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Group 12 metal complexes of (2-piperazine-1-yl-ethyl)-pyridin-2-yl-methylene-amine: rare participation of terminal piperazine N in coordination leads to structural diversity

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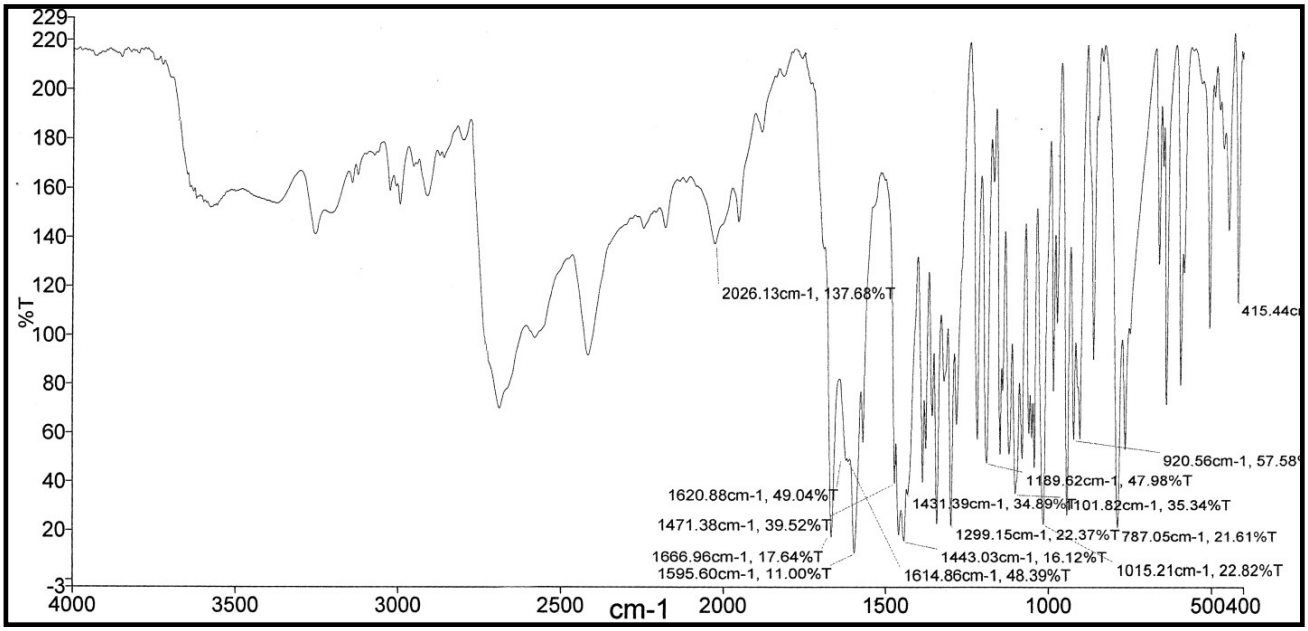

Fig. S1 Ir spectra of complex **1**

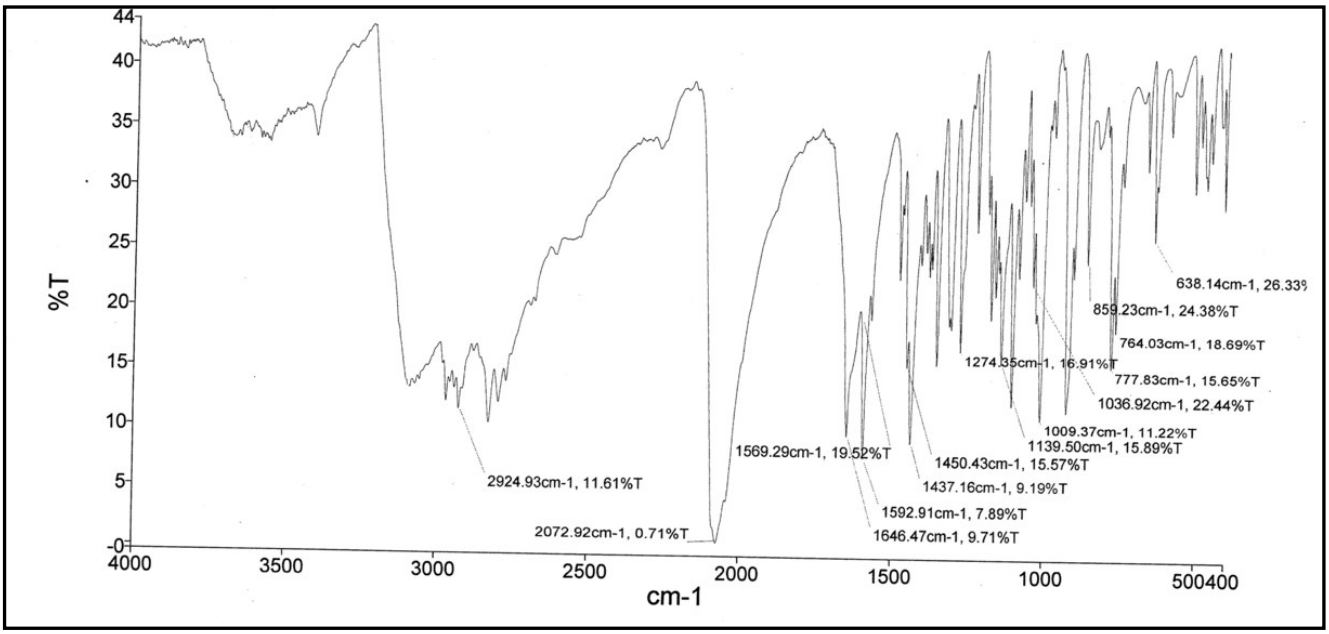

Fig. S2 Ir spectra of complex **2**

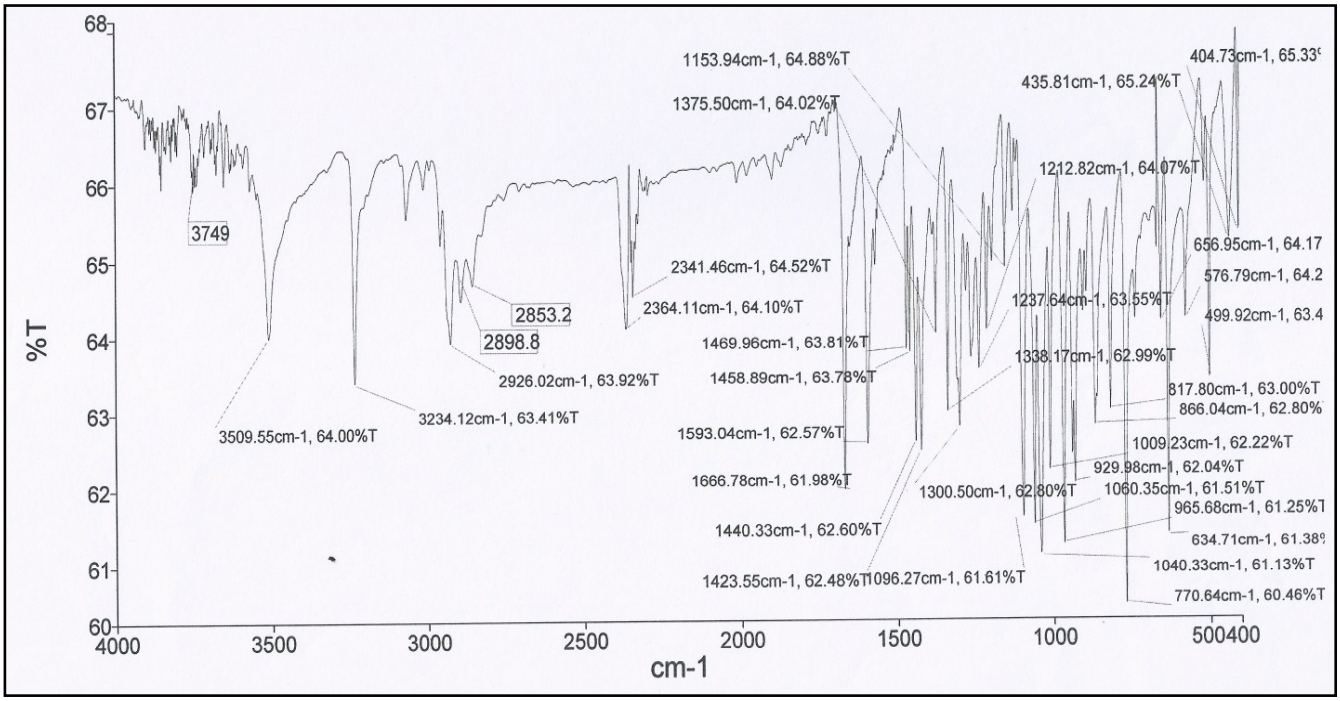

Fig.S3 Ir spectra of complex **3**

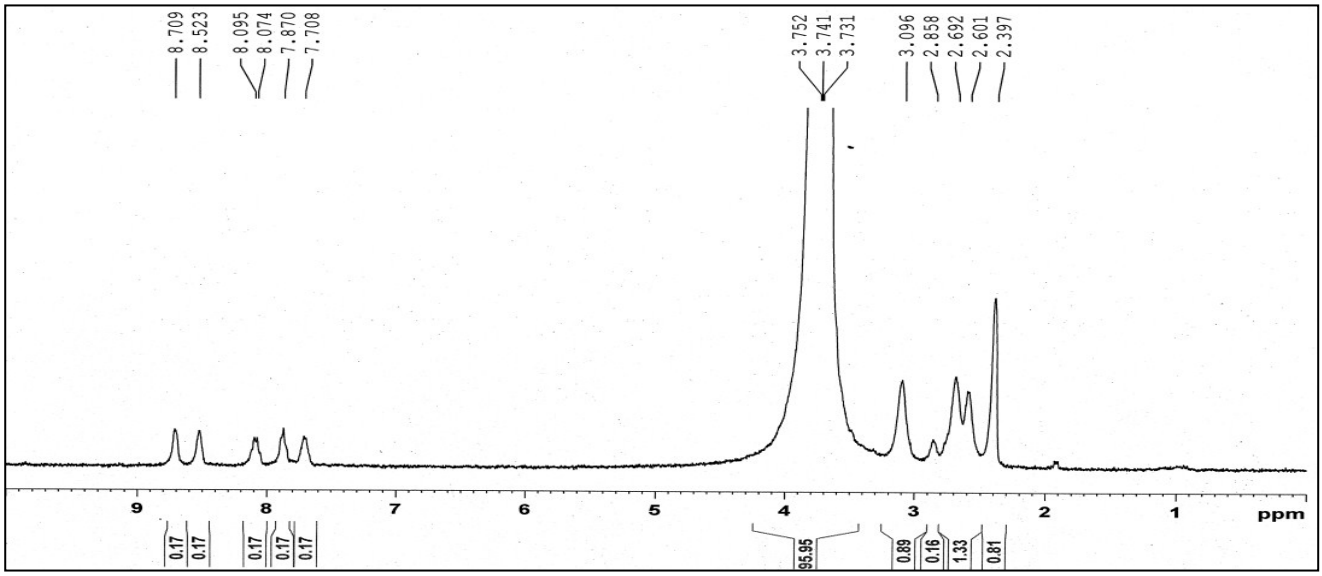

Fig. S4 ^{1}H NMR spectrum of complex **1**

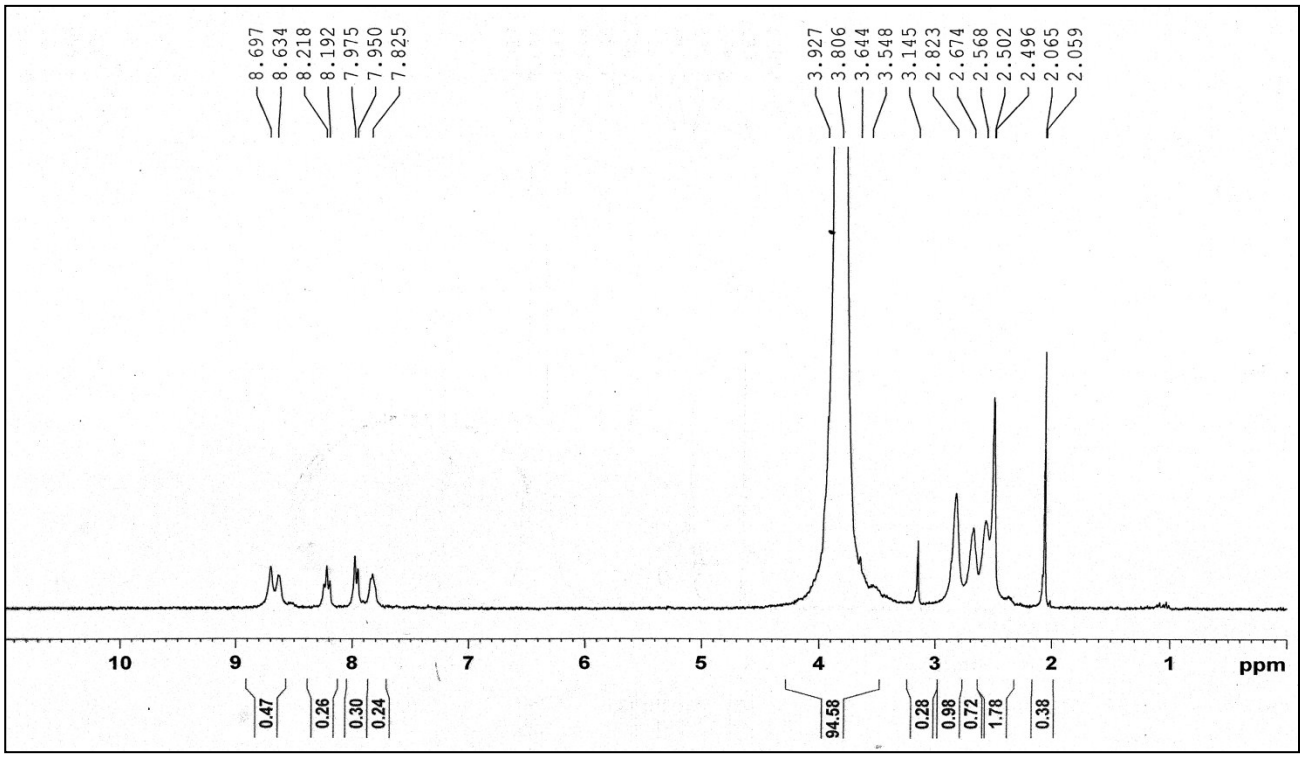

Fig .S5 ^{1}H NMR of complex **2**

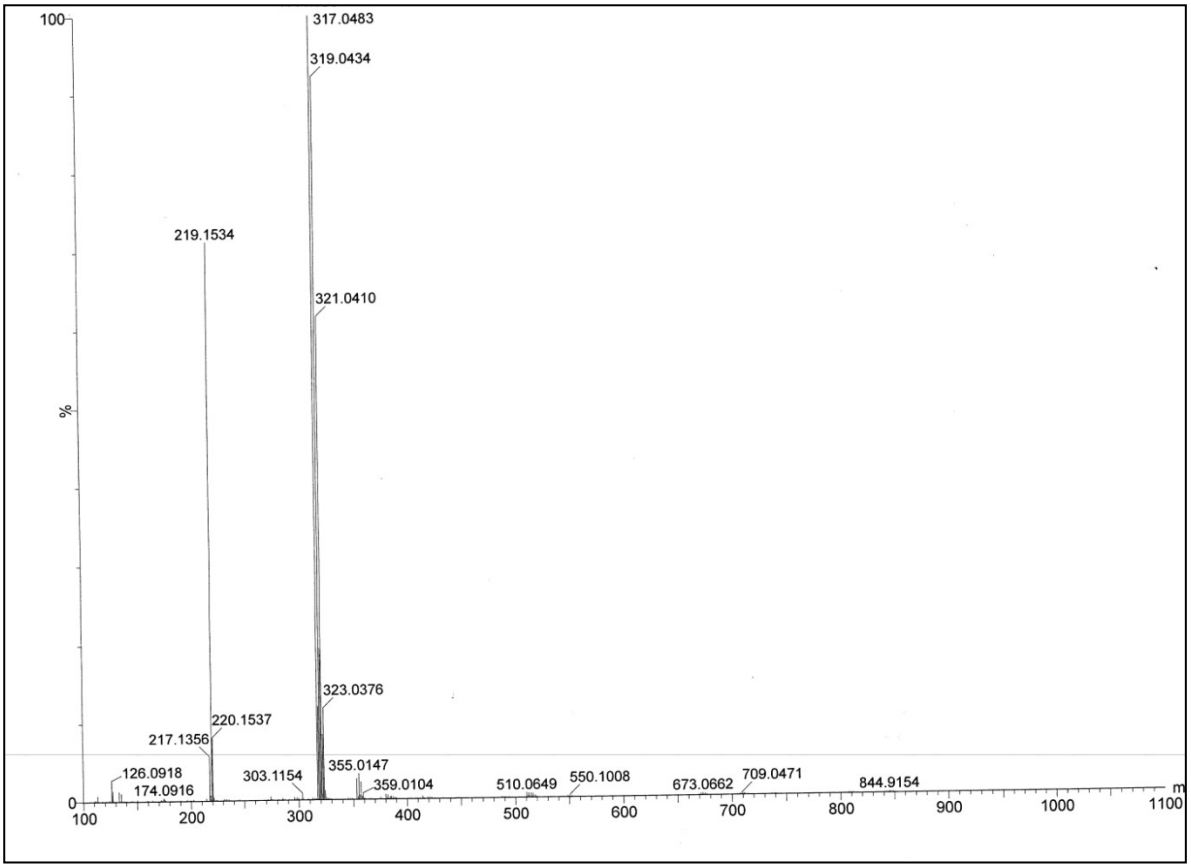

Fig. S6 Mass spectra of complex **1**

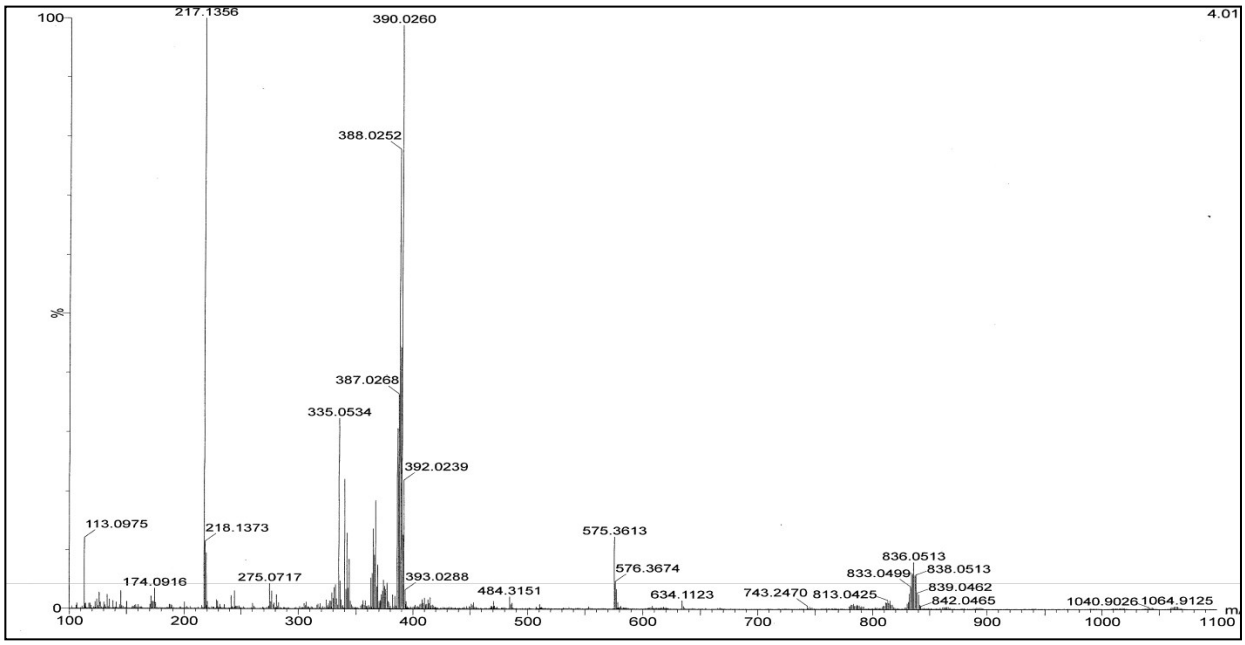

Fig. S7 Mass spectra of complex **2**

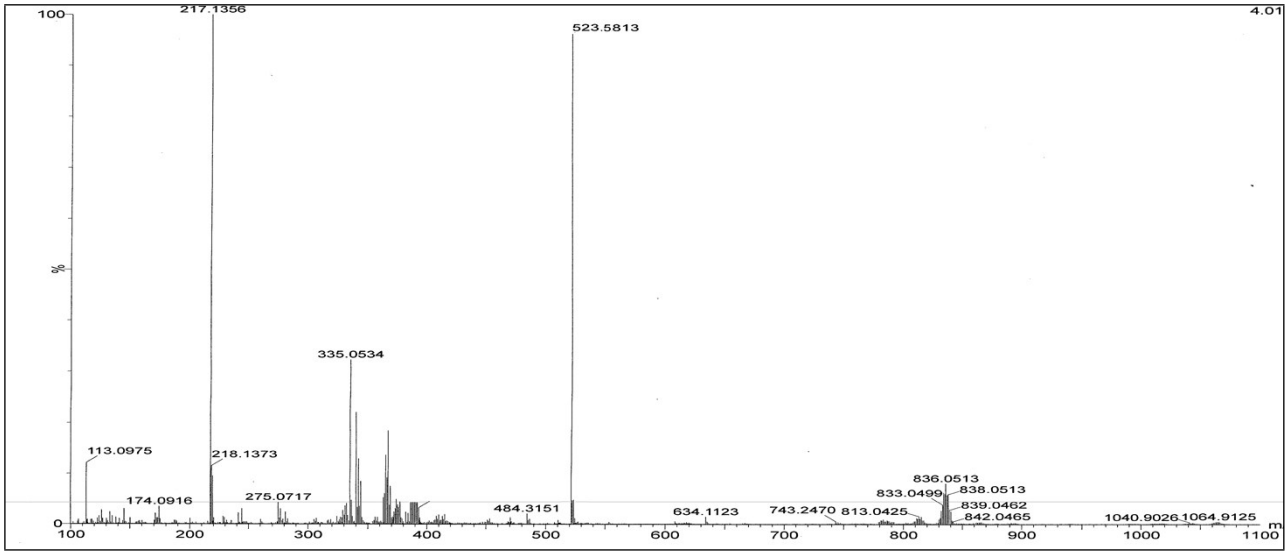

Fig . **S8** Mass spectra of complex **3**

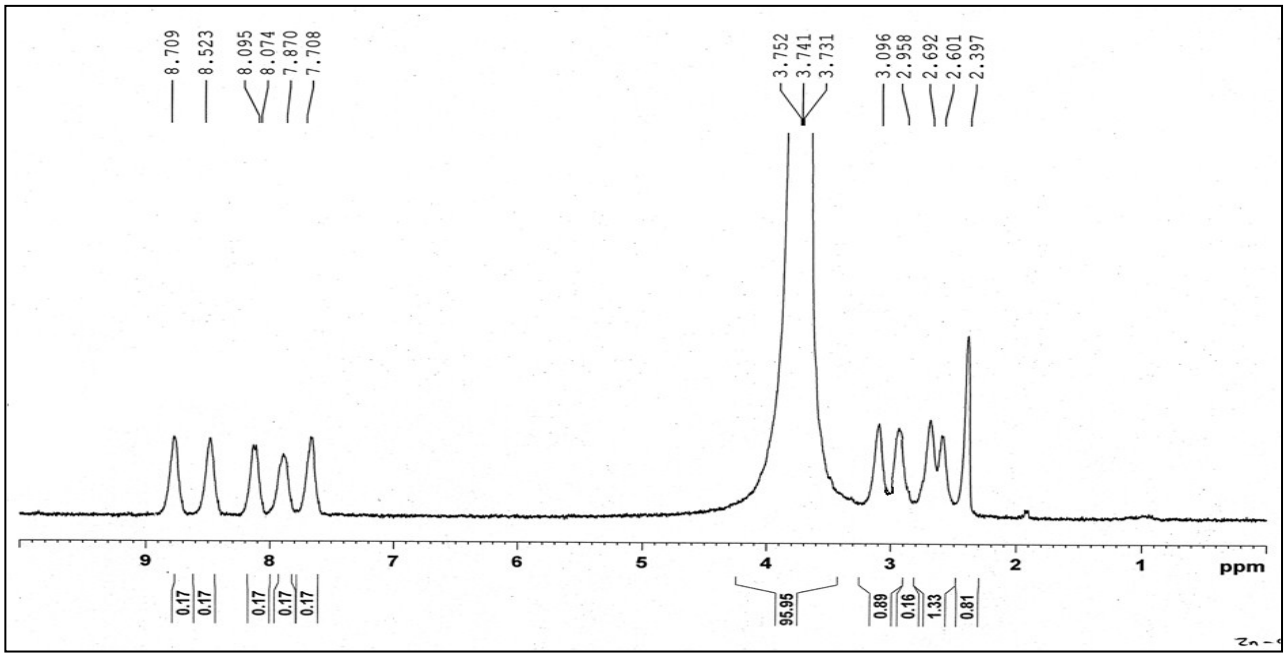

Fig .S9 ^{1}H NMR spectra of complex **3**

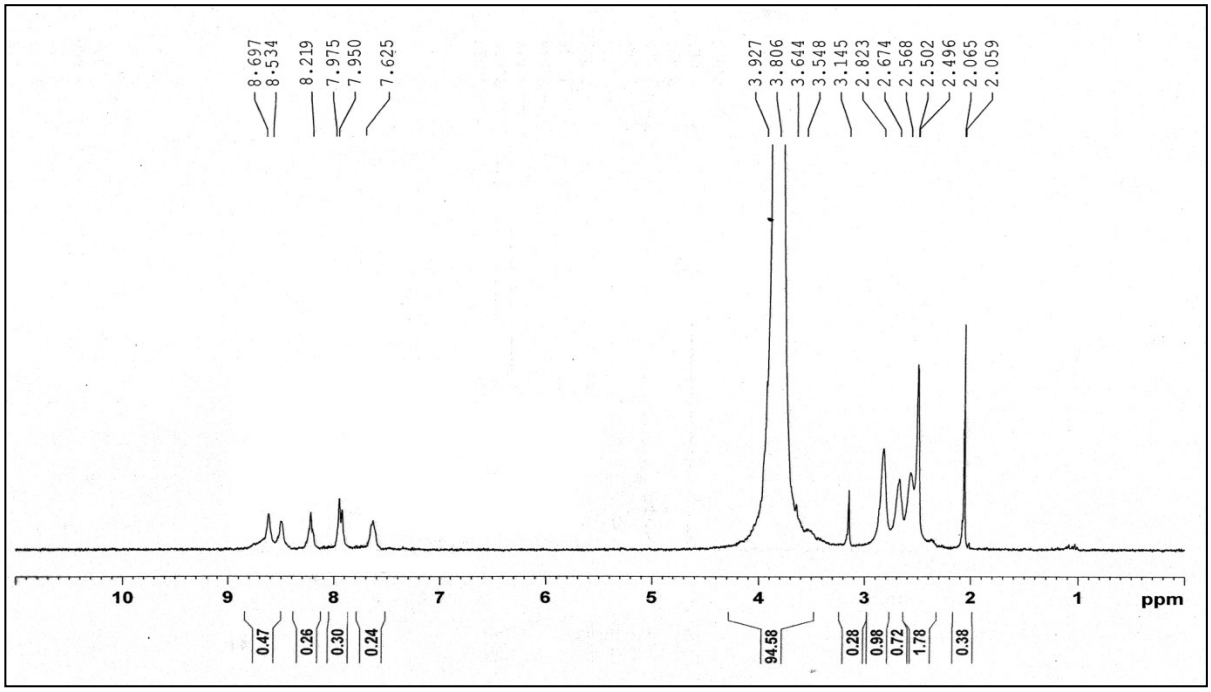

Fig. S10 ^{1}H NMR spectra of ligand(**HL**)

Table. S1 Relative Gibbs free enegies in solution for compounds involved in the reaction shown in the Scheme 1. The energy for $\mathbf{A}^{Cl}$ is arbitrarily taken to zero. All energies are in kcal/mol.

Compds	$[MCl(MeOH)L]^+$		
	Zn	Cd	Hg
$[MCl_2L]$ ($\mathbf{A}^{Cl}$)	0.00	0.00	0.00
$[MCl_2L^*]$ (*exchanging chelate ligand*)	-0.39	+0.85	+0.33
$[M(\kappa N\text{-}NCS)_2L]$ ($\mathbf{A}^{N}$)	+29.39	+39.88	+44.54
$[M(\kappa S\text{-}NCS)_2L]$ ($\mathbf{A}^{S}$)	+47.64	+44.84	+40.08
$[MCl_2(MeOH)L]$ ($\mathbf{B}^{Cl}$)	+13.66	+10.79	+15.01
$[M(\kappa N\text{-}NCS)_2(MeOH)L]$ ($\mathbf{B}^{N}$)	+42.91	+48.59	+58.29
$[M(\kappa S\text{-}NCS)_2(MeOH)L]$ ($\mathbf{B}^{S}$)	+59.51	+55.64	+55.86
$[MCl(MeOH)L]^+$ (**C**)	+59.20	+39.82	+28.74
[MCl(MeO)L] (**D**)	-7.53	-3.36	-11.99
½ $[M_2Cl_2(MeOH)_2L_2]^{2+}$ (**CC**)	+44.41	+41.10	+37.11
½ $[M_2Cl_2(MeO)_2L_2]$ (**DD**)	-6.98	-0.37	-4.82

Table .S2. Main geometric parameters for the optimized mononuclear structures. Distances in angstroms, angles in degrees.

M	**Zn**	**Cd**	**Hg**	**Zn**	**Cd**	**Hg**	**Zn**	**Cd**	**Hg**
Compds		$[MCl_2L]$ (**A**^{Cl})			$[M(\kappa N\text{-}NCS)_2L]$ (**A**^{N})			$[M(\kappa S\text{-}SCN)_2L]$ (**A**^{S})	
M-N_{Py}	2.323	2.574	2.786	2.388	2.545	2.801	2.375	2.588	2.793
M-N_{Im}	2.159	2.411	2.587	2.145	2.391	2.581	2.118	2.364	2.524
M-N_{Pip}	2.698	2.701	2.904	2.482	2.590	2.919	2.578	2.648	2.862
M-X	2.229	2.413	2.404	1.912	2.127	2.085	2.340	2.524	2.502
	2.230	2.424	2.411	1.914	2.156	2.093	2.361	2.559	2.518
X-M-X	134.1	141.0	157.6	132.1	133.4	159.7	126.7	130.9	148.4
M-X-C	-	-	-	169.7	140.5	136.9	99.0	100.0	101.7
				172.6	137.6	134.0	93.9	93.6	97.1
S_{TBP} [a]	2.84	3.46	4.85	2.47	3.58	5.39	2.95	4.31	5.02
S_{SPY} [a]	4.45	5.92	7.22	4.49	4.57	6.23	4.12	4.36	6.18
Compds		$[MCl_2(MeOH)L]$ (**B**^{Cl})			$[M(\kappa N\text{-}NCS)_2(MeOH)L]$ (**B**^{N})			$[M(\kappa S\text{-}SCN)_2(MeOH)L]$ (**B**^{S})	
M-N_{Py}	2.346	2.547	2.719	2.324	2.512	2.577	2.354	2.531	2.624
M-N_{Im}	2.708	2.754	3.012	2.449	2.573	2.696	2.427	2.587	2.756
M-N_{Pip}	2.244	2.508	2.694	2.265	2.455	2.559	2.274	2.483	2.595
M-O_{MeOH}	2.210	2.401	2.614	2.208	2.400	2.556	2.237	2.433	2.657
M-$X_{Py,Im}$	2.350	2.496	2.479	2.030	2.239	2.257	2.459	2.627	2.602
	2.324	2.501	2.472	2.014	2.223	2.254	2.508	2.666	2.649
X-M-X	108.9	121.1	138.3	105.4	109.9	116.7	100.1	105.4	113.3
M-X-C	-	-	-	148.2	138.2	130.2	101.2	99.3	98.7
				152.8	141.7	134.4	97.6	93.4	93.9
S_{OCT} [a]	1.95	3.28	5.40	1.16	2.02	2.74	1.53	2.09	2.92
S_{TPR} [a]	13.73	9.63	7.98	12.81	10.79	9.96	15.03	14.38	12.81

[a] Continuous shape measurements from ideal trigonal bipyramidal (S_{TBP}), square pyramidal (S_{SPY}), octahedral (S_{OCT}), or trigonal prismatic (S_{TPR}) geometries.

Table. S3. Main geometric parameters for the optimized binuclear structures. Distances in angstroms, angles in degrees.

M	**Zn**	**Cd**	**Hg**	**Zn**	**Cd**	**Hg**
Compds	$[MCl(MeOH)L]^+$ (**C**)			[MCl(MeO)L] (**D**)		
M-N_{Pip}	2.008	2.217	2.179	2.135	2.421	2.653
M-O_{Me}	2.030	2.312	2.614	1.818	2.022	2.034
M-Cl	2.120	2.304	2.303	2.164	2.345	2.350
Cl-M-N_{Pip}	137.5	153.1	171.6	108.1	104.2	95.5
Cl-M-O_{Me}	113.2	105.5	99.9	152.5	164.2	175.2
N_{Pip}-M-O_{Me}	109.2	101.4	89.5	99.3	91.6	89.4
S_{TRI} [a]	2.96	4.81	6.00	1.08	2.99	5.62
S_{LIN} [a]	2.19	0.82	0.23	4.81	1.88	0.21
S_{VTET} [b]	5.82	7.52	8.60	4.01	5.86	8.20
S_{DVTET} [b]	6.27	9.34	12.76	2.79	6.15	11.46
Compds	$[M_2Cl_2(MeOH)_2L_2]^{2+}$ (**CC**)			$[M_2Cl_2(MeO)_2L_2]$ (**DD**)		
M···M	3.207	3.598	3.959	3.051	3.684	3.686
M-N_{Pip} [c]	2.017	2.284	2.196	2.082	2.359	2.257
M-O_{Me} [c]	2.240	2.238	2.528	1.874	2.042	2.077
M-Cl	2.352 2.358	2.551 2.551	2.401 2.965	2.357 2.385	2.577 2.647	2.789 2.811
Cl-M-Cl [c]	94.2	90.3	85.5	93.1	89.2	92.8
M-Cl-M [c]	85.8	89.7	94.5	78.1	89.6	82.3
N_{Pip}-M-O_{Me} [c]	109.7	106.7	91.0	122.7	112.5	161.6
θ [d]	180.0	180.0	180.0	135.5	164.5	145.2
S_{TET} [a,c]	1.06	2.29	4.37	0.91	1.57	5.18
S_{SS} [a,c]	7.42	6.74	3.34	7.70	6.97	2.64
S_{LIN} [a,c]	18.34	25.54	29.21	10.64	8.76	17.42
S_{DVTET} [b,c]	0.62	2.23	4.14	0.64	1.00	1.40

[a] Continuous shape measures from ideal tetrahedral (S_{TET}), seesaw (S_{SS}), trigonal (S_{TRI}), or lineal (S_{LIN}) geometries. [b] Continuous shape measures from one or two vacant positions in an ideal tetrahedron (S_{VTET}, S_{DVTET}), or trigonal (S_{VTRI}) geometries. [c] Average value. [d] The θ value is defined as the bent angle between MCl_2 planes.