

Electronic Supplementary Information (ESI)

Seven-coordinate anion complex with a tren-based urea: Binding discrepancy of hydrogen sulfate in solid and solution states

Avijit Pramanik^a, Bethtrice Thompson^a, Trina Hayes^a, Kimberly Tucker^a, Douglas R. Powell^b, Peter V. Bonnesen^c, Erick D. Ellis^a, Ken S. Lee^a, Hongtao Yu^a and Md. Alamgir Hossain^{*a}

^aDepartment of Chemistry and Biochemistry, Jackson State University, Jackson, MS 39212, ^bDepartment of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019,

^cChemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Email: alamgir@chem.jsums.edu

Synthesis of L: Tris(2-aminoethyl)amine (300 mg, 2.05 mmol) was added with *p*-cyanophenyl isocyanate (886 mg, 6.15 mmol) in chloroform at room temperature under constant stirring. The mixture was refluxed for 3 h. The precipitate was collected by filtration, washed by chloroform, and dried under vacuum to give a white solid (1.067 gm, 90% yield). MP: 249° C, IR (KBr disk) $\nu_{\max}/\text{cm}^{-1}$ 3329 (NH), 2220 (CN), 1665 (CO). δ_{H} (500 MHz; DMSO-*d*₆; TSP) 9.14 (3H, s, Ar-NH), 7.67 (6H, d, $J = 8.5$ Hz, ArH), 7.58 (6H, d, $J = 8.5$ Hz, ArH), δ 6.39 (3H, t, $J_1 = 5.50$ Hz, $J_2 = 5.05$, CH₂NH), 3.24 (6H, m, $J_1 = 6.10$ Hz, $J_2 = 5.95$, $J_3 = 5.90$, NHCH₂), 2.64 (6H, t, $J_1 = 6.55$ Hz, $J_2 = 6.45$, NCH₂). δ_{C} (125 MHz; DMSO-*d*₆; TSP) δ 154.93 (CO), 145.37 (C_{Ar}), 133.58 (CH_{Ar}), 119.99 (CN_{Ar}), 118.01 (CH_{Ar}), 102.75 (C_{Ar}) 54.05 (NHCH₂), 37.86 (NCH₂). ESI-MS(+ve): m/z 579.1 (MH⁺). Anal. Found: C, 62.20; H, 5.24; N, 24.28. Calcd. for C₃₀H₃₀N₁₀O₃: C, 62.27; H, 5.23; N, 24.21%.

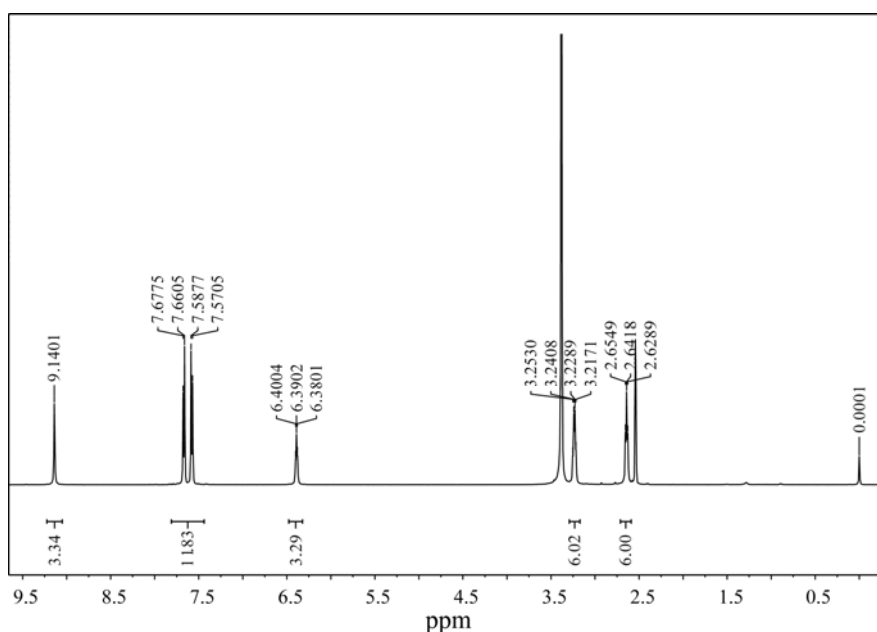


Figure S1. ¹H NMR spectra of L in DMSO-*d*₆.

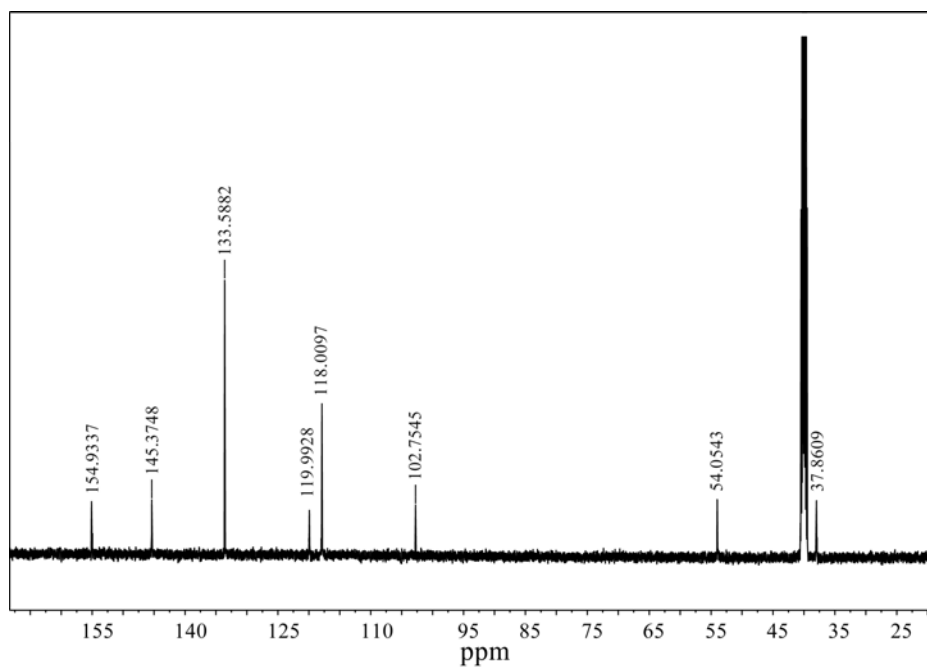


Figure S2. ^{13}C NMR spectra of **L** in $\text{DMSO-}d_6$.

tripodal urea_cyano_1 #1 RT: 0.02 AV: 1 NL: 1.45E7
T: + c Full ms [215.00-1000.00]

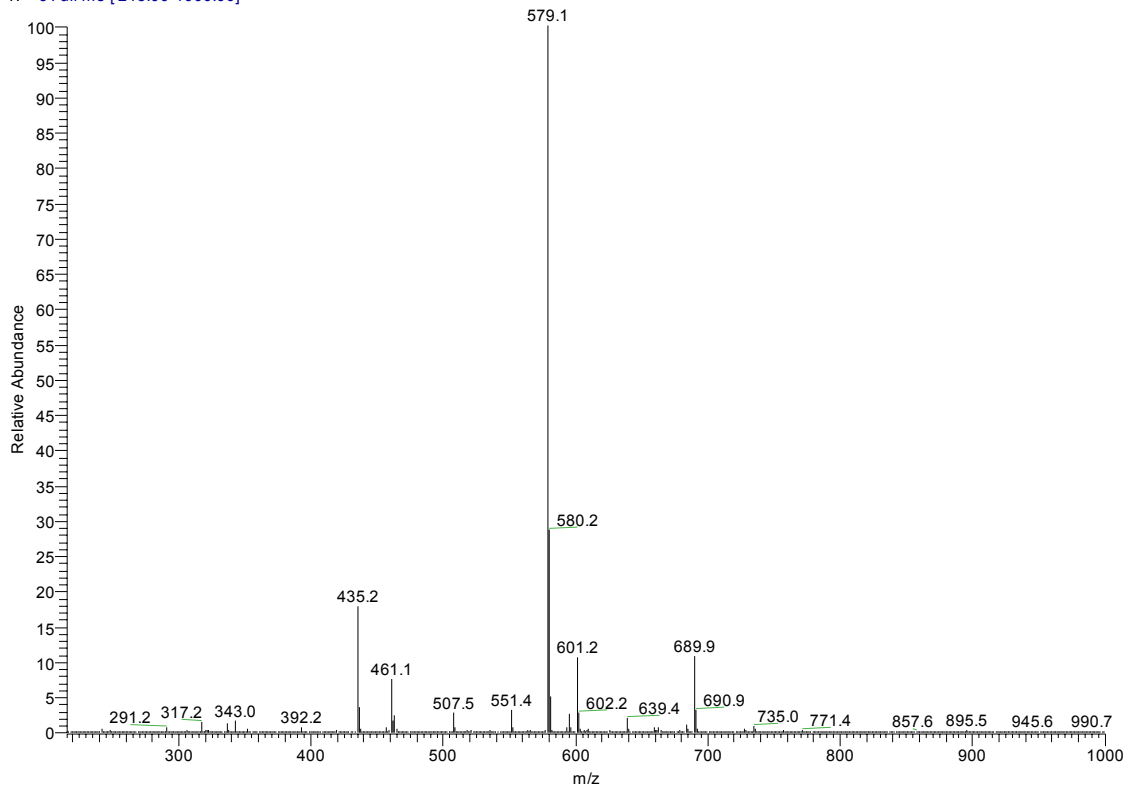


Figure S3. ESI-MS (+ve) spectra of **L**

Synthesis of $[\text{HL}]^+ \cdot [\text{HSO}_4]^-$. To a stirred solution of **L** (100 mg) in EtOH (50 mL) was added 52% H_2SO_4 (0.5 mL) dropwise. After the mixture was stirred for 30 min at room temperature, a white precipitate formed was filtered, washed with diethyl ether, and dried under vacuum (105.2 mg, 90% yield). δ_{H} (500 MHz; $\text{DMSO-}d_6$; TSP) 9.40 (3H, s, ArNH), 7.63 (6H, d, $J = 9.0$ Hz, ArH), 7.59 (6H, d, $J = 9.00$ Hz, ArH), δ 6.82 (3H, m, $J_1 = 5.55$ Hz, $J_2 = 5.60$, CH_2NH), 3.56 (6H, m, $J_1 = 5.65$, Hz, $J_2 = 5.65$, $J_3 = 5.65$, NHCH_2), 3.47 (1H, s, N^+H), 3.43 (6H, t, $J_1 = 5.80$ Hz, $J_2 = 6.1$, NCH_2). δ_{C} (125 MHz; $\text{DMSO-}d_6$; TSP) 155.73 (CO), 144.98 (C_{Ar}), 133.63 (CH_{Ar}), 119.79 (CN_{Ar}), 118.10 (CH_{Ar}), 103.23 (C_{Ar}), 53.45 (NCH_2CH_2) 34.86 (NCH_2CH_2). Single-crystals suitable for X-ray diffraction were obtained from slow evaporation of a CH_3OH -water (1:1) mixture solution of the compound after one week.

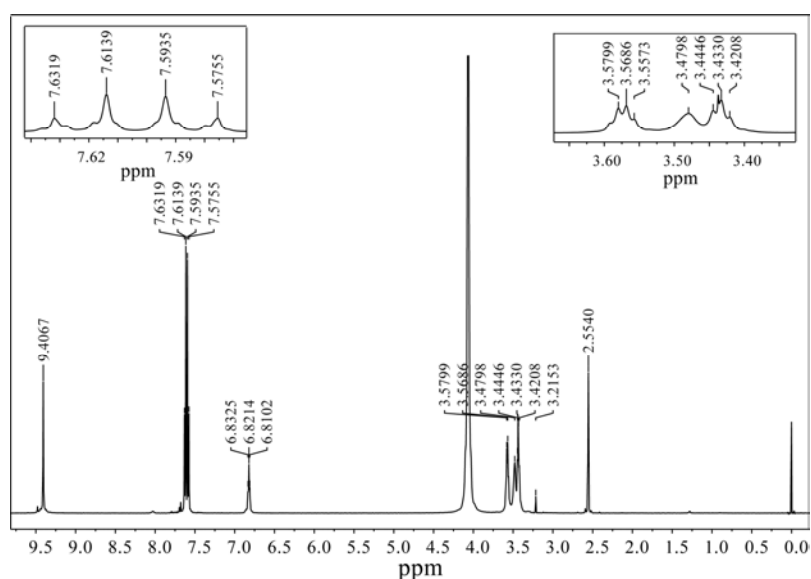


Figure S4. ^1H NMR spectra of $[\text{LH}]^+ \cdot [\text{HSO}_4]^-$ in $\text{DMSO-}d_6$.

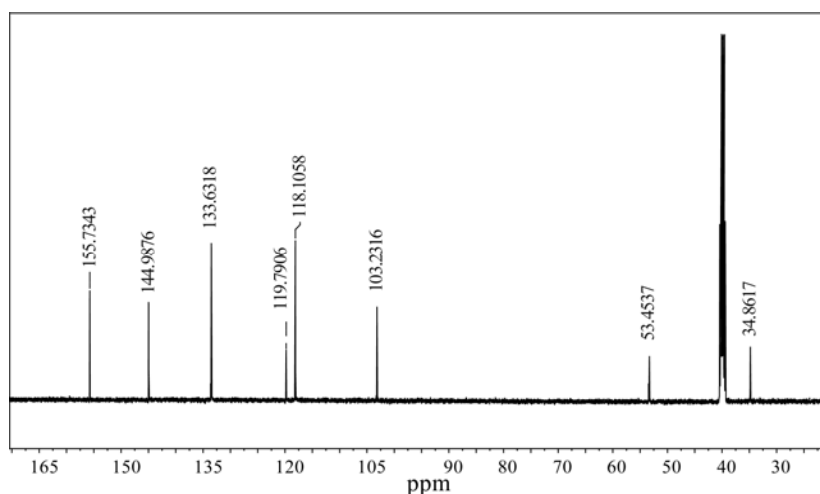


Figure S5. ^{13}C NMR spectra of $[\text{LH}]^+ \cdot [\text{HSO}_4]^-$ in $\text{DMSO-}d_6$.

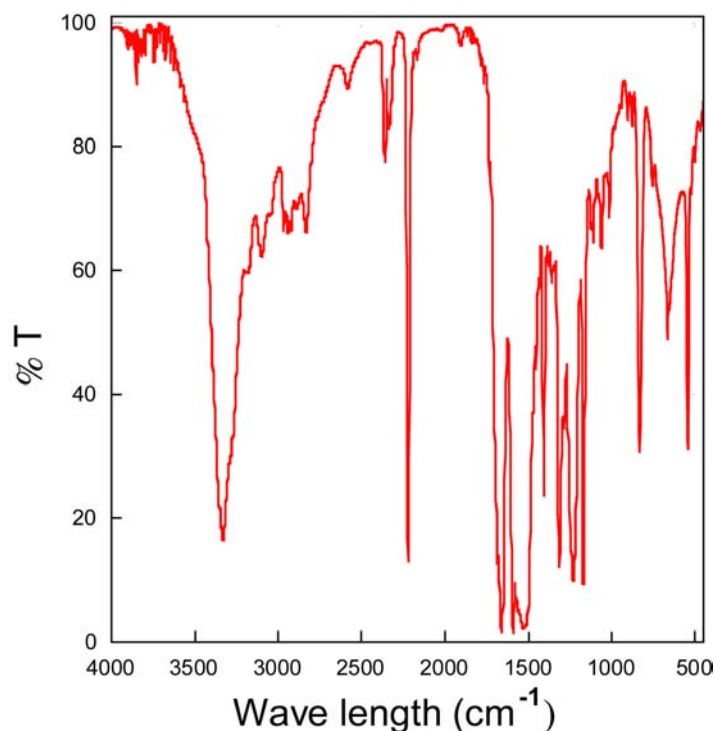


Figure S6. FT-IR spectra of **L**.

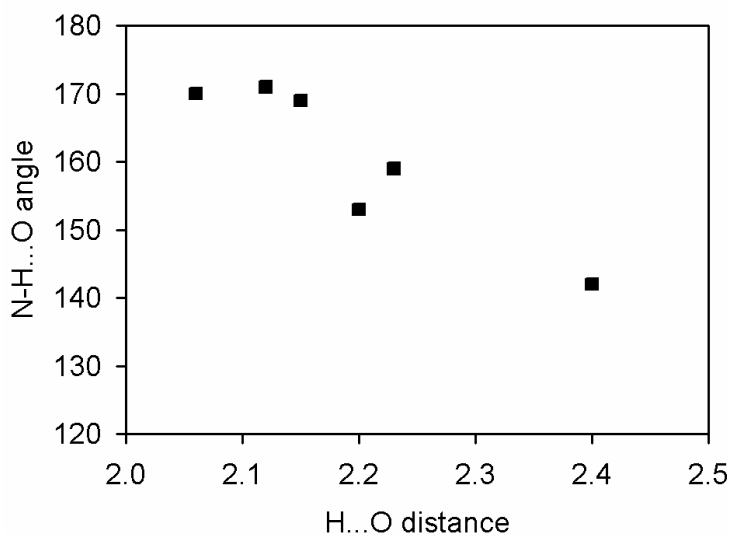


Figure S7. The correlation of H...O distances and N-H...O angles for NH...O hydrogen bonds with $d_{N...O} < 3.2 \text{ \AA}$ in the bisulfate complex of **L**.

Binding Constant (K): Binding constants were obtained by ^1H NMR titrations of **L** with different anions in $\text{DMSO-}d_6$. All the measurements were carried out using 500 MHz Varian at room temperature. Initial concentrations were $[\text{ligand}]_0 = 2 \text{ mM}$, and $[\text{anion}]_0 = 20 \text{ mM}$. Sodium salt of 3-(trimethylsilyl) propionic-2,2,3,3- d_4 acid (TSP) in DMSO was used as an external reference in a capillary tube. Each titration was performed by 14 measurements. Association constants (K) were calculated using Sigma Plot software, using the equations: $\Delta\delta$

$= ([A]_0 + [L]_0 + 1/K - ([A]_0 + [L]_0 + 1/K)^2 - 4[L]_0[A]_0)^{1/2} \Delta\delta_{\max} / 2[L]_0$ (where **L** = ligand and **A** = anions). An error limit in *K* was less than 10%.

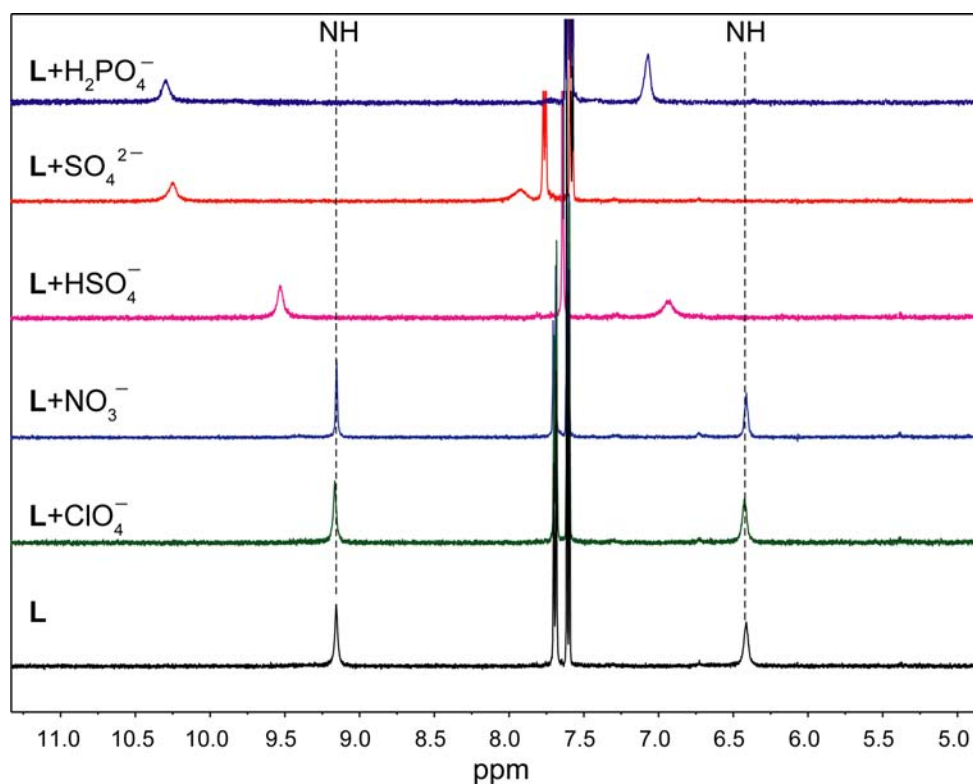


Figure S8. Partial ^1H NMR spectra of **L** (2mM) in absence and presence of an anion showing two NH peaks. An equivalent amount of *n*-Bu₄NClO₄, *n*-Bu₄NNO₃, *n*-Bu₄NHSO₄, ZnSO₄ or *n*-Bu₄NH₂PO₄ was added in DMSO-*d*₆.

Table S1. Binding constants ($\log K$) of tripodal *tris*-urea receptor (**L**) with various oxo-anions.

Anion	$\log K$
SO ₄ ²⁻	4.70
H ₂ PO ₄ ⁻	4.20
HSO ₄ ⁻	3.0
ClO ₄ ⁻	No binding
NO ₃ ⁻	No binding

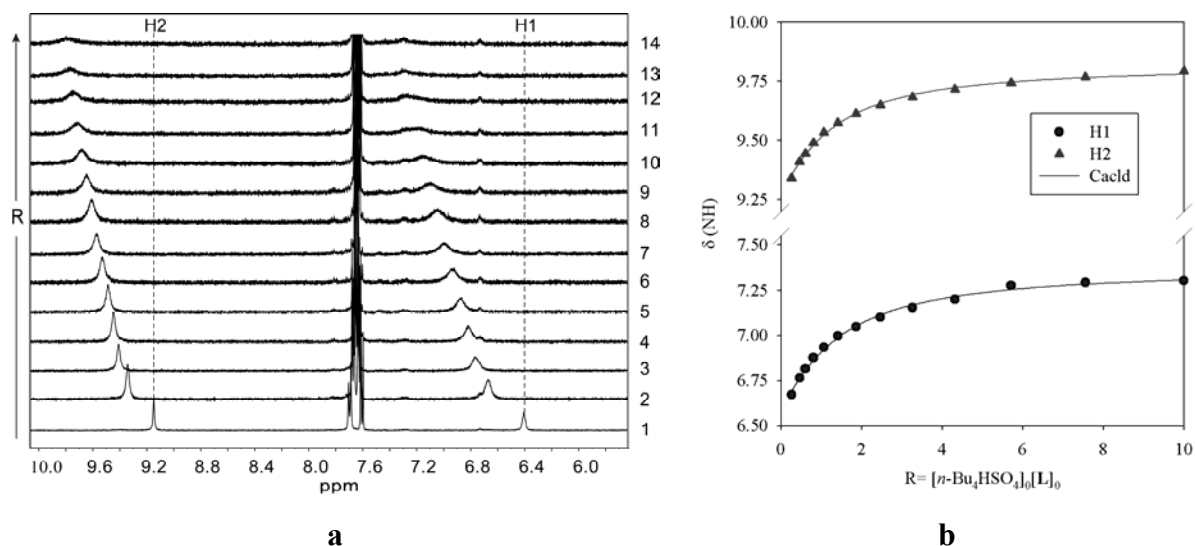


Figure S9. (a) ¹H NMR spectra of **L** (2mM) with an increasing amount of TBAHSO₄ ($R = [\text{TBAHSO}_4]_0/[\text{L}]_0$) in DMSO-*d*₆. (b) Titration curves of **L** with TBAHSO₄ showing changes in the chemical shifts of NH are shown against the increasing amount of anions. H1 = CH₂NHCO and H2 = CONHAr.

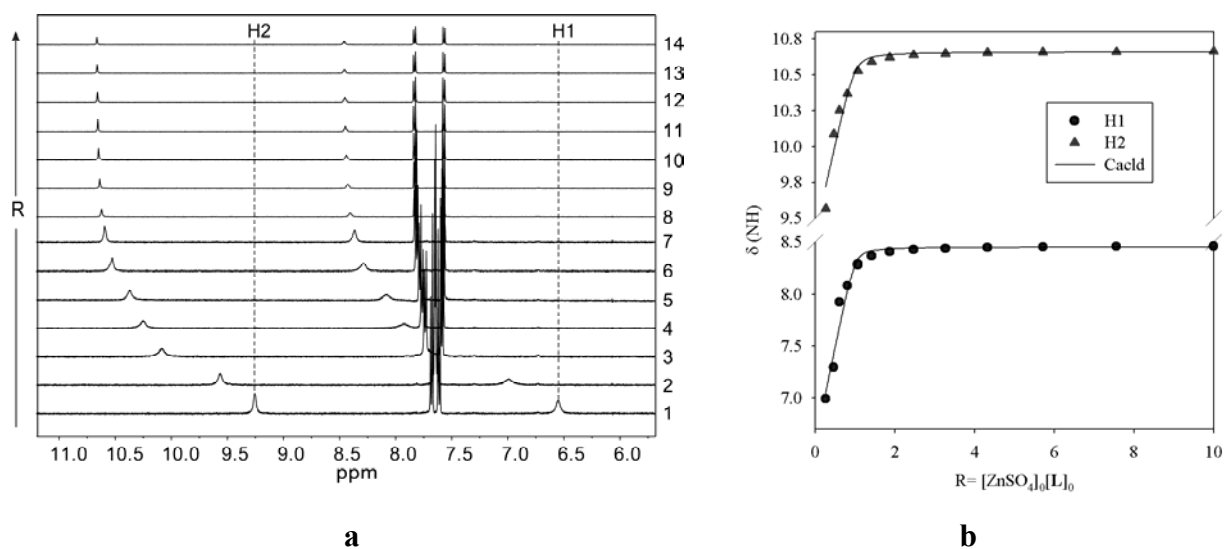


Figure S10. (a) ¹H NMR spectra of **L** (2mM) with an increasing amount of ZnSO₄ ($R = [\text{ZnSO}_4]_0/[\text{L}]_0$) in DMSO-*d*₆. (b) Titration curves of **L** with ZnSO₄ showing changes in the chemical shifts of NH are shown against the increasing amount of anions. H1 = CH₂NHCO and H2 = CONHAr.

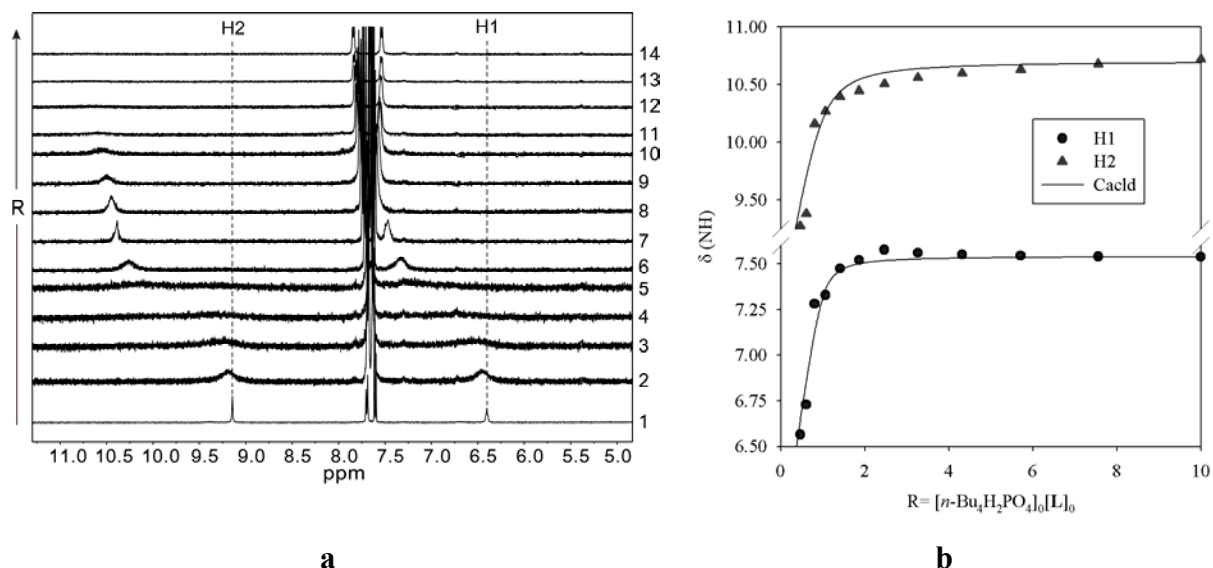


Figure S11. (a) ¹H NMR spectra of L (2mM) with an increasing amount of TBAH₂PO₄ (R = [TBAH₂PO₄]₀/[L]₀) in DMSO-*d*₆. (b) Titration curves of L with TBAH₂PO₄ showing changes in the chemical shifts of NH are shown against the increasing amount of anions. H1 = CH₂NHCO and H2 = CONHAr.

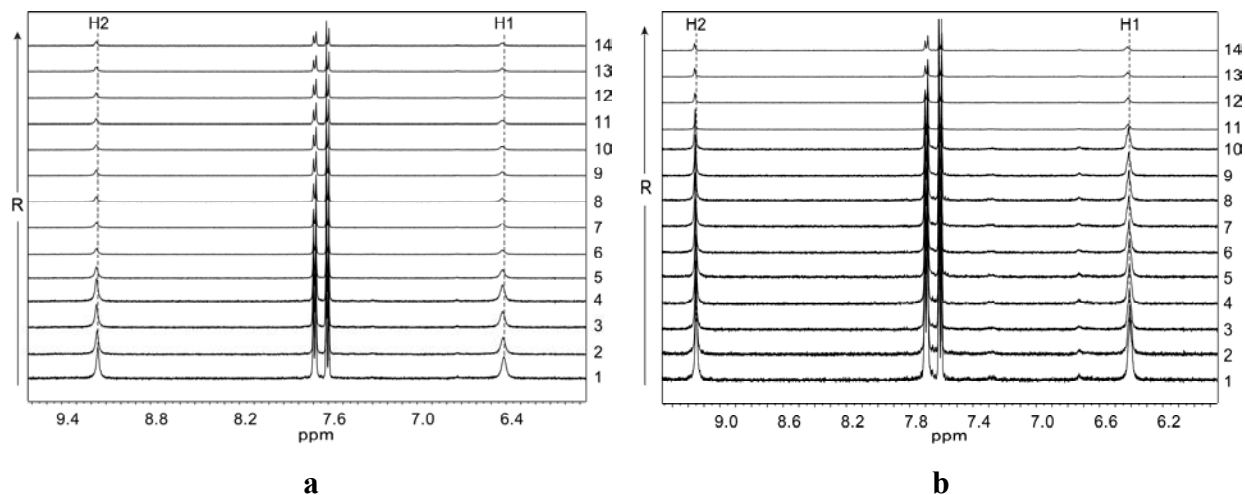


Figure S12. ¹H NMR spectra of L (2mM) with an increasing amount of (a) TBAClO₄ (R = [TBAClO₄]₀/[L]₀) and (b) TBANO₃ (R = [TBANO₃]₀/[L]₀) in DMSO-*d*₆. (No apparent binding was observed from these titrations)

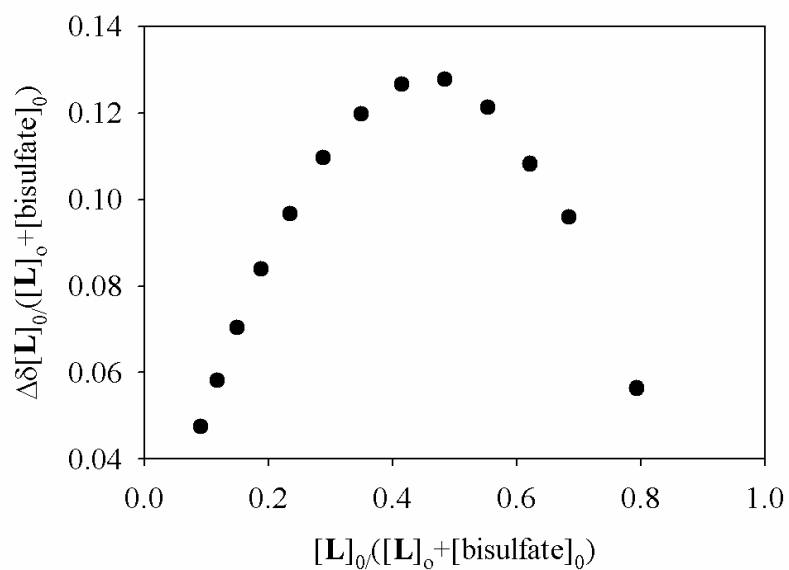


Figure S13. Job's plot of **L** with TBAHSO₄ in DMSO-*d*₆ showing a maximum at 0.5 mole fraction of **L**. The shift change ($\delta\Delta$) in the H2 (CONHAr) was followed for the Job's plot.