# Unusual Recognition and Separation of Hydrated Metal Sulfates, $[M_2(\mu\text{-}SO_4)_2(H_2O)_n$, M = $Zn^{II}$, $Cd^{II}$, $Co^{II}$, $Mn^{II}]$ by a Ditopic Receptor

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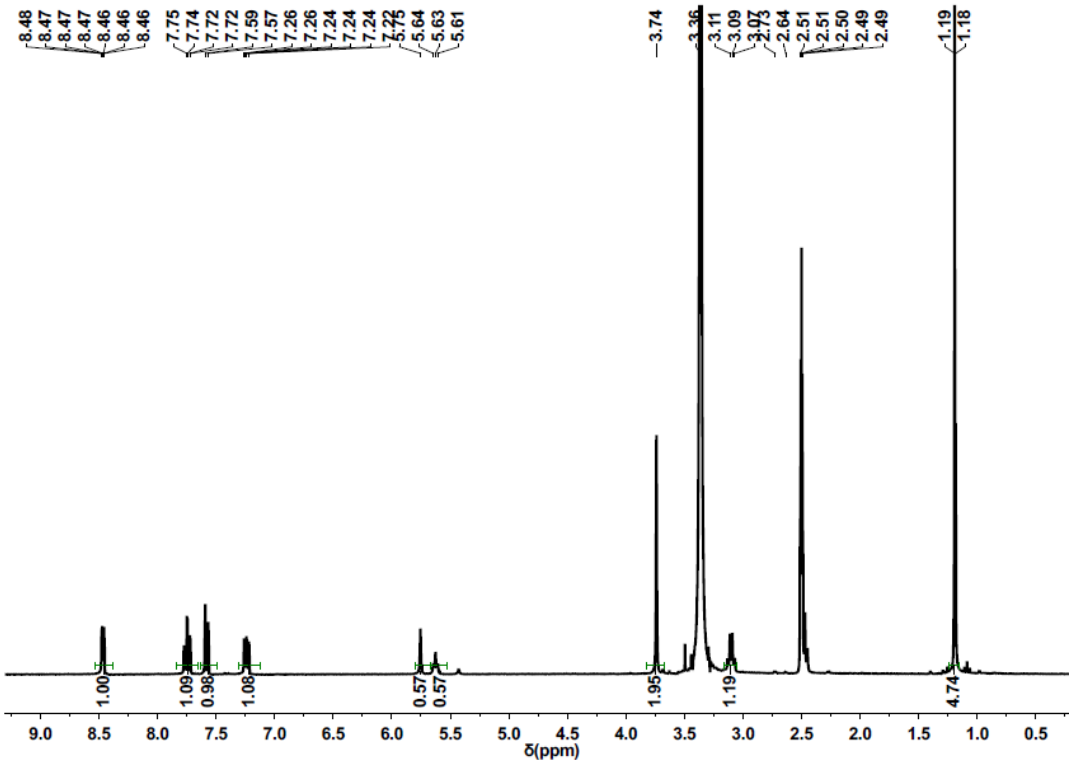


**Figure S1.** $^{1}$H-NMR Spectrum of **L1** in DMSO-$d_6$ at 298K.

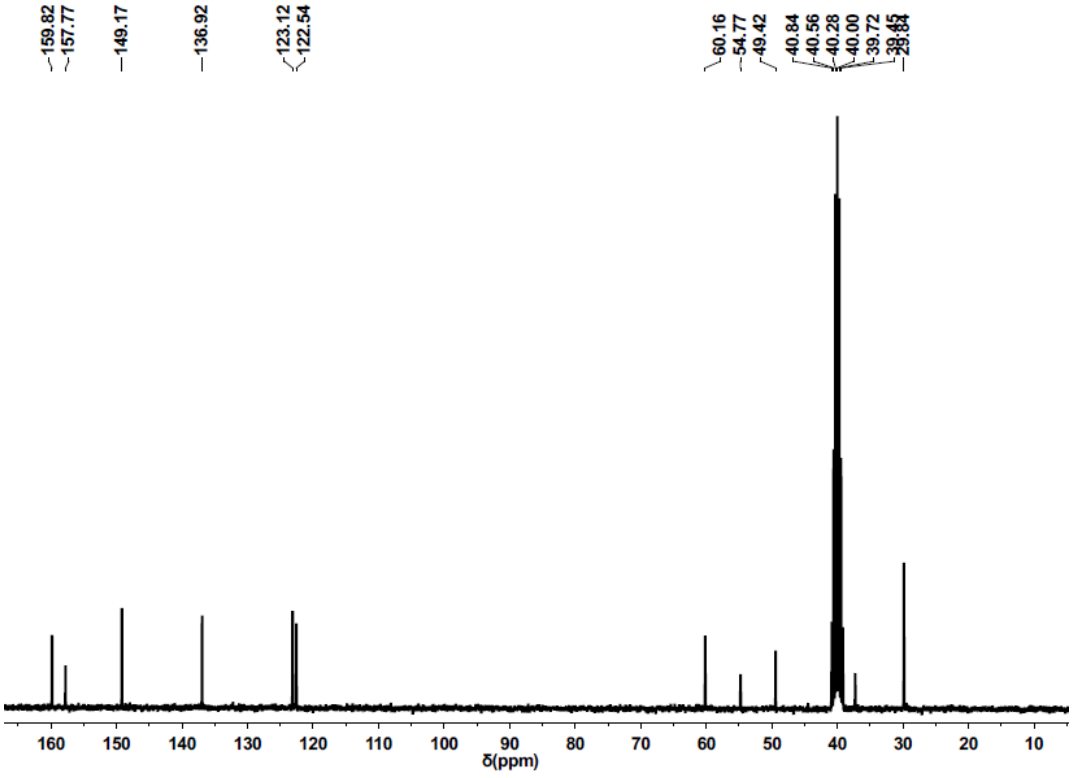


**Figure S2.** $^{13}$C-NMR Spectrum of **L1** in DMSO-$d_6$ at 298K.

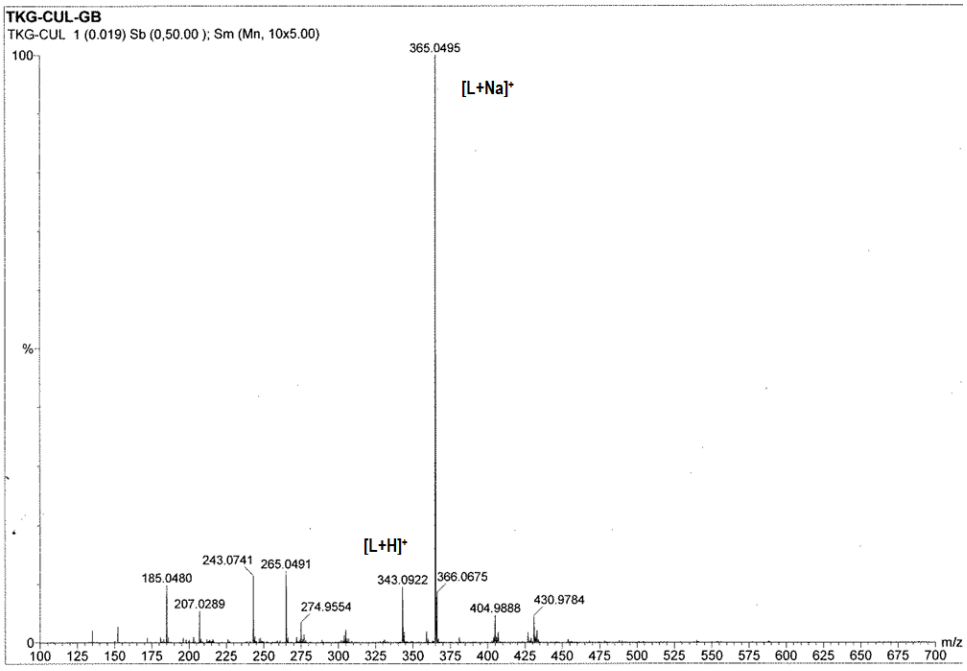


**Figure S3.** ESI-MS(+ve) Mass Spectrum of **L1**.

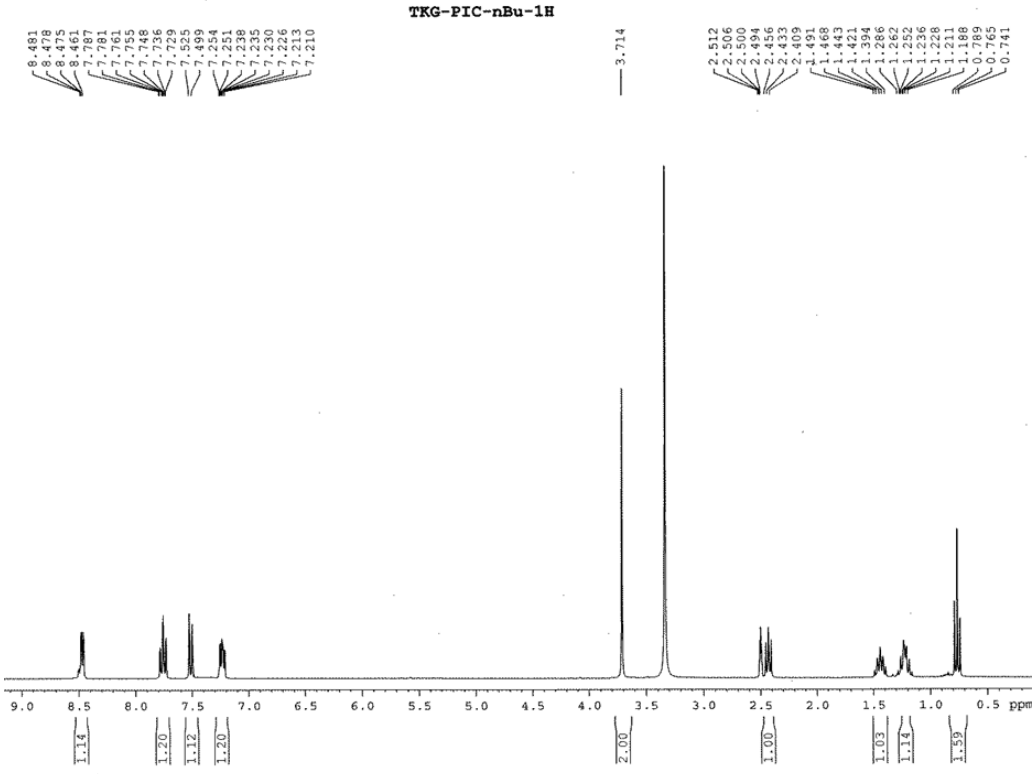


**Figure S4.** $^{1}$H-NMR Spectrum of **L2** in DMSO-$d_6$ at 298K.

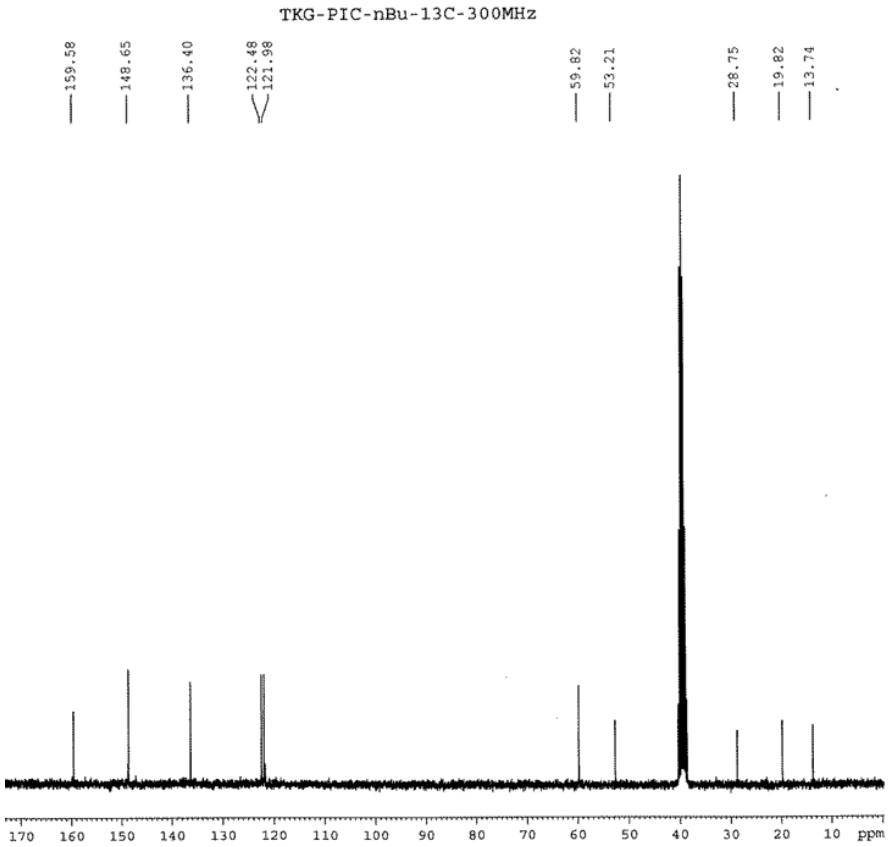


**Figure S5.** $^{13}$C-NMR Spectrum of **L2** in DMSO-$d_6$ at 298K.

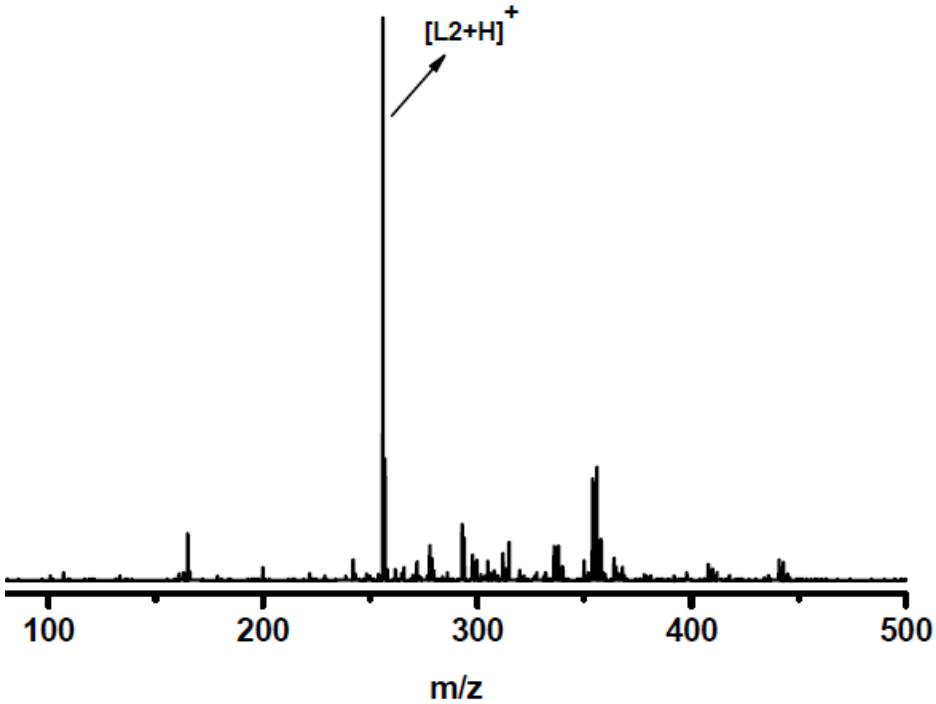


**Figure S6.** ESI-MS(+ve) Mass Spectrum of **L2**.

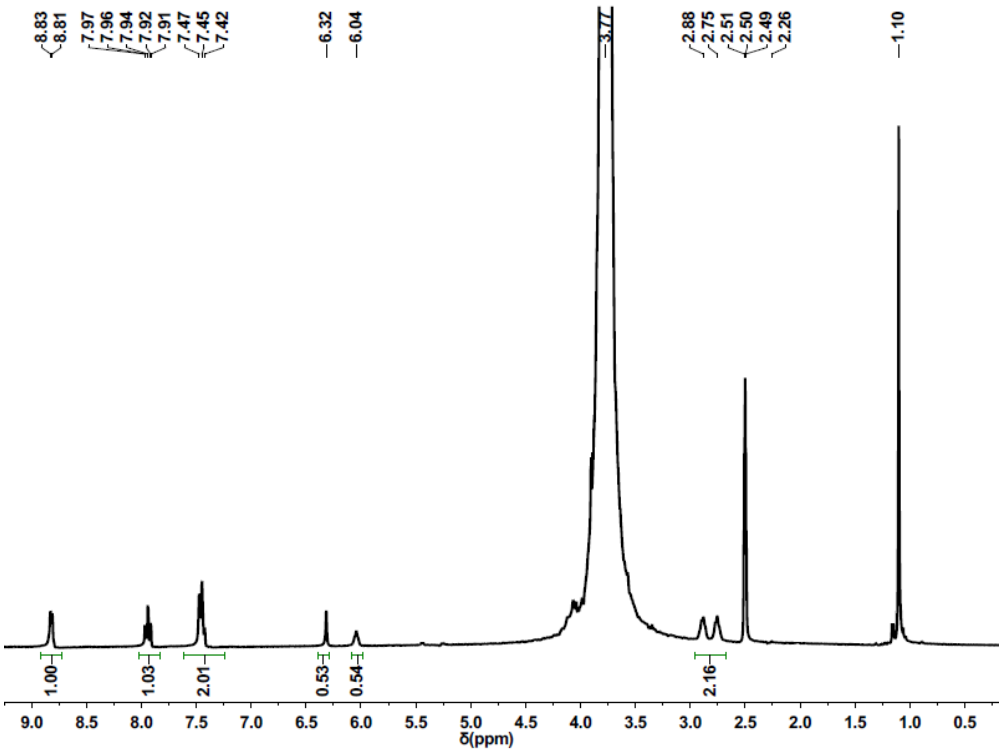


**Figure S7.** $^{1}$H-NMR Spectrum of complex **1** in DMSO-$d_6$ at 298K.

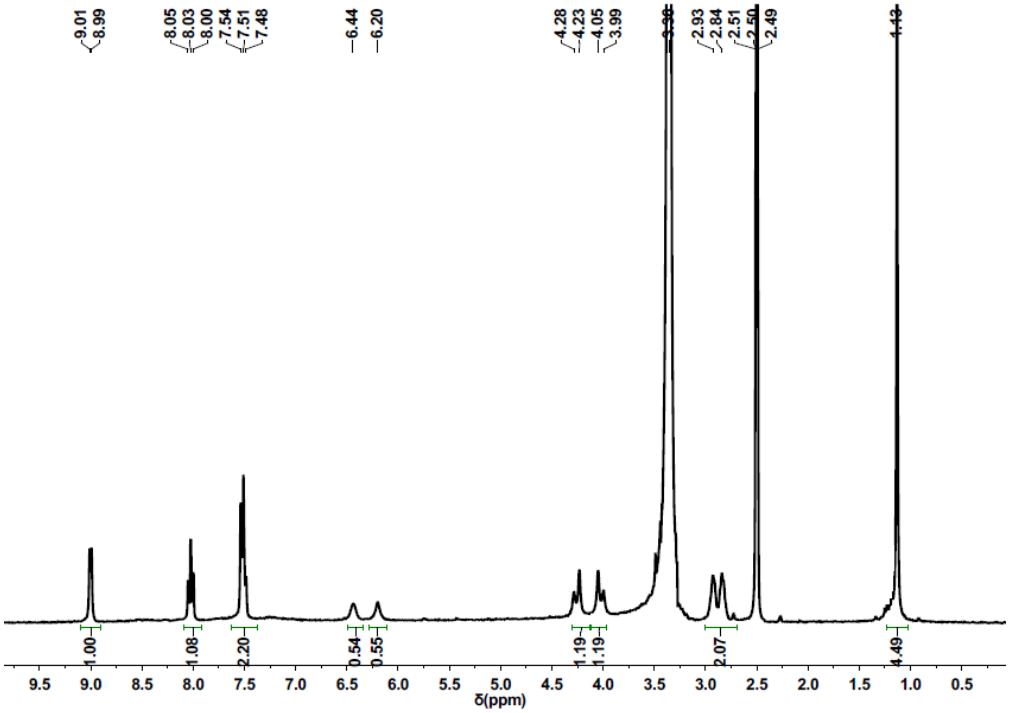


**Figure S8.** $^{1}$H-NMR Spectrum of complex **2** in DMSO-$d_6$ at 298K.

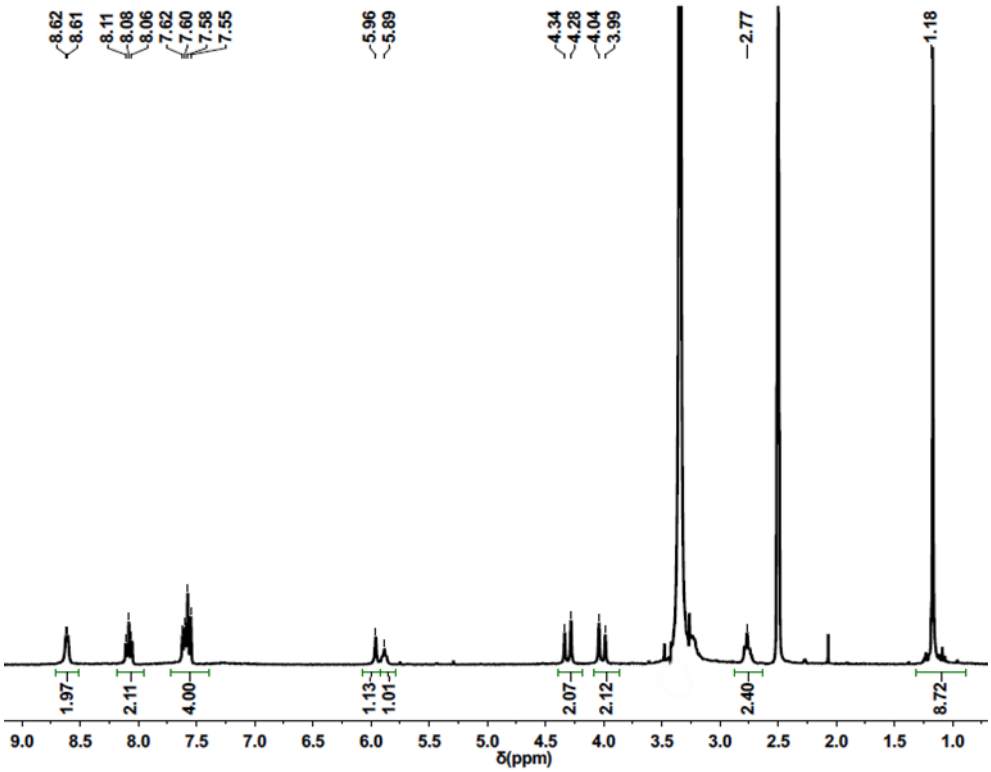


**Figure S9.** $^{1}$H-NMR Spectrum of complex **3** in DMSO-$d_6$ at 298K.

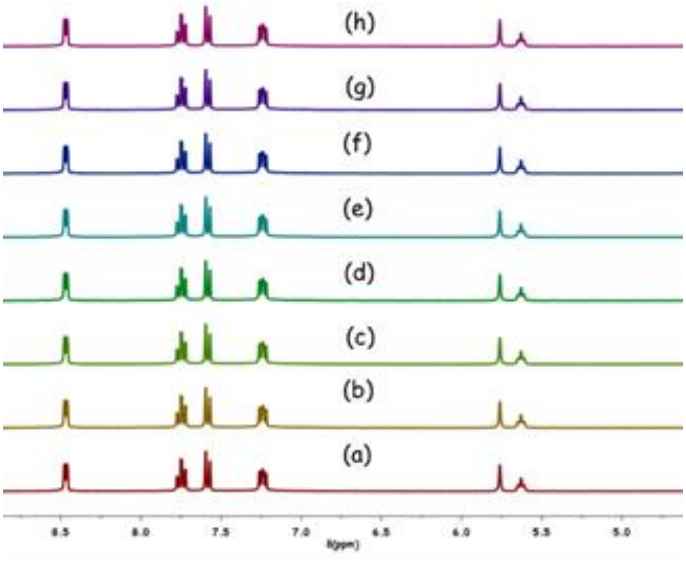


**Figure S10.** Qualitative & Partial $^{1}$H-NMR spectra of (a) free **L1** (b) **L1** (5.37mM) with TBACl (60.18mM) (c) **L1** (5.84mM) with TBABr (57.52mM) (d) **L1** (6.13mM) with TBAOAC (58.62mM) (e) **L1** (5.16mM) with $TBAH_2PO_4$ (54.58mM) (f) **L1** (6.28mM) with $(TBA)_2SO_4$ (64.23mM) (g) **L1** (5.69mM)with $TBAHSO_4$ (61.28mM)(h) **L1** (6.38mM)with TBAOH (50.12mM) in DMSO-$d_6$ at 298k.

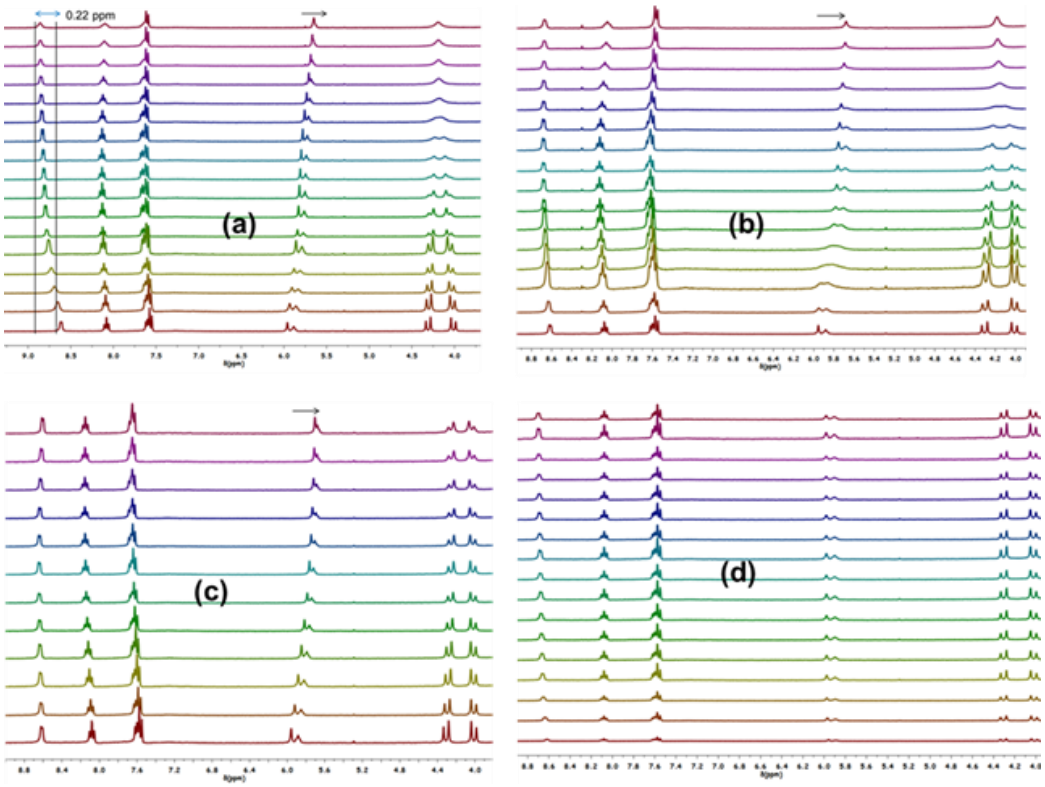


**Figure S11.** $^{1}$H- NMR titration profile of complex **5** (5.65mM) in DMSO-$d_6$ with (a) 36.4 mM TBACl in DMSO-$d_6$ (b) 37.1 mM TBAOAC in DMSO-$d_6$ (c) 42.4 mM $(TBA)_2SO_4$ (d) 35.2 mM $TBANO_3$ in DMSO-$d_6$ DMSO-$d_6$ at 298K in 300MHz.

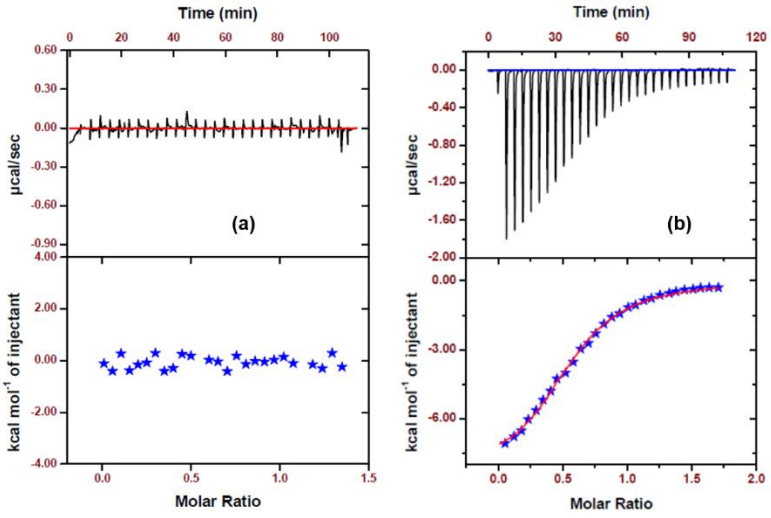


**Figure S12.** Isothermal calorimetric titration plot of (a) a solution of $(TBA)_2SO_4$ (0.8771mm) to a solution of **L1** (0.1253mm), (b) $ZnCl_2$ (0.8696 mm) to a solution of **L1** (0.1087 mm),The upper panel shows the heat pulses experimentally observed in each titration. The lower panel reports the respective time integrals translating as he heat evolved for each aliquot and its coherence to the 1:1 binding model.

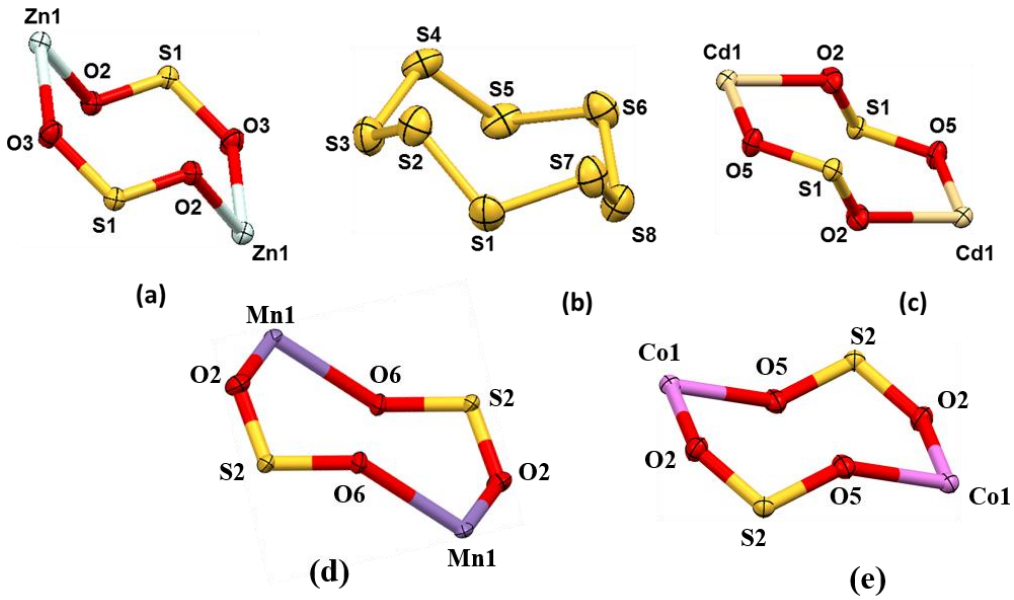


**Figure S13.** Truncated ORTEP view of (a) Zig- Zag $Zn^{II}_2S_2O_4$ unit in Complex **1**, (b) Molecular S8 (c) Zig- Zag $Cd^{II}_2S_2O_4$ unit in Complex **2**, (d) Zig- Zag $Mn^{II}_2S_2O_4$ unit in Complex **4**, (e) Zig-Zag $Co^{II}_2S_2O_4$ unit in Complex **3**.

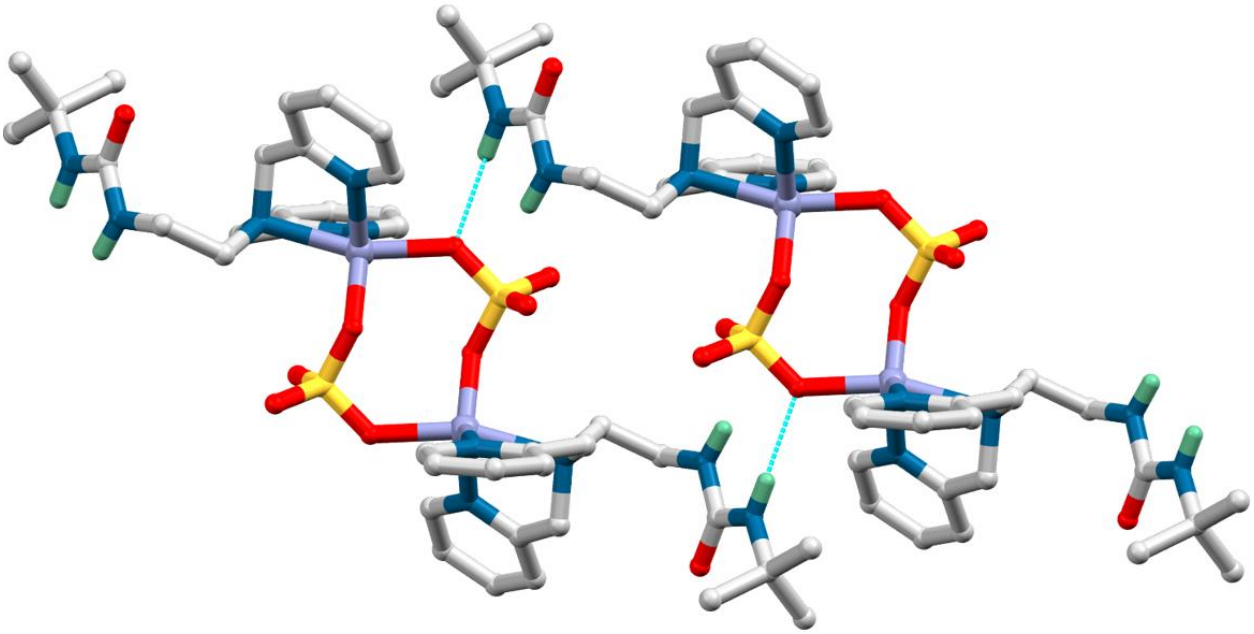

**Figure S14.** ORTEP view of complex **1** showing H-bonding interaction of $SO_4^{2-}$ with N-H protons of urea moiety in complex **1**. H-atoms except those of urea moiety are omitted for clarity. The structure is drawn at 50% probability level.

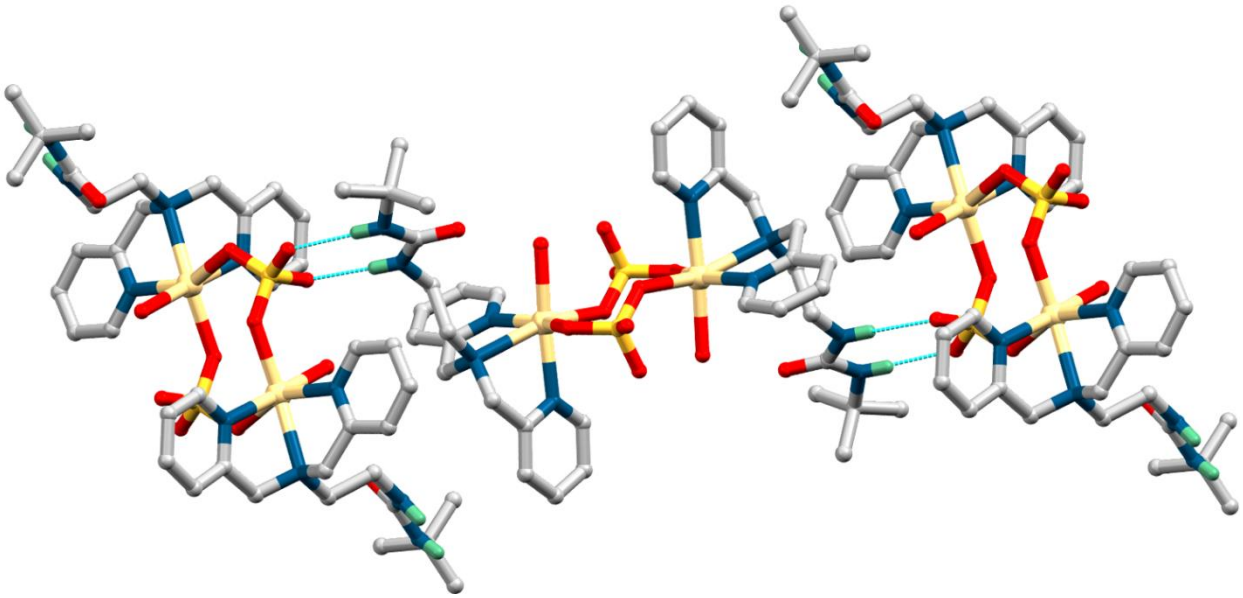

**Figure S15.** ORTEP view of complex **2** showing H-bonding interaction of $SO_4^{2-}$ with N-H protons of urea moiety. H-atoms except those of Urea moiety are omitted for clarity. The structure is drawn at 50% probability level.

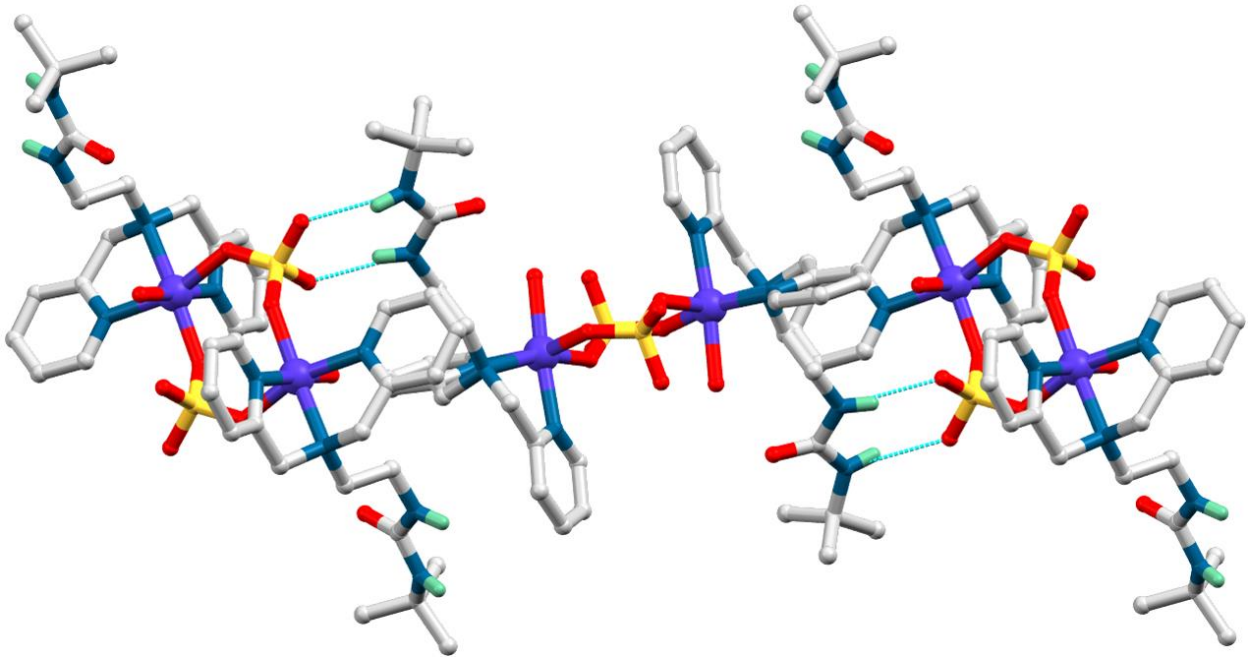

**Figure S16.** ORTEP view of complex **3** showing H-bonding interaction of $SO_4^{2-}$ with N-H protons of urea moiety. H-atoms except those of Urea moiety are omitted for clarity. The structure is drawn at 50% probability level.

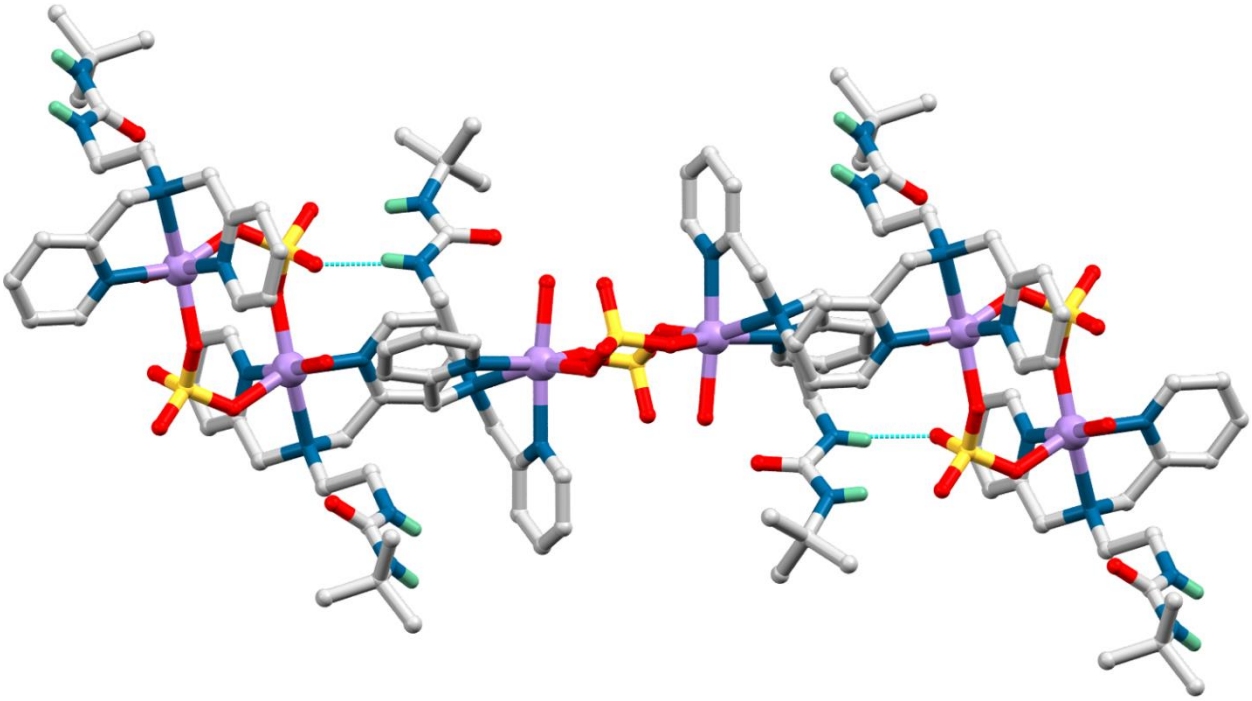

**Figure S17.** ORTEP view of complex **4** showing H-bonding interaction of $SO_4^{2-}$ with N-H protons of urea moiety. H-atoms except those of Urea moiety are omitted for clarity. The structure is drawn at 50% probability level.

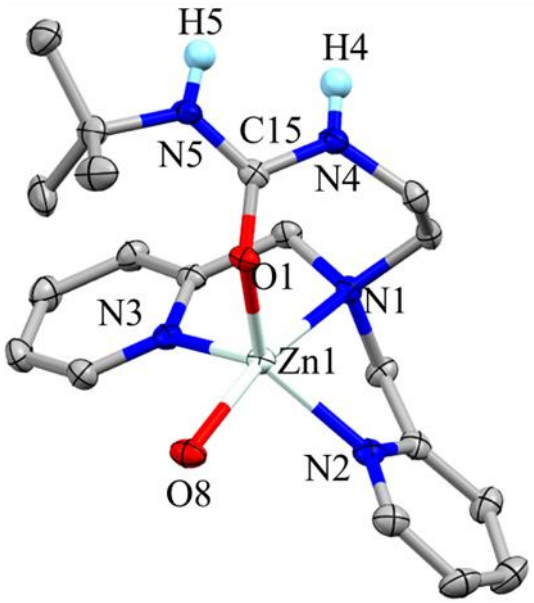


**Figure S18.** ORTEP diagram of Complex **5,** (**L1**)Zn($CF_3SO_3$)$_2$. H-atoms except that of urea moiety are omitted for clarity and the structure is drawn at 50% probability level.

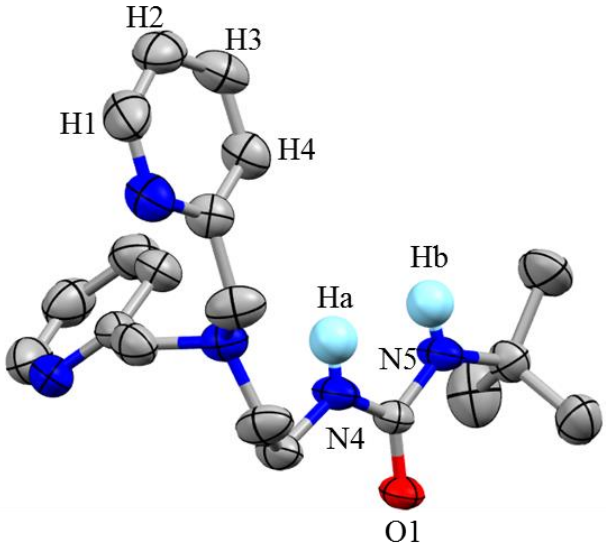


**Figure S19.** ORTEP view of **L1** is shown. Hydrogen atoms, except those of the urea group, are omitted for clarity. All the thermal ellipsoids are drawn at 50% probability level.

**Table S1.** Selected bond distances (Å) and angles (deg) for **1-5** [a]

| **Complex 1** | | | |
|---|---|---|---|
| **M-L** | **d (M-L) [Å]** | **L-M-L** | **< (L-M-L) [°]** |
| Zn1- N1 | 2.242(2) | N1 -Zn1-N2 | 78 |
| Zn1 - N2 | 2.067(2) | N1- Zn1- N3 | 79 |
| Zn1- N3 | 2.052( 2) | N1- Zn1- O1 | 100 |
| Zn1 - O1 | 1.992(1) | N1- Zn1-O8 | 166 |
| Zn1 - O8 | 2.078(2) | N2- Zn1- N3 | 124 |
| | | N2- Zn1- O1 | 129 |
| | | N2 - Zn1- O8 | 90 |
| | | N3- Zn1- O1 | 105 |
| | | N3- Zn1- O8 | 100 |
| | | O1- Zn1- O8 | 92 |
| **Complex 2** | | | |
| **M-L** | **d (M-L) [Å]** | **L-M-L** | **< (L-M-L) [°]** |
| Cd1- O2 | 2.2549 ( 12) | O2 - Cd1 - O1 | 89 |
| Cd1 - O1 | 2.2986 ( 13) | O2 - Cd1 - N3 | 90 |
| Cd1 - N3 | 2.3245 ( 15) | O2 - Cd1 - N1 | 93 |
| Cd1 - N1 | 2.3245 ( 15) | O2 - Cd1 - N2 | 156 |
| Cd1 - N2 | 2.4531 ( 13) | O1 - Cd1 - N3 | 175 |
| Cd1 -O5$^{\#2}$ | 2.2604 (12) | O1 - Cd1 - N1 | 92 |
| | | O1 - Cd1 - N2 | 110 |
| | | N3 - Cd1 - N1 | 93 |
| | | N3 - Cd1 - N2 | 72 |
| | | N1 - Cd1 - N2 | 73 |

| Complex 3 | | | |
|---|---|---|---|
| **M-L** | **d (M-L) [Å]** | **L-M-L** | **< (L-M-L) [°]** |
| Co1 - O2 | 2.0635(17) | O2 -Co1 -O3 | 85.33(7) |
| Co1 -O3 | 2.1468(17) | O2 -Co1 -O5 | 102.63(7) |
| Co1 -O5 | 2.0809(18) | O2 -Co1 -N1 | 162.25(8) |
| Co1 -N1 | 2.134(2) | O2 -Co1 -N2 | 87.39(7) |
| Co1 -N2 | 2.248(2) | O2 -Co1 -N3 | 89.79(7) |
| Co1 -N3 | 2.121(2) | O3 -Co1 -O5 | 88.52(7) |
| **Complex 4** | | | |
| **M-L** | **d (M-L) [Å]** | **L-M-L** | **< (L-M-L) [°]** |
| Mn1- O2 | 2.138(5) | O2 -Mn1 -O5 | 85.56(18) |
| Mn1 – O6 | 2.134(5) | O2 -Mn1 -O6 | 109.24(17) |
| Mn1 – O5 | 2.202(5) | O2 -Mn1 -N3 | 91.2(2) |
| Mn1 – N3 | 2.244(6) | O2 -Mn1 -N4 | 156.8(2) |
| Mn1 – N5 | 2.389(6) | O2 -Mn1 -N5 | 85.60(18) |
| Mn1 – N4 | 2.258(6) | O5 -Mn1 -O6 | 87.59(18) |
| | | O5 -Mn1 -N3 | 175.06(18) |
| | | O5 -Mn1 -N4 | 91.09(19) |
| | | O5 -Mn1 -N5 | 111.06(18) |
| | | O6 -Mn1 -N3 | 89.9(2) |
| | | | |
| **Complex 5** | | | |
| **M-L** | **d (M-L) [Å]** | **L-M-L** | **< (L-M-L) [°]** |
| Zn1 - N2 | 2.263(2) | N2 - Zn1- N1 | 77 |
| Zn1 - N1 | 2.089(2) | N2 - Zn1 - N3 | 77 |
| Zn1 - N3 | 2.047(2) | N2 - Zn1 - O2 | 101 |
| Zn1 - O2 | 1.960(1) | N1 - Zn1 - N3 | 121 |
| Zn1- O3 $^{\#1}$ | 2.053(1) | N1 - Zn1 - O2 | 106 |
| | | N3 - Zn1 - O2 | 130 |

[a]Symmetry transformations used to generate equivalent atoms: [#1], -x,-y,-z+1; [#2], -x+1,-y, -z+1

**Table S2.** Hydrogen bonding data of complexes **1-4**.

| **Complex 1** | | |
|---|---|---|
| **D - H····A** | **d (D····A) [Å]** | **<(D - H····A) [°]** |
| N6 -H6····O4 | 3.074(3) | 153 |
| N5 -H5····O3 | 3.028(3) | 168 |
| **Complex 2** | | |
| **D - H····A** | **d (D····A) [Å]** | **<(D - H····A) [°]** |
| N5 -H1N····O4 | 2.922(2) | 171 |
| N4 -H2N····O3 | 2.897(2) | 167 |
| **Complex 3** | | |
| **D - H····A** | **d (D····A) [Å]** | **<(D - H····A) [°]** |
| N4 -- H4A···· O4 | 2.886(3) | 165.00 |
| N5 -- H5A···· O6 | 2.947(3) | 160.00 |
| **Complex 4** | | |
| **D - H····A** | **d (D····A) [Å]** | **<(D - H····A) [°]** |
| N1 -- H1···· O4 | 3.096(8) | 174.00 |
| N2 -- H2····O3 | 2.850(7) | 171.00 |

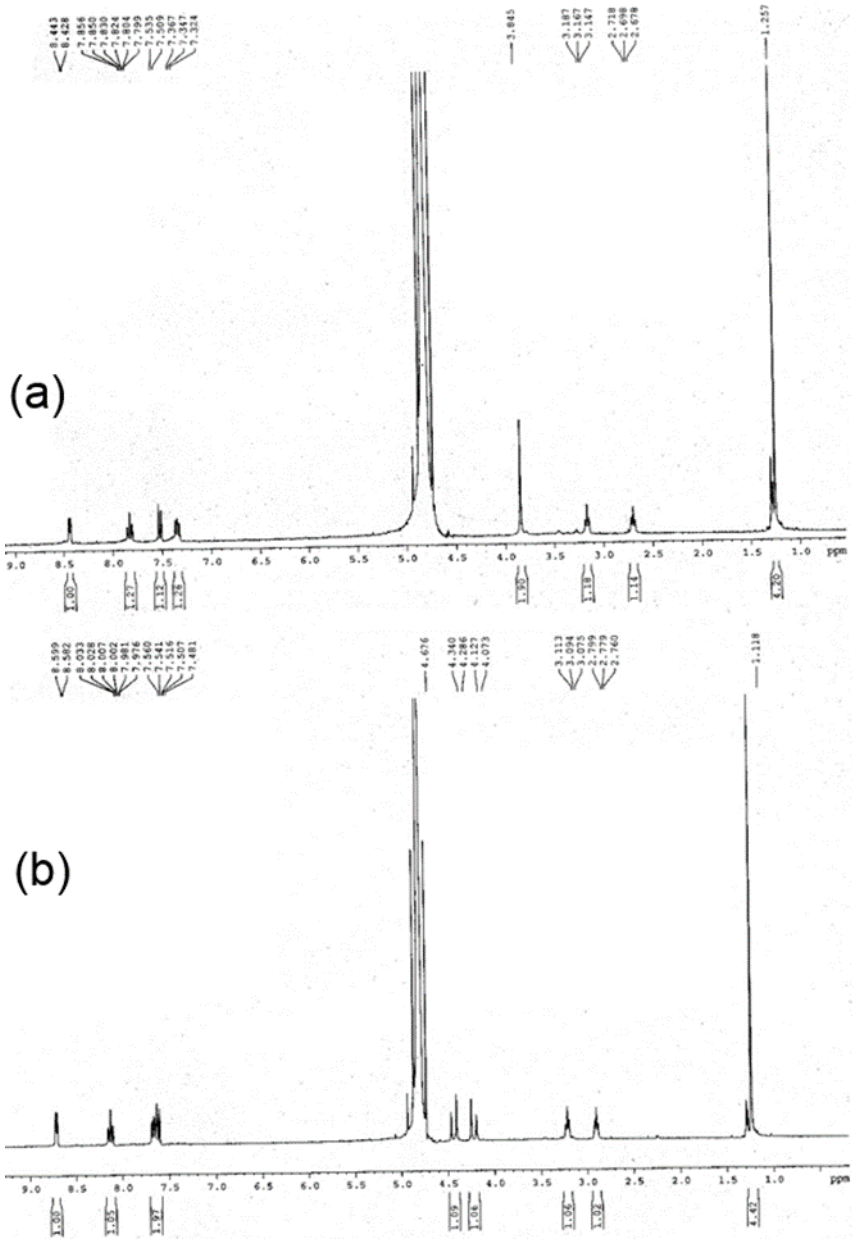


**Figure S20.** $^{1}$H-NMR spectra of (a) **L1** in $D_2O$ (b) 1:1 mixture of **L1** and $ZnSO_4$ in $D_2O$.

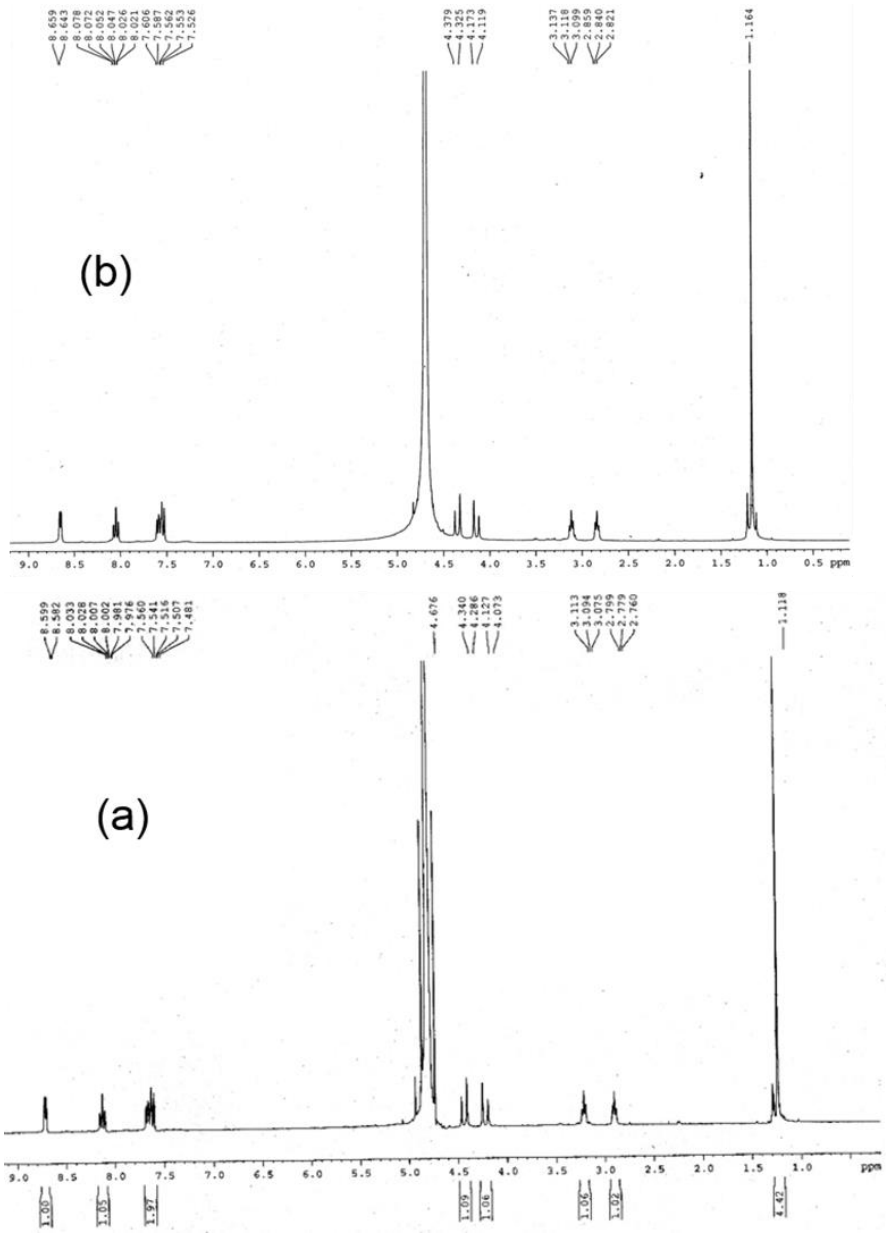


**Figure S21.** $^{1}$H-NMR spectra in $D_2O$ of (a) crystal of complex **1** (b) crystal obtained from mixture of **L1** and mixture of several competing $Zn^{II}$ from pure water medium.

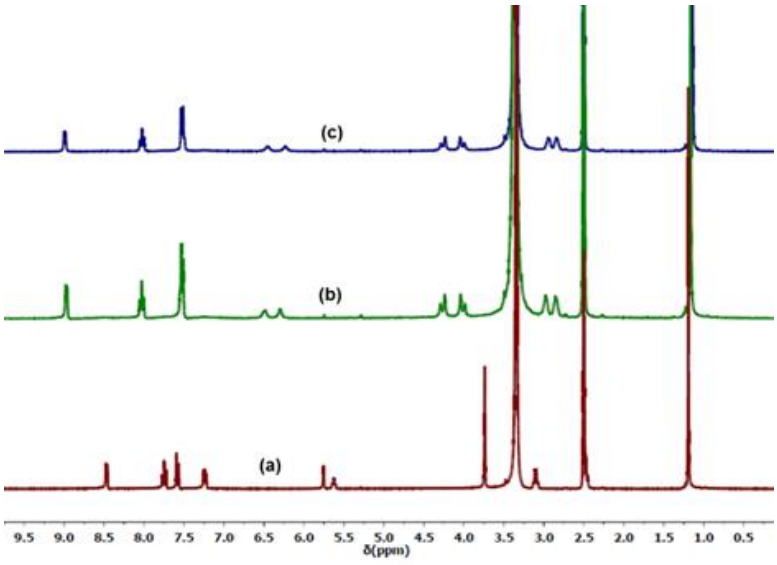


**Figure S22.** Selective formation of $Zn^{II}$-sulfate complex in solution from mixture of several competing Zn(II) salts at 298K. (a) $^{1}$H-NMR of free **L1** (b) $^{1}$H-NMR of 1:1 solution of **L1** and $ZnSO_4$ (C) $^{1}$H-NMR of **L1** and equimolar mixture of various Zn(II) Salts.

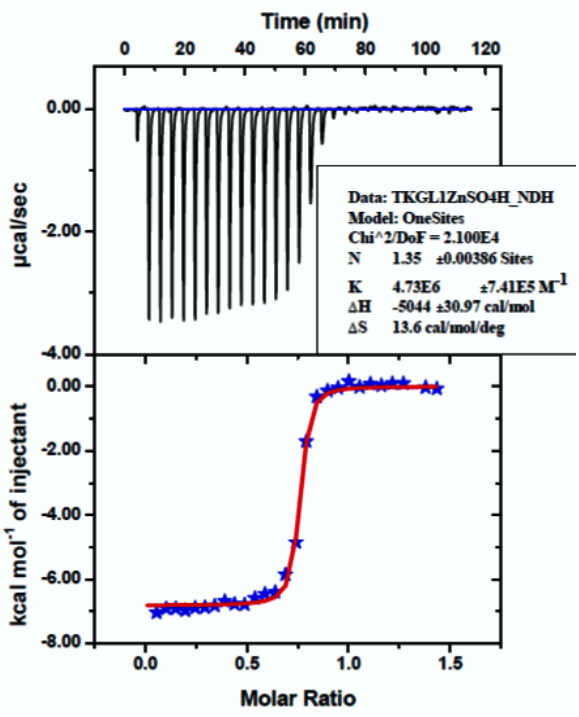


**Figure S23.** Isothermal Titration Calorimetric plot for the addition of a solution of (a) $ZnSO_4$ (4.287 mm) to a solution of **L1** (0.618 mm) in HEPES buffer at 298K. The upper panel shows the heat pulses as experimentally observed in each titration. The lower panel reports the respective time integrals translating as the heat evolved for each aliquot and its coherence to the one site binding model.

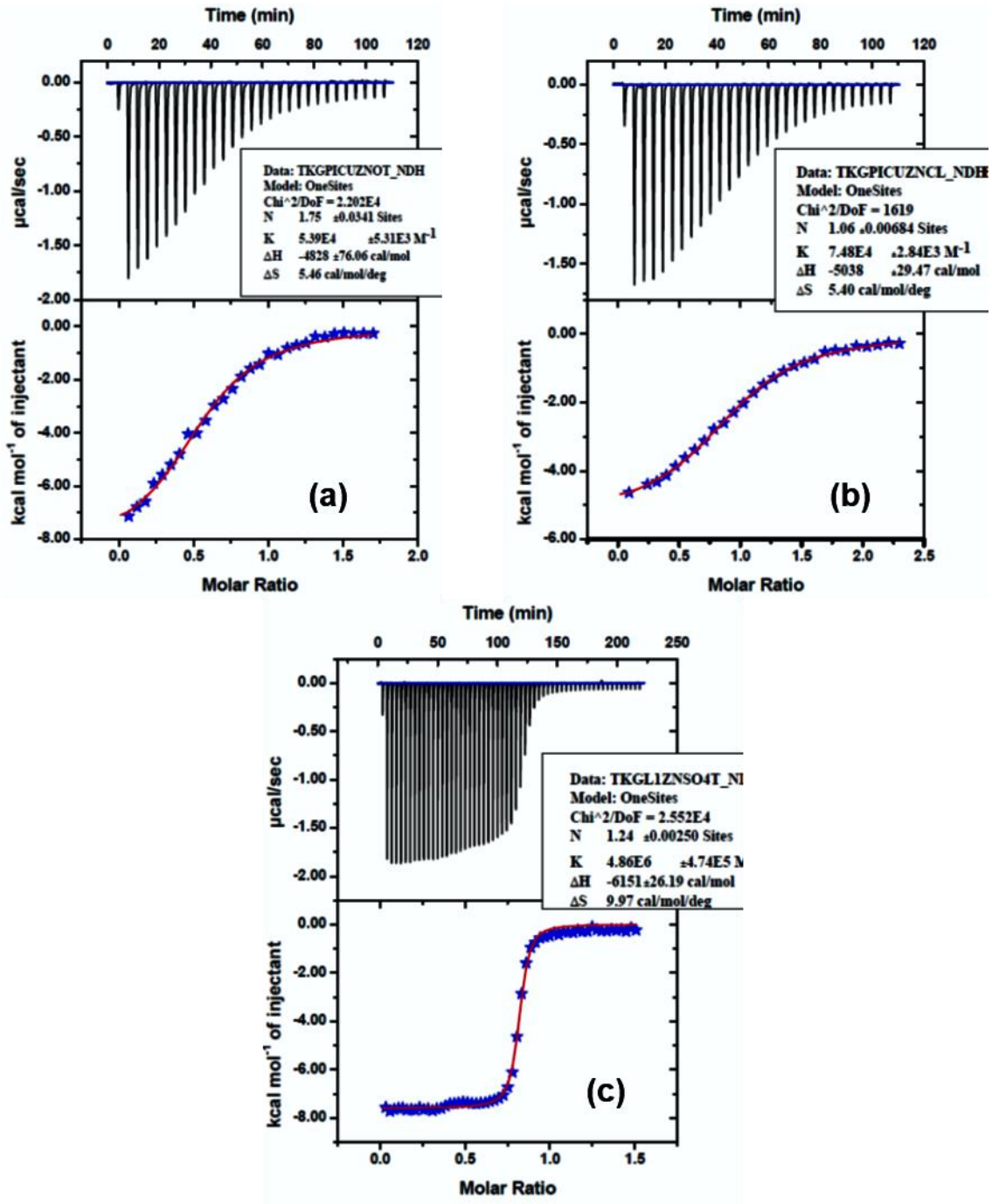


**Figure S24.** Isothermal Titration Calorimetric plot in 10% $H_2O$/DMSO binary solvent mixture at 298 K for the addition of a solution of (a) $ZnCl_2$ (8.421 mm) to a solution of **L1** (0.991 mm), (b) $Zn(ClO_4)_2$ (7.52mm) to a solution of **L1** (0.625mm), (c) $ZnSO_4$ (6.09) to a solution of **L1** (0.812mm).the upper panel shows the heat pulses experimentally observed in each titration. The lower panel reports the respective time integrals translating as the heat evolved for each aliquot and its coherence to the one site binding model.

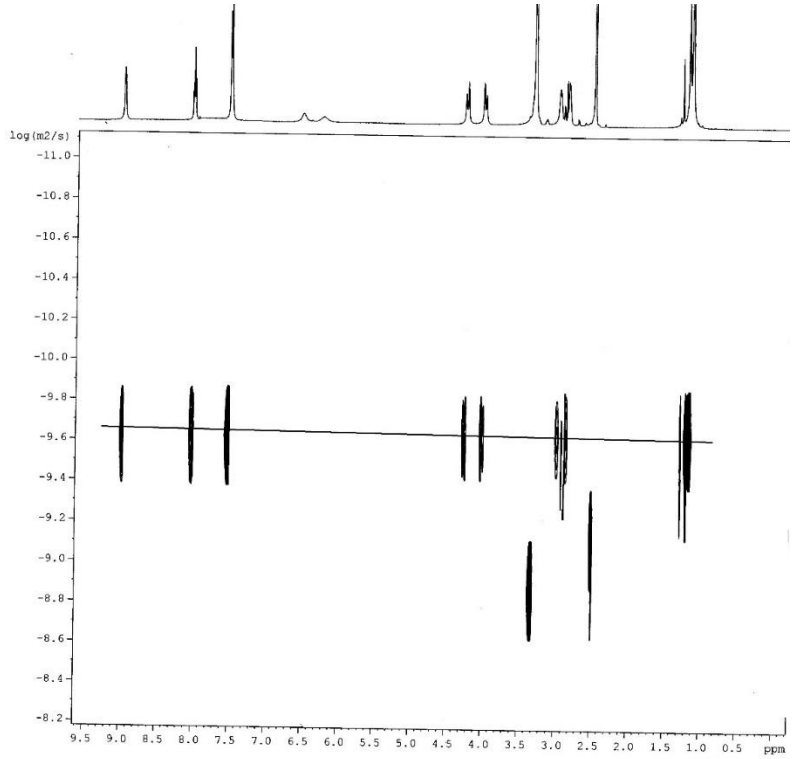


**Figure S25.** $^{1}$H-DOSY NMR of 1:1 mixture of **L1** and $ZnSO_4$ in DMSO-$d_6$.

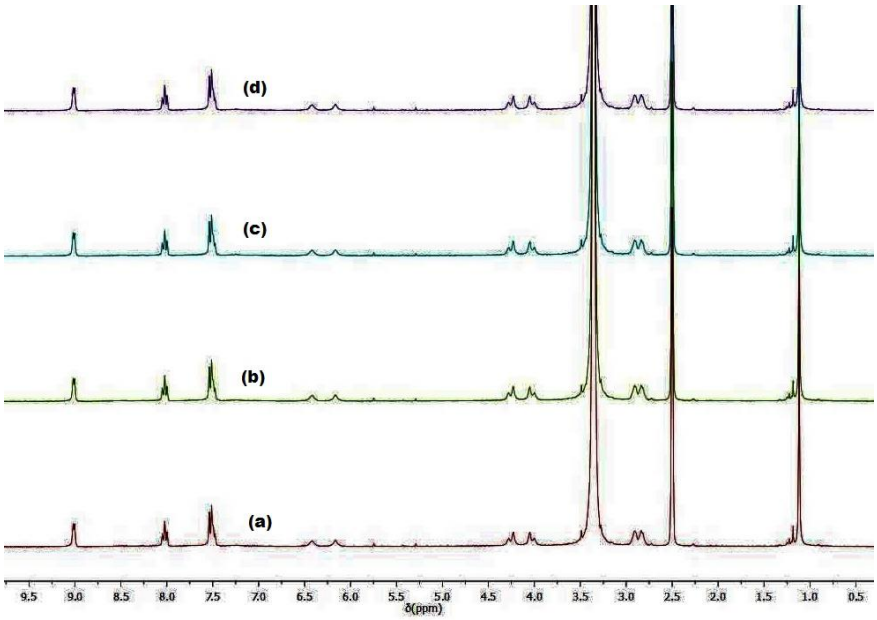


**Figure S26**. $^{1}$H-NMR dilution experiment of complex **1**. (a) [**1**] = 7.8 x $10^{-3}$ (M); (b) [**1**] = 3.9 x $10^{-3}$; (c) [**1**] = 9.7 x $10^{-4}$ (M); (d) [**1**] = 4.8 x $10^{-4}$ (M).

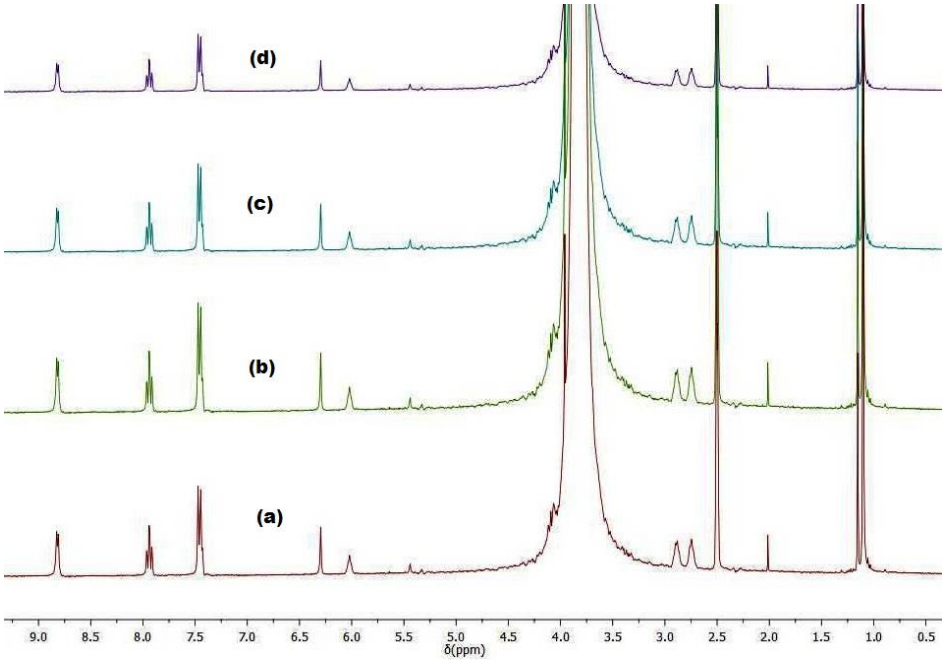


**Figure S27**. $^{1}$H-NMR dilution experiment of complex **2**. (a) [**2**] = 9.1 x $10^{-3}$ (M); (b) [**2**] = 4.6 x $10^{-3}$; (c) [**2**] = 1.1 x $10^{-4}$ (M); (d) [**2**] = 3.8 x $10^{-4}$ (M).