421, 3156, 3061, 3027, 2917, 2851, 1635, 1602, 1497, 1454, 1395, 1349, 1205, 1164, 1094, 998, 829, 748, 701, 619 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d6): δ 7.99-7.85 (m, 15H, Ar-H), 4.5 (bs, 6H, Bn-H), 3.23 (bs, 6H, NH-CH_2), 3.19 (bs, 6H, N-CH_2).

^{13}C NMR (125 MHz, DMSO-d6, DEPT): δ 137.69 (3 X C, Ar-C-CH_2), 128.94 (6 X CH, Ar-C), 128.52 (3 X CH, Ar-C), 127.58 (3 X CH, Ar-C), 52.97 (3 X CH_2, Bn-CH_2), 51.40 (3 X CH_2, NH-CH_2), 42.94 (3 X CH_2, N-CH_2).

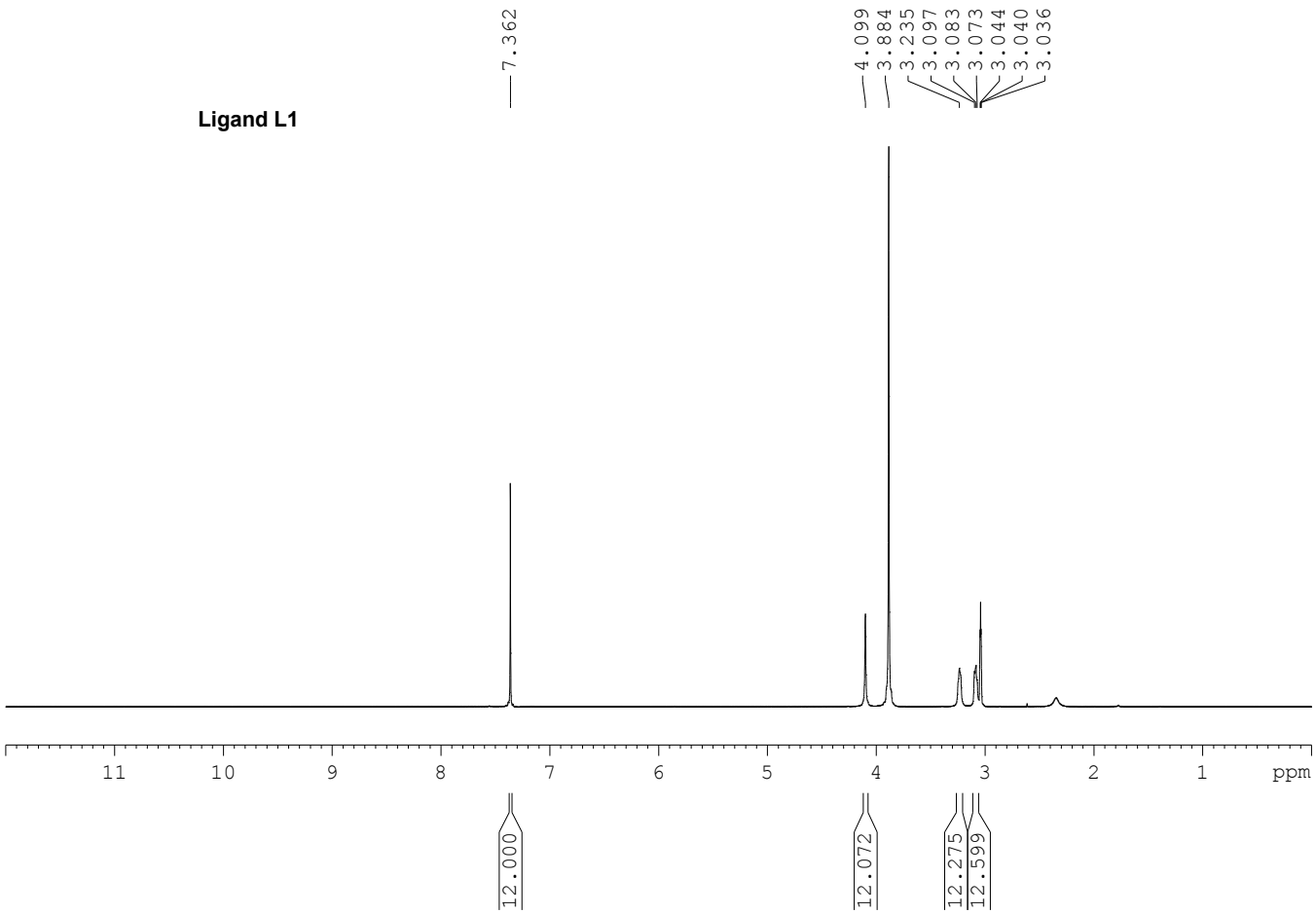


Figure S-1. 400 MHz ^{1}H NMR spectrum of Ligand **L1** in DMSO-d6.

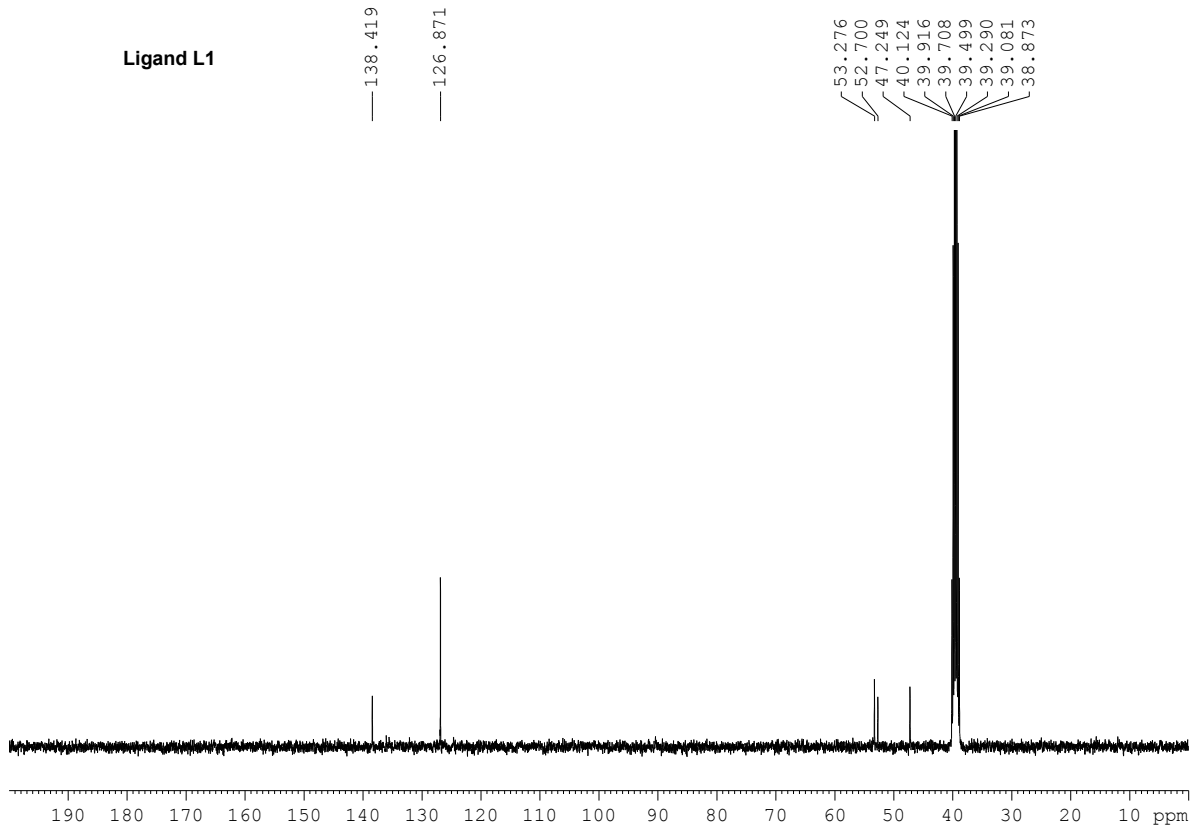


Figure S-2. 100 MHz ^{13}C NMR spectrum of Ligand **L1** in DMSO-d6.

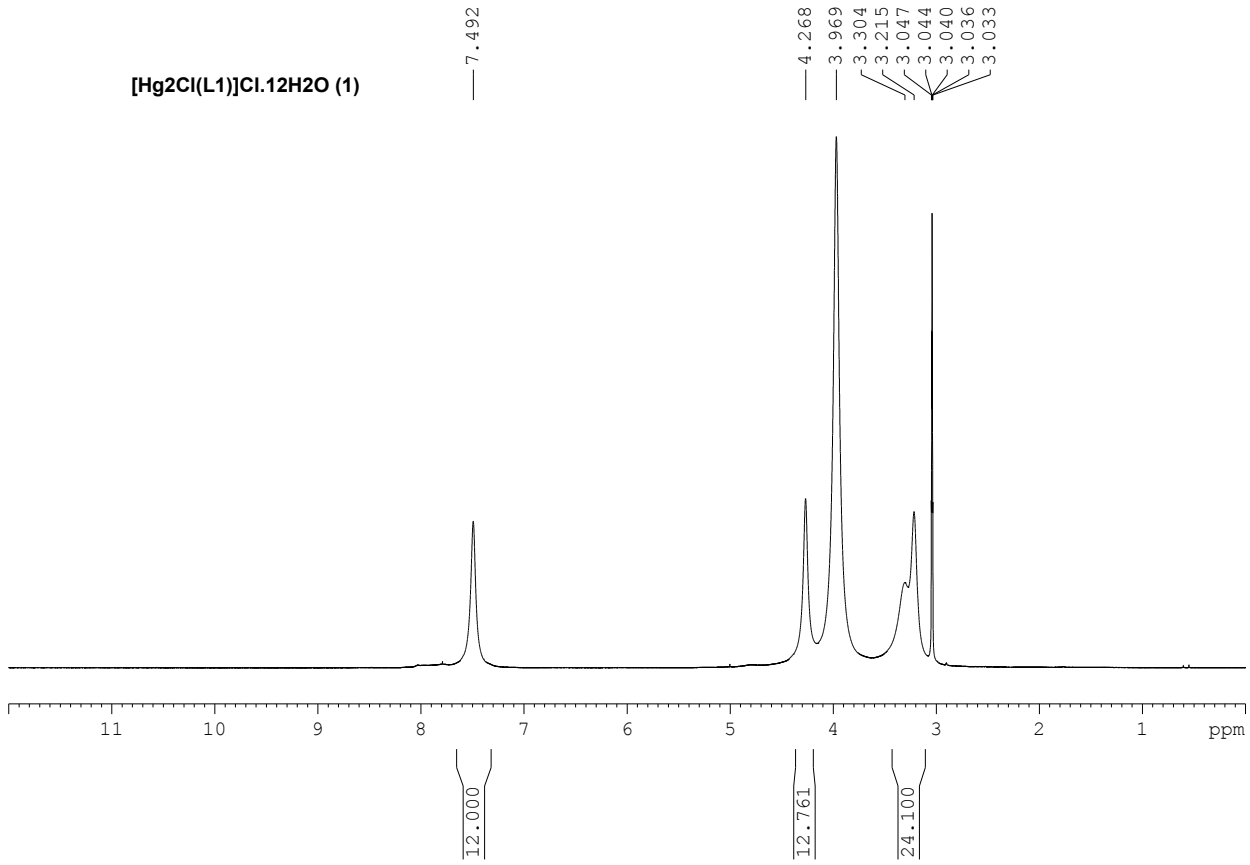


Figure S-3. 500 MHz ^{1}H NMR spectrum of $[Hg_2Cl(\mathbf{L1})]Cl.12H_2O$, **1** in DMSO-d6.

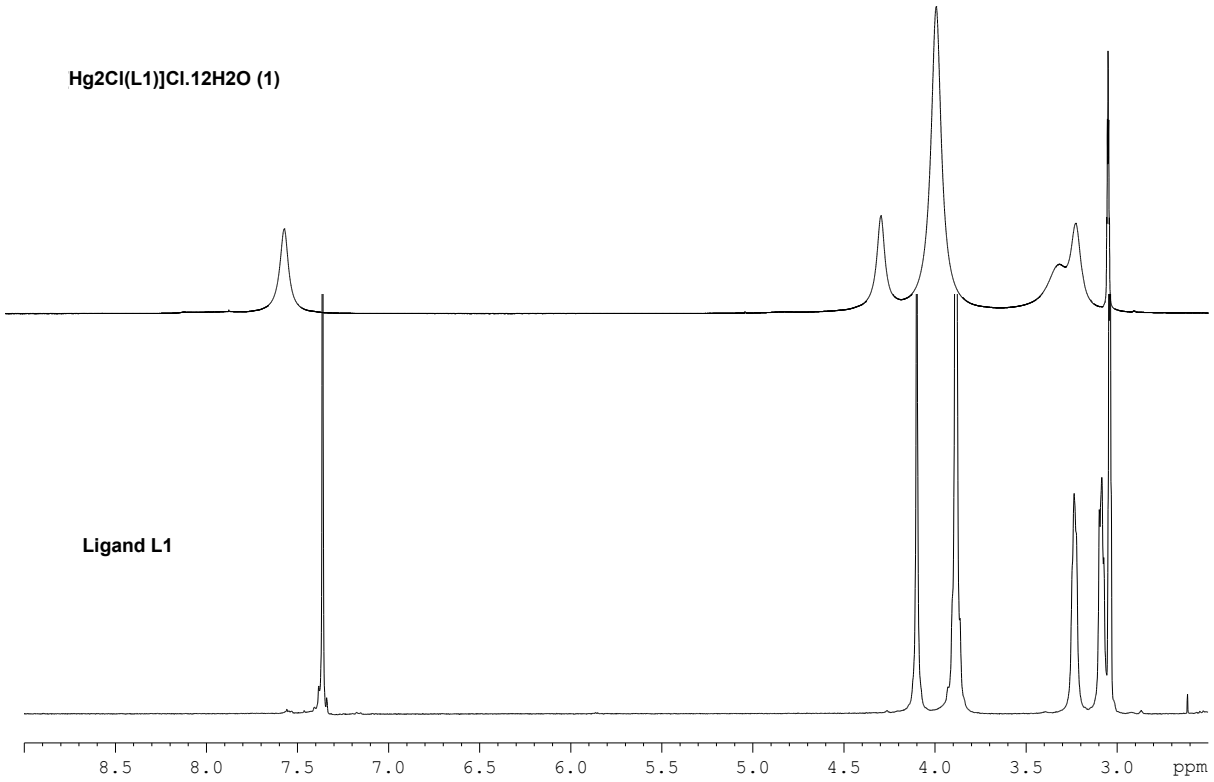


Figure S-4. Stacking diagram of ^{1}H NMR spectrum of Ligand **L1** and $[Hg_2Cl(\mathbf{L1})]Cl.12H_2O$, **1**.

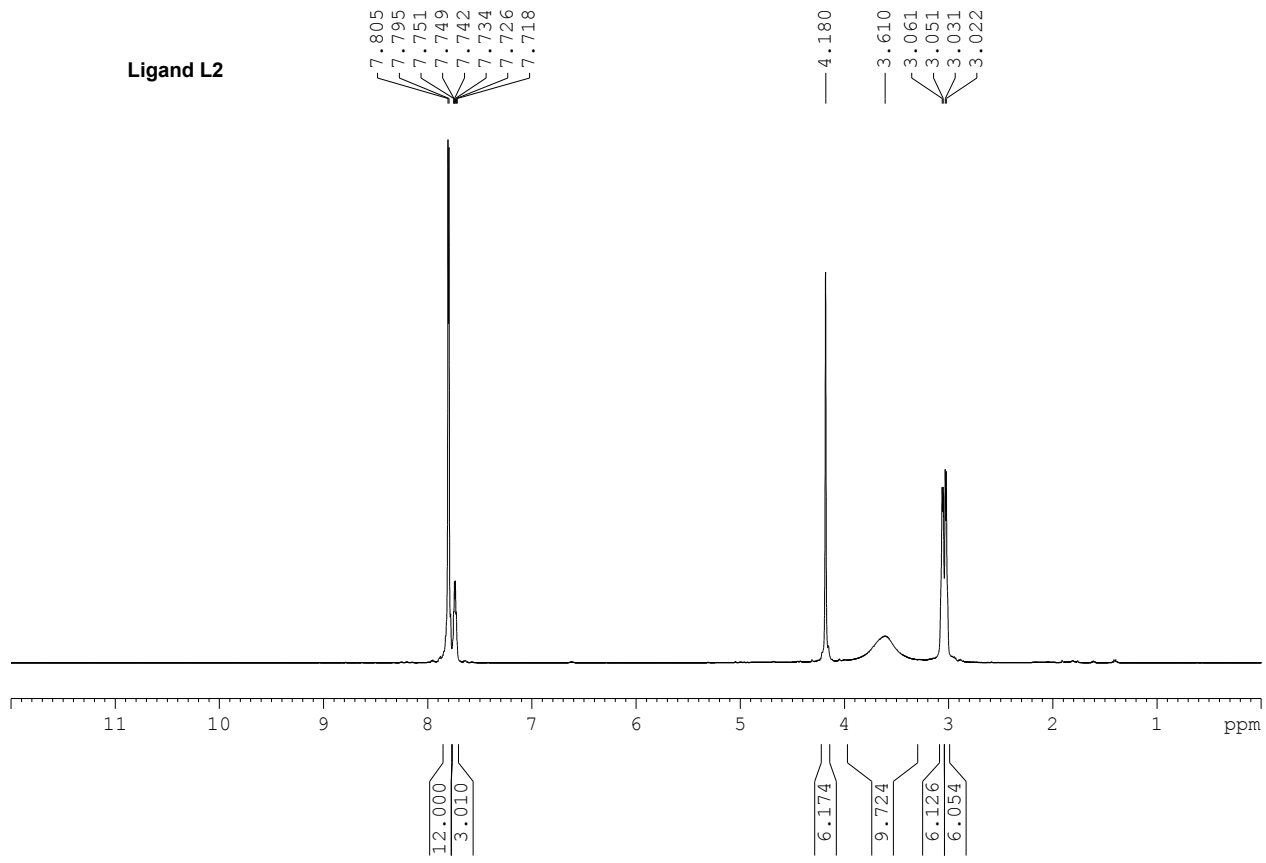


Figure S-5. 500 MHz ^{1}H NMR spectrum of Ligand **L2** in DMSO-d6.

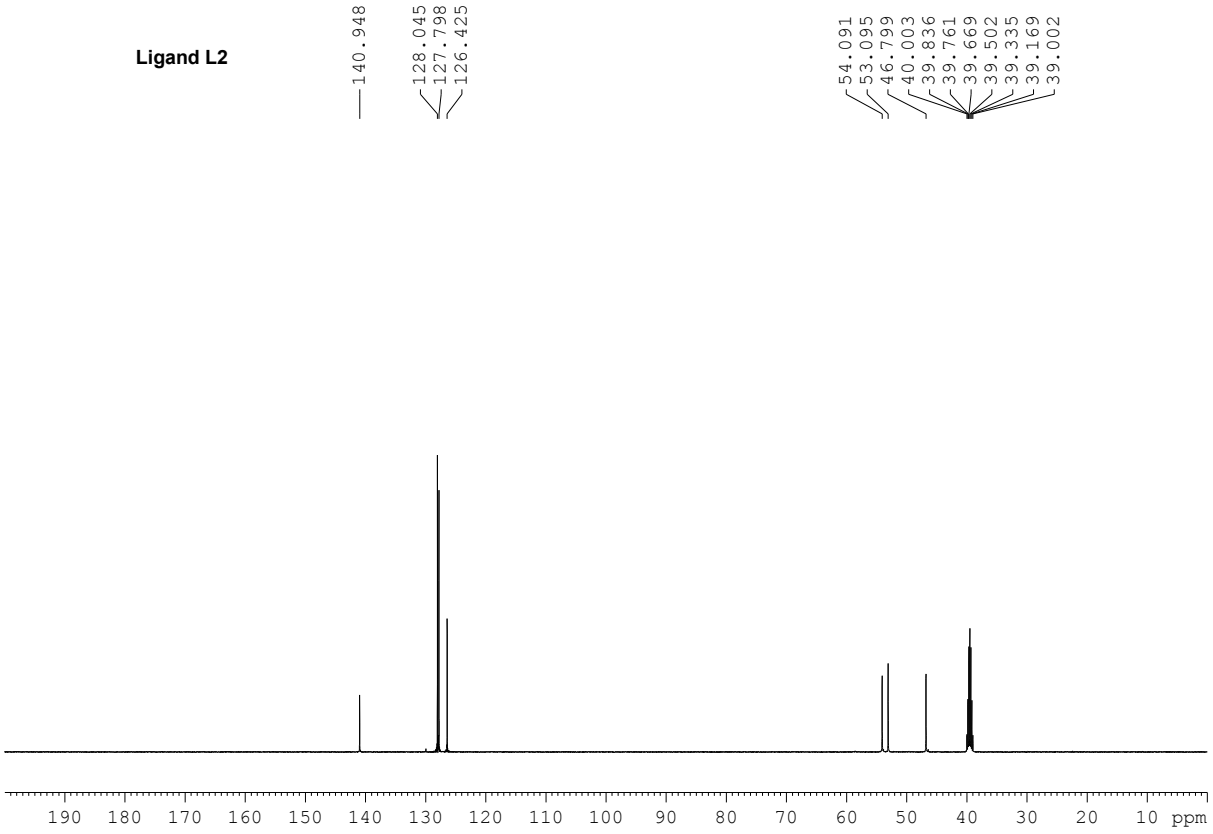


Figure S-6. 125.76 MHz ^{13}C NMR spectrum of Ligand **L2** in DMSO-d6.

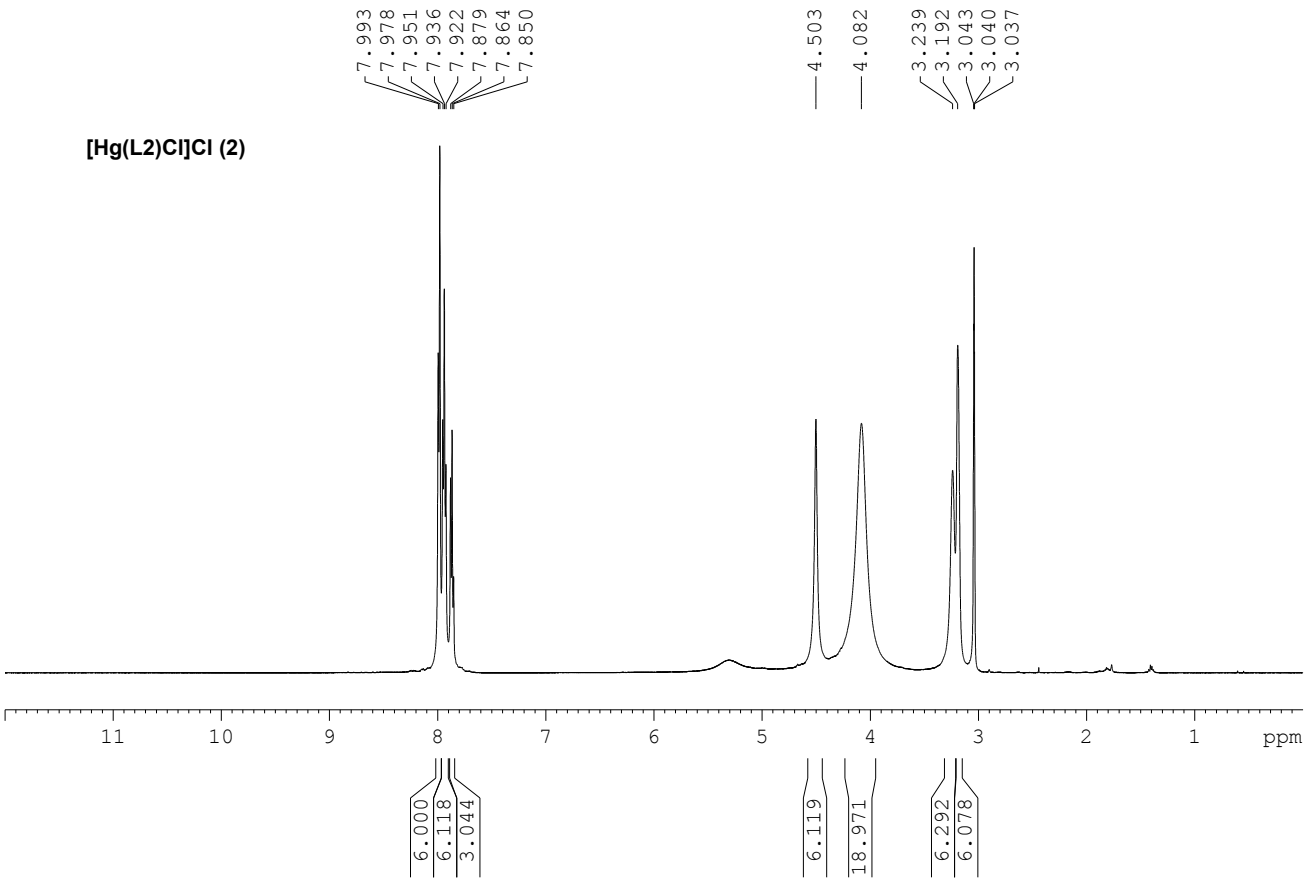


Figure S-7. 500 MHz ^{1}H NMR spectrum of [Hg(**L2**)Cl]Cl, **2** in DMSO-d6.

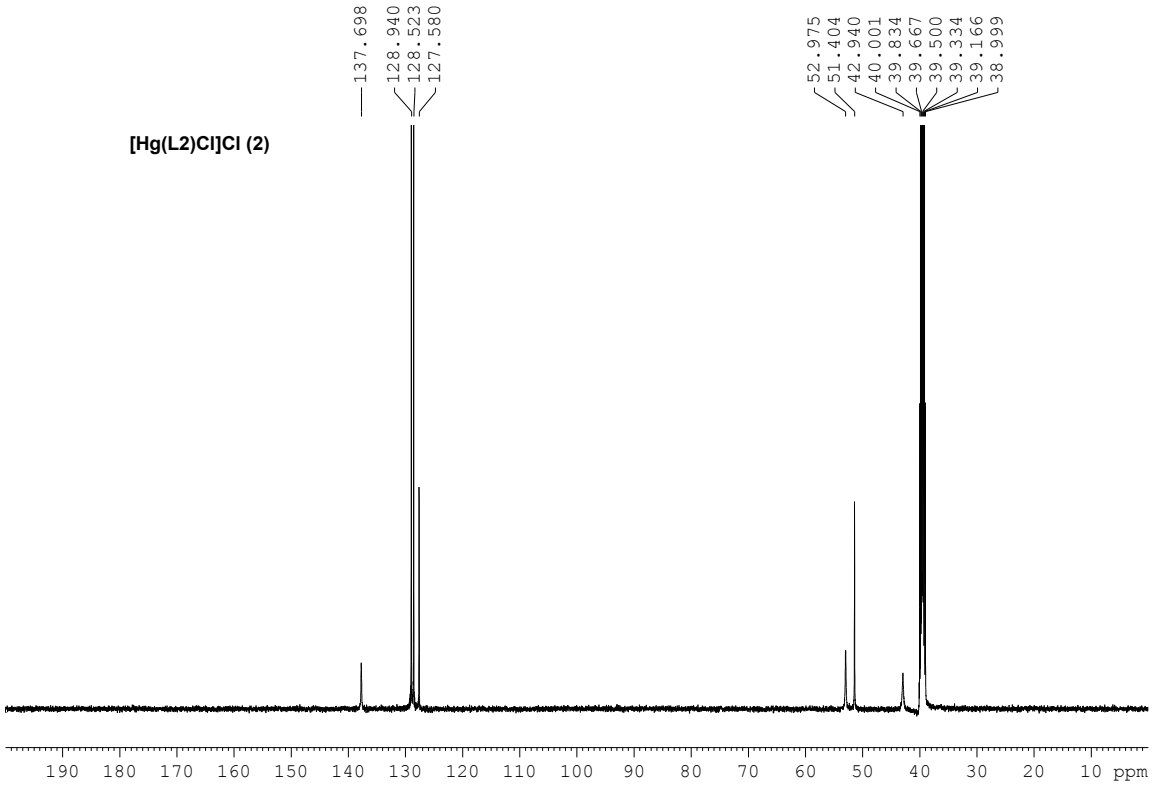


Figure S-8. 125.76 MHz ^{13}C NMR spectrum of [Hg(**L2**)Cl]Cl, **2** in DMSO-d6.

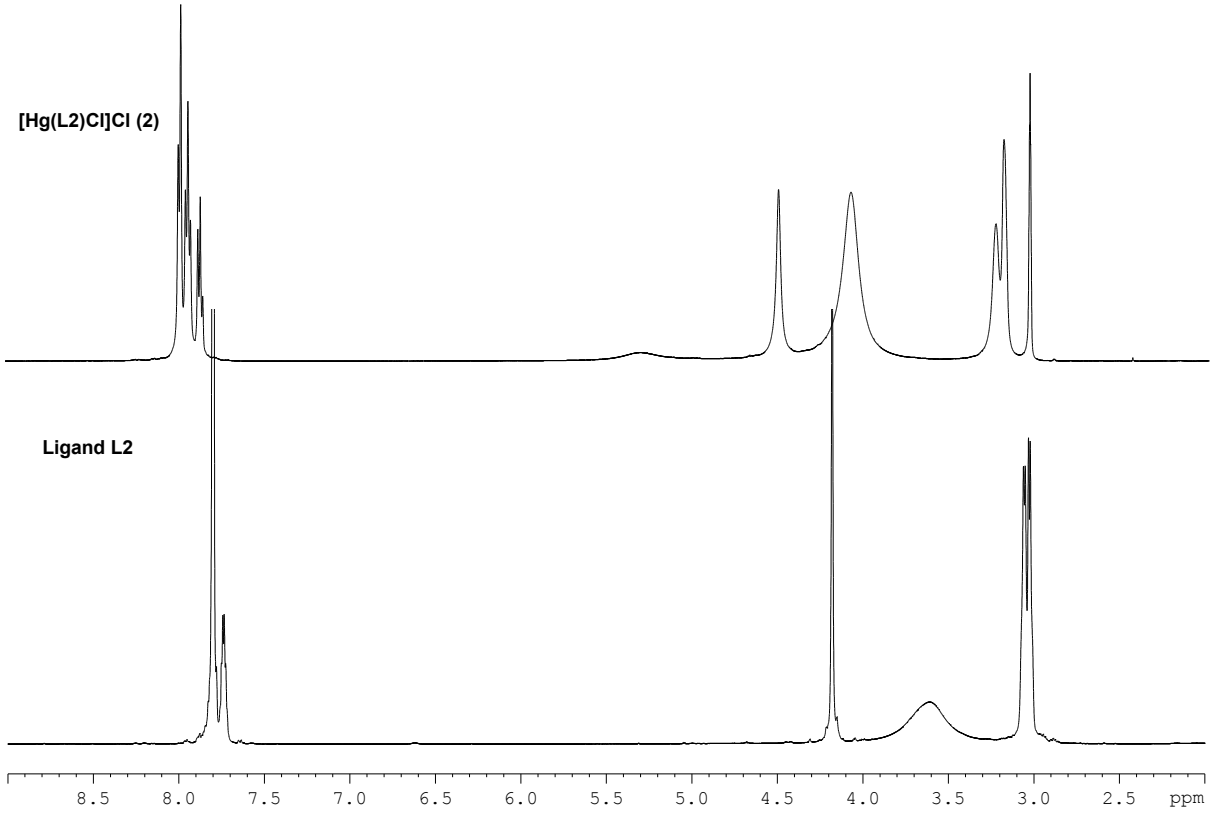
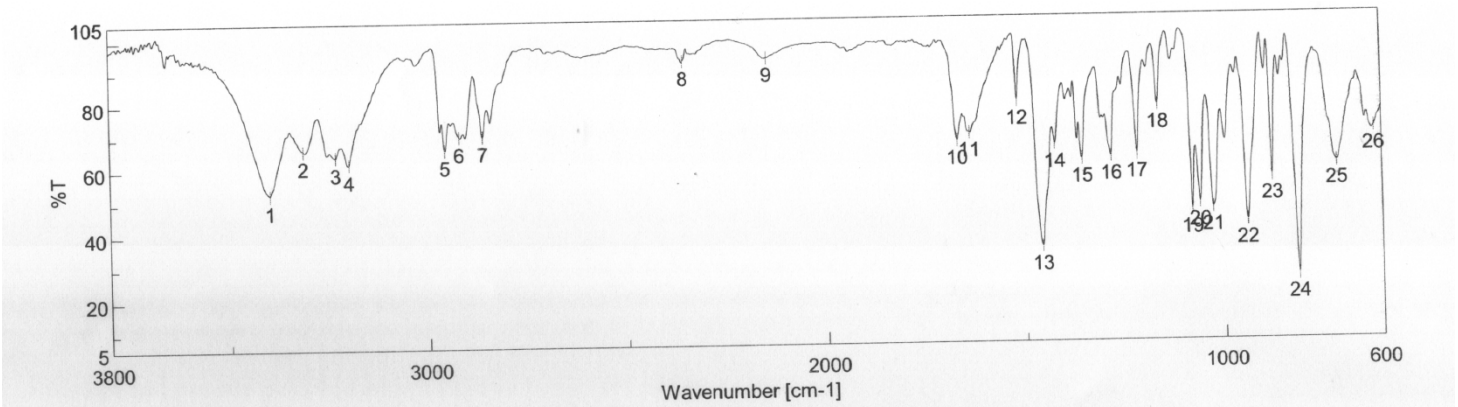


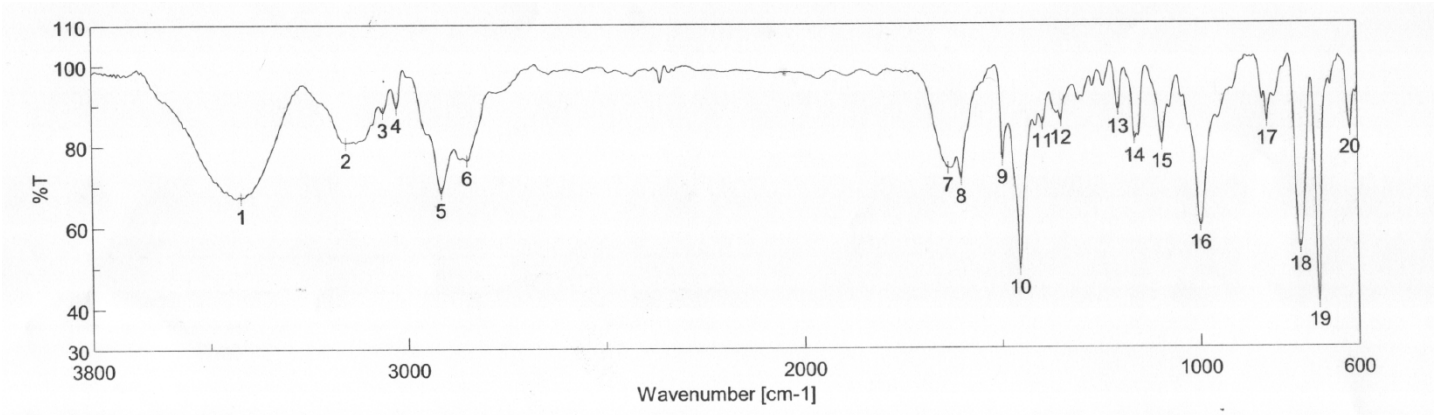
Figure S-9. Stacking diagram of ^{1}H NMR spectrum of Ligand **L2** and [Hg(**L2**)Cl]Cl, **2**.



[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3398	52.3763	2	3312	65.9028	3	3231	63.8242
4	3197	61.4718	5	2956	65.624	6	2921	69.5903
7	2861	69.676	8	2356	92.119	9	2145	92.9818
10	1668	66.5795	11	1637	68.8956	12	1518	78.5399
13	1457	34.0104	14	1423	65.1194	15	1355	60.5011
16	1281	61.2741	17	1215	61.7571	18	1162	76.7853
19	1078	44.6329	20	1059	46.8077	21	1027	45.2571
22	940	41.2065	23	877	54.5846	24	811	24.5064
25	713	58.8522	26	619	69.2262			

Figure S-10. IR spectrum of $[Hg_2Cl(\mathbf{L1})]Cl.12H_2O$, **1**.



[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3421	67.005	2	3156	80.5974	3	3061	88.0258
4	3027	89.221	5	2917	68.2208	6	2851	76.1883
7	1635	74.1415	8	1602	71.3655	9	1497	76.0303
10	1454	48.9427	11	1395	84.8013	12	1349	85.6334
13	1205	88.2881	14	1164	81.1595	15	1094	79.6992
16	998	59.7705	17	829	85.2892	18	748	54.3061
19	701	40.6542	20	619	83.0488	21	481	88.0098
22	438	89.614	23	419	84.1651			

Figure S-11. IR spectrum of [Hg(L2)Cl]Cl, **2**.

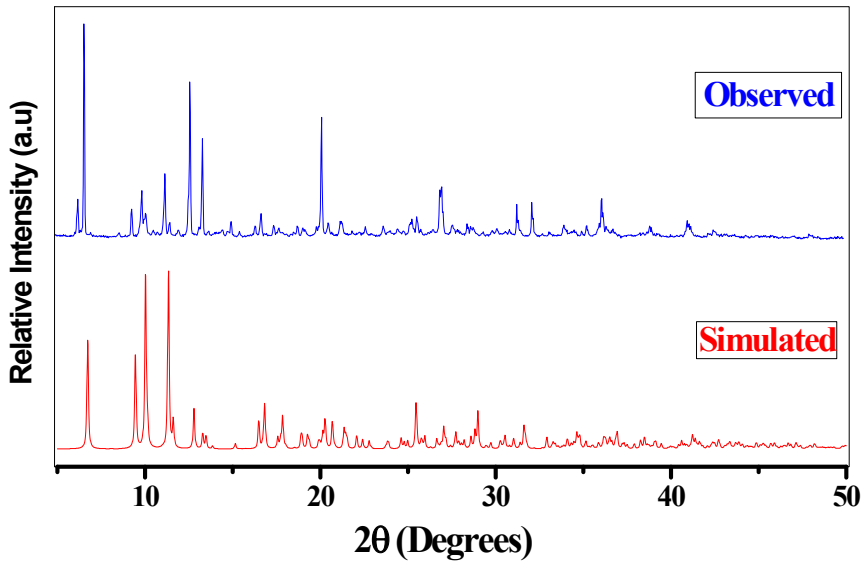


Figure S-12. Observed and Simulated PXRD pattern of $[Hg_2Cl(\mathbf{L1})]Cl.12H_2O$, **1**.

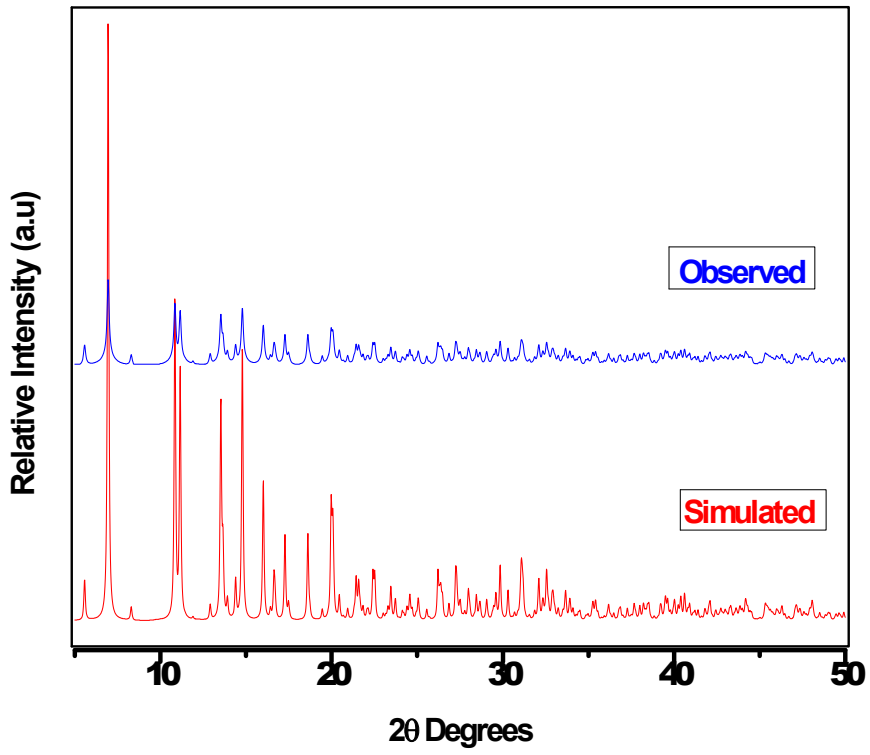


Figure S-13. Observed and Simulated PXRD pattern of [[Hg(**L2**)Cl]Cl, **2**.

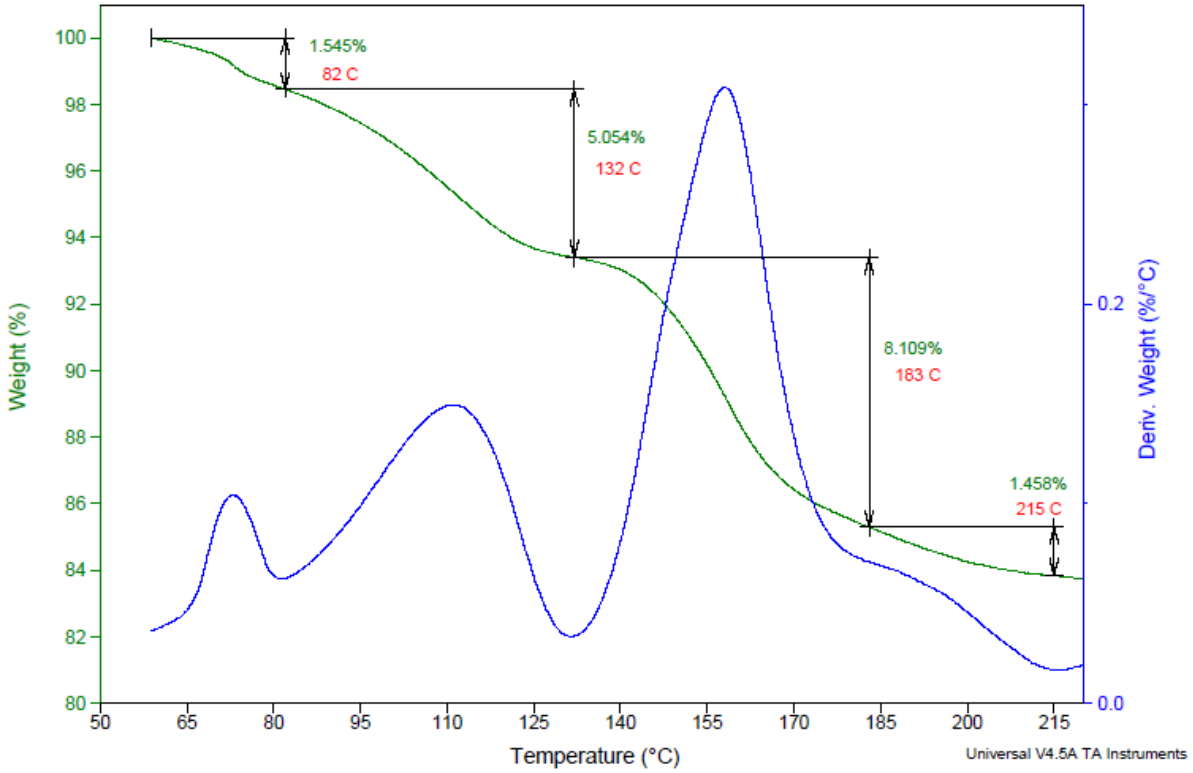


Figure S-14. TGA Curve for $[Hg_2Cl(L1)]Cl.12H_2O$, **1**.

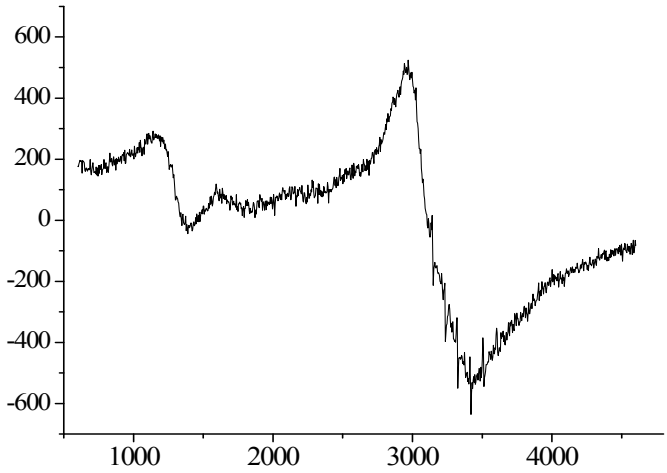


Figure S-15. The powder EPR spectra of $[Hg_2Cl(L1)]Cl.12H_2O$, **1.** (X- band, RT, calibrated using diphenylpicrylhydrazyl (DPPH).

Table S-1. Crystal data and structure refinement parameters for the complexes **1** and **2**.

Compounds	**1**	**2**
Empirical Formula	$C_{36}\ H_{52}\ Cl_2\ Hg_2\ N_8\ O_{12}$	$C_{27}\ H_{38}\ Cl_{1.5}\ Hg\ N_4\ O$
Formula Weight	1260.93	688.38
Crystal System	Monoclinic	Monoclinic
Space Group	C2/c	P 21/c
a (Å)	10.1044(5)	16.052(9)
b (Å)	18.7022(8)	21.298(12)
c (Å)	26.5462(12)	8.932(5)
α (°)	90.00	90.00
β (°)	98.448(2)	99.10(2)
γ (°)	90.00	90.00
Volume (Å)^3	4962.1(4)	3015(3)
Z	4	4
Wavelength (Å)	0.71073	0.71073
Temperature(K)	298(2)	298(2)
Calculated density (g/cm^3)	1.688	1.516
Absorption coefficient (mm^{-1})	6.348	5.262
F(000)	2456	1366
Crystal Dimensions (mm)^3	0.42 X 0.38 X 0.35	0.35 X 0.20 X 0.18
θ range for data collection (°)	1.551 to 24.999	1.602 to 25.00
Limiting indices	-12 ≤ h ≤12, -18 ≤ k ≤ 22, -31 ≤ l ≤ 31	-18 ≤ h ≤18, -25 ≤ k ≤ 25, -9 ≤ l ≤ 10
Reflections collected / unique	14135/4350	15883/5040
Data / restraints / Parameter	4350/0/281	5040/ 6/ 279
GOF	1.017	1.025
Final [a]*R* indices [*I*>2σ (*I*)]	*R*1 = 0.0407	*R*1 = 0.0871
	*wR*2 = 0.1012	*wR*2 = 0.2432
R indices (all data)	*R*1 = 0.0509	*R*1 = 0.1549
	*wR*2 = 0.1059	*wR*2 = 0.3047
CCDC	785896	966453