Supporting information for

C_3 Symmetric vanadium(III) complexes with *O,N*-chelating hexadentate tripodal ligands of pyrazolone

Sanjay Parihar,[a] R. N. Jadeja[a]* and Vivek K. Gupta[b]

[a] *Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda,Vadodara 390 002, India.*

E-mail: rajendra_jadeja@yahoo.com

Post-Graduate Department of Physics, University of Jammu, Jammutawi 180 006, India.

Contents:

Experimental section

Materials and characterization

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. Pyrazolone derivatives were obtained from Nutan Dye Chem. Sachin, Surat. Tris(2-aminoethyl)amine was purchased from Sigma-Aldrich. Dry DMF, vanadyl sulfate, benzyl alcohol, $POCl_3$, hexane and 30% aqueous H_2O_2 were purchased from Merck and used as received.

The synthesized tripodal ligands and their vanadium(III) complexes were characterized by ^1H & ^{13}C NMR, ESI-MS, single crystal XRD, FT-IR, UV-Vis, LC-MS and elemental analyses. ^1H & ^{13}C NMR spectra were recorded on Avance-III 400 MHz Bruker FT-NMR instrument. Elemental analyses of C, H, and N were determined using a Perkin Elmer series-II 2400 elemental analyzer. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet at Department of Chemistry, Jadavpur University, Kolkata. Single-crystal structures of L^1 and L^2 were determined using BRUKER SMART APEX (CCD) diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71073). Crystallograpic data of complex [VL^1] were recorded on a Xcalibur, Eos, Gemini diffractometer equipped with a graphite-monochromated Cu Kα radiation (λ = 1.54184). FT-IR spectra of ligands and complexes were recorded as the KBr pellet on the Perkin Elmer Fourier transform (FT-IR) spectrum RX 1 spectrometer. Electronic spectra were recorded on a Perkin Elmer Lambda 35 UV-Vis spectrometer. LC-MS spectra were recorded on a Waters Micromass Q-Tof Micro instrument at SAIF, Panjab University, Chandigarh.

Synthesis of tripodal ligands

Synthesis of 3-methyl-5-oxo-1-(p-tolyl)-4,5-dihydro-1H-pyrazole-4-carbaldehyde (1a)

A mixture of 9.4 g. (0.05 mol.) of 3-methyl-1-tolyl-2-pyrazolin-5-one and 10 ml. of dry *N,N'*-dimethylformamide was cooled to 0 °C in a ice bath. Then, 5.5 ml (0.06 mol.) of phosphoryl chloride ms added dropwise at such a rate as to maintain the temperature between 5-15 °C. After the addition was complete, the reaction mixture was heated on the steam bath for 1.5 h. The mixture was then poured into 500 ml. of ice-water mixture. The resulting mixture was allowed to stand overnight at room temperature. The yellow solid product was collected by filtration, washed with water and dried to afford 1a. Yield of 8.3 g. (77%) ESI-

MS: $[M]^+$: 216.14; ^{1}H NMR (400 MHz $CDCl_3$): δ 2.39 (*s*, 3H), 2.43 (*s*, 3H), 7.25 (*d*, *J* = 8.4 Hz, 2H), 7.65 (*d*, *J* = 8.4 MHz, 2H), 8.49 (*s*, 1H), 9.56 (*s*, 1H). ^{13}C NMR (400 MHz CDCl3): δ 184.77, 158.37, 148.80, 136.93, 134.44, 129.68, 120.94, 105.52, 21.02, 12.32. Elemental analyses (%): found: C 66.68, H 5.64, N 12.96; calcd: C 66.65, H 5.59, N 12.96.

Synthesis of 3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazole-4-carbaldehyde (1b)

Using a similar method to 1a, compound 1b was obtained with a Yield: 8.41 g. (83.3%) ESI-MS: $[M]^+$: 202.14; ^{1}H NMR(400 MHz $CDCl_3$): δ 2.44 (*s*, 3H), 7.28-7.34 (*m*, 1H), 7.45-7.49 (*m*, 2H), 7.79-7.82 (*m*, 2H), 9.07 (*s*, 1H), 9.99 (*s*, 1H). ^{13}C NMR (400 MHz CDCl3): δ 12.38, 105.66, 120.89, 126.97, 129.17, 136.90, 148.99, 158.76, 184.57. Elemental analyses (%): found: C 65.41, H 5.13, N 13.86; calcd: C 65.34, H 4.98, N 13.85.

Synthesis of tripodal ligand L^1

Aldehyde 1a (0.648 g, 3 mmol) and 40 ml methanol were added to a 3-neck 100 mL round-bottom flask equipped with a magnetic stirrer. The aldehyde was dissolved by heating the solution. A dropping funnel containing diluted Tris(2-aminoethyl)amine (0.142 mL, 1 mmol) with 10 mL of dry MeOH was fitted in to the 3-neck round-bottom flask. Tris(2-aminoethyl)amine solution was added dropwise allowing for complete dispersion of each drop between the additions with constant stirring under N_2 atmosphere. After all tris(2-aminoethyl)amine solution was added, the yellow solution was allowed to stir at reflux temperature for another 6 h. The light yellow compound precipitated was filtered, washed with methanol and dried under vacuum. The product was recrystallized in warm MeCN at RT. Yield 84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.96 (s, 3H), 2.33 (s, 3H), 2.2.92-2.89 (t, *J* = 5.2, 4.8 MHz, 2H), 3.56 (s, 2H), 7.15-7.17 (d, J = 8.4 MHz, 2H), 7.63-7.66 (d, *J* = 12 MHz, 1H), 7.83-7.85 (d, *J* = 8.4 MHz, 2H), 9.90 (s, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 12.28, 20.96, 48.72, 56.57, 100.44, 118.98, 129.22, 133.76, 136.62, 148.05, 152.28, 165.46. Elem. anal. Calcd. for $C_{42}H_{48}N_{10}O_3$: C 68.09, H 6.53, N 18.91; found C 68.12, H 6.56, N 18.92. ESI-MS: *m/z* $[M]^+$ 740.39; found 741.41 $[M+H]^+$.

Synthesis of tripodal ligand L^2

Tripodal ligand L^2 was synthesized by the procedure similar to L^1. Yield 81%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.97 (s, 1H), 2.85-2.88 (*t*, *J* = 5 MHz, 2H), 3.52 (*s*, 2H), 7.09-7.13 (*m*, 1H), 7.33-7.37 (*m*, 2H), 7.65-7.67 (*d*, *J* = 10.4 MHz, 1H), 7.96-7.98 (*d*, *J* = 8 MHz, 2H), 9.88 (*s*, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 12.80, 47.99, 54.72, 99.20, 117.66, 123.57,

129.01, 140.02, 153.91, 165.43. Elem. Anal. Calcd. for $C_{39}H_{42}N_{10}O_3$: C 67.03, H 6.06, N 20.04; found C 67.08, H 6.09, N 67.08. ESI-MS: m/z $[M]^+$ 698.34; found 699.31 $[M+H]^+$.

Synthesis of complex [V(L^1)]

To a well stirred hot ethanolic solution of tripodal ligand L^1 (0.740 g, 1 mmol), an ethanolic solution of VOSO4·5H2O (0.253 g, 1 mmol) was added drop wise. An ethanolic solution of NaOH (0.20 g in 10 mL) was added drop wise to the reaction mixture till green precipitates of complex were observed (pH = 8-9). The reaction was further stirred on reflux temperature for 1 h. The precipitates were filtered, washed with hot distilled water and then ethanol, and dried under a vacuum. The obtained complex was designated as VL^1. Yield 421.7 g (53.5%). Elem anal. Calcd for $C_{42}H_{45}N_{10}O_3V$: C 63.95, 5.75, 17.76; found C 64.26, H 5.72, N 17.46. LC-MS: m/z 788.41 $[M]^+$, 789.41 $[M+H]^+$, 811.44 $[M+Na]^+$.

Synthesis of complex [V(L^2)]

To a well stirred hot ethanolic solution of tripodal ligand L^2 (0.698 g, 1 mmol), an ethanolic solution of vanadyl acetylacetonate (0.256 g, 1 mmol) was added drop wise. An ethanolic solution of NaOH (0.20 g in 10 mL) was added drop wise to the reaction mixture till green precipitates of complex observed (pH = 8-9). The reaction was further stirred on reflux temperature for 1 h. The precipitates were filtered, washed with hot distilled water and then ethanol, and dried under a vacuum. The obtained complex was designated as VL^2. Yield 0.343 g (46%). Elem anal. Calcd for $C_{39}H_{39}N_{10}O_3V$: C 62.73, 5.26, 18.76; found C 62.53, H 5.58, N 18.18. LC-MS: m/z 746.45 $[M]^+$, 747.42 $[M+H]^+$, 769.48 $[M+Na]^+$.

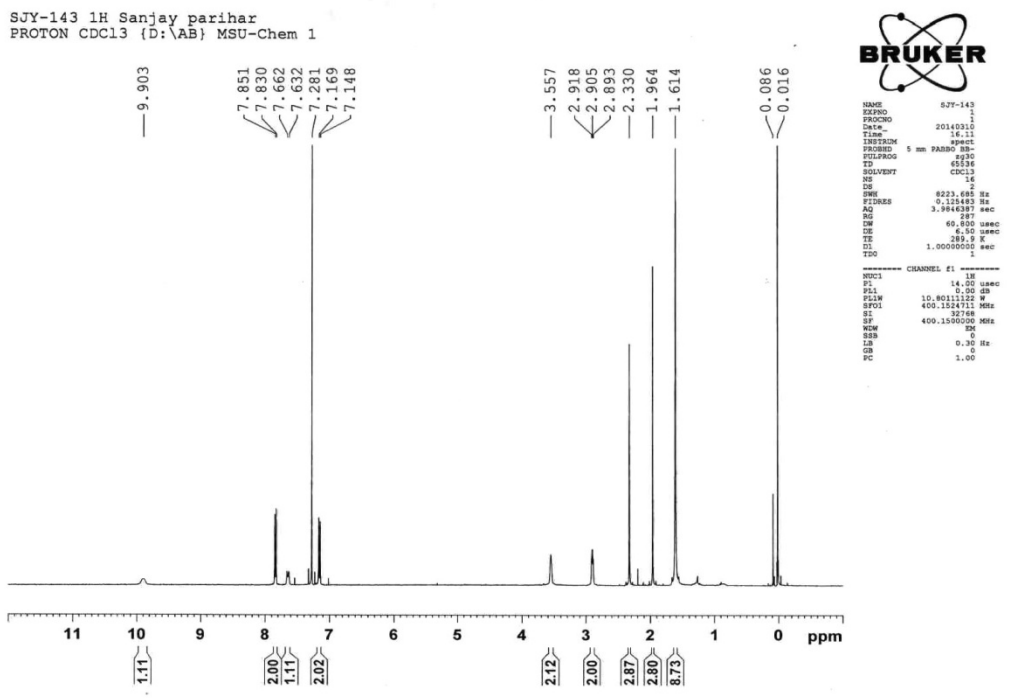

Figure S1: ^{1}H NMR spectra of tripodal ligand L[1]

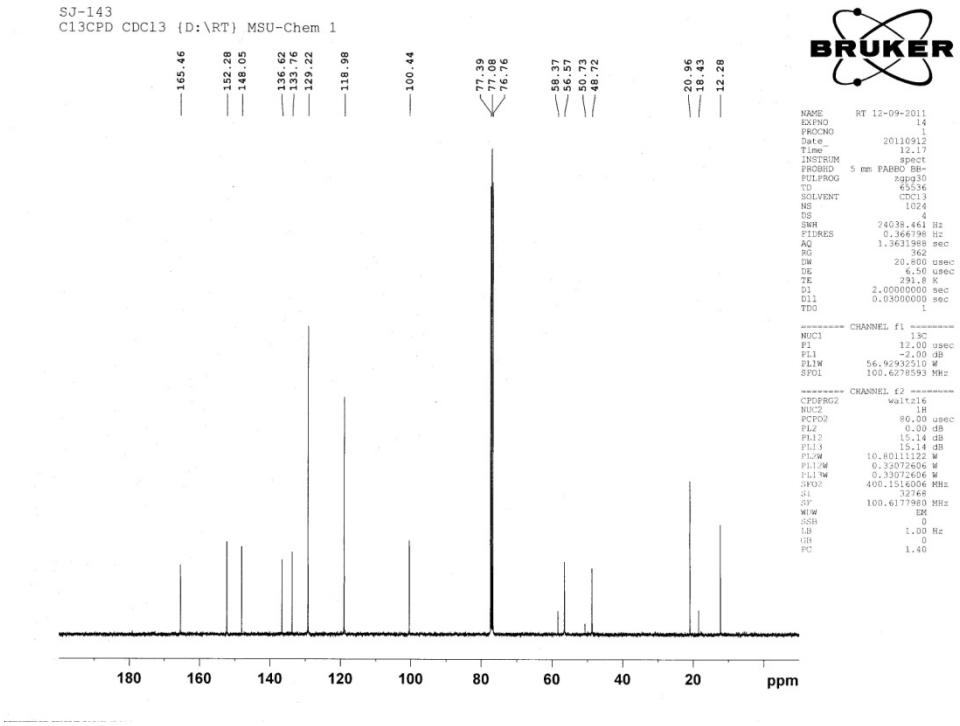

Figure S2: ^{13}C NMR spectra of tripodal ligand L[1]

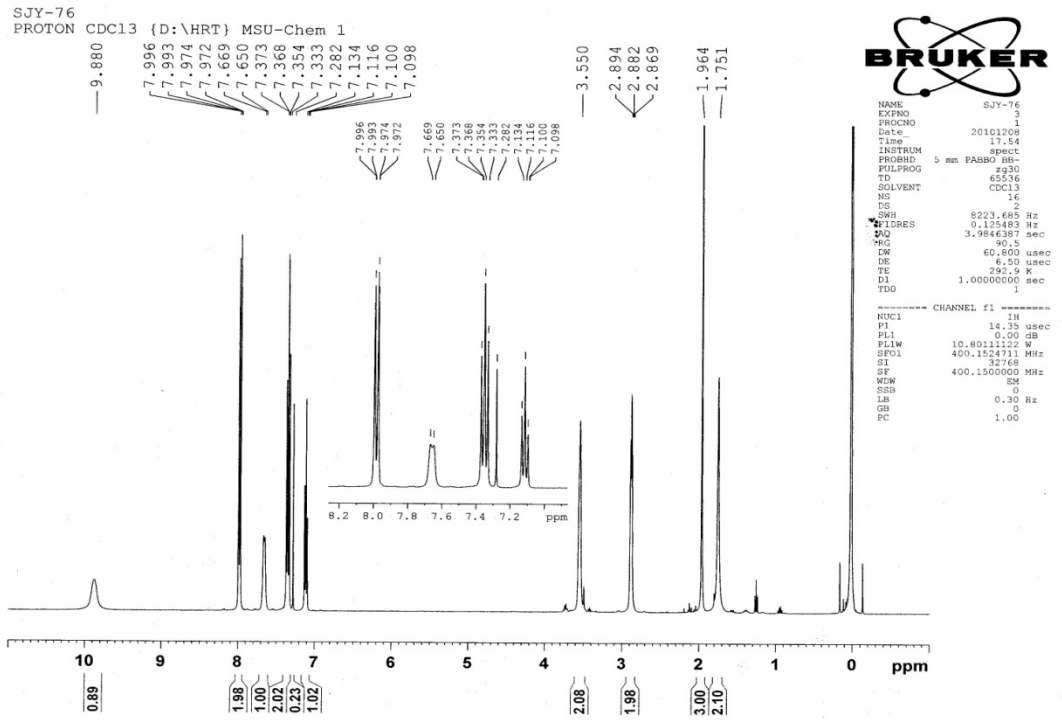

Figure S3: ^{1}H NMR spectra of tripodal ligand L^2

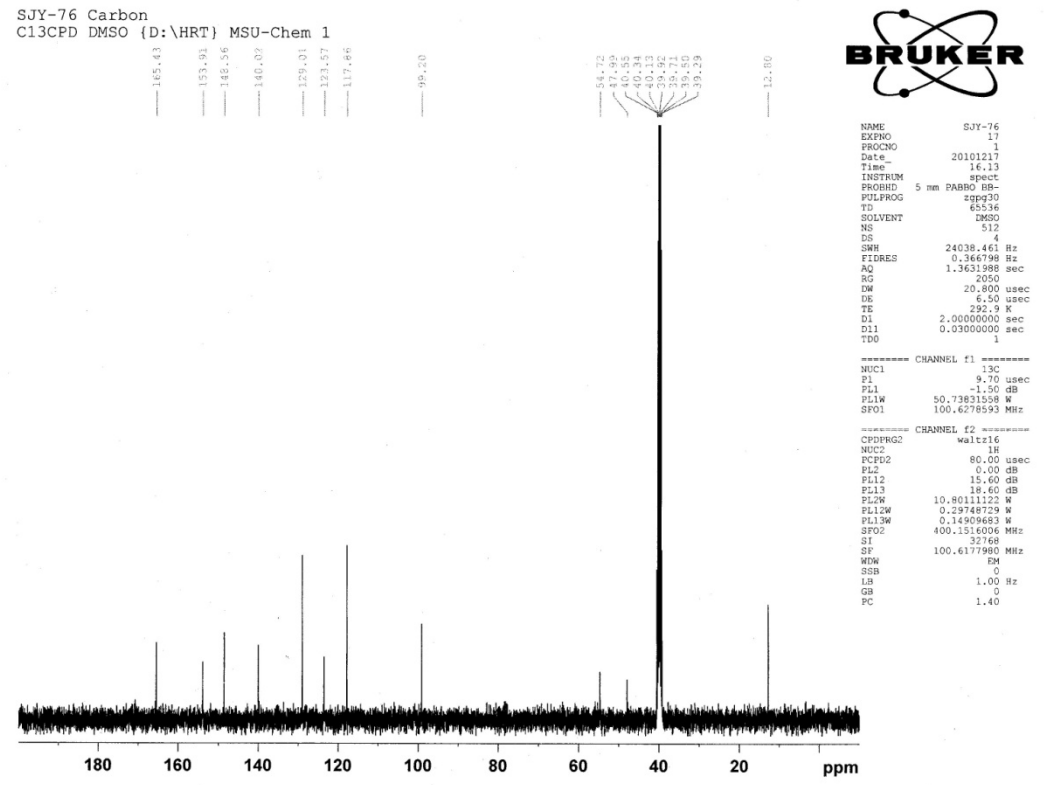

Figure S4: ^{13}C NMR spectra of tripodal ligand L^2

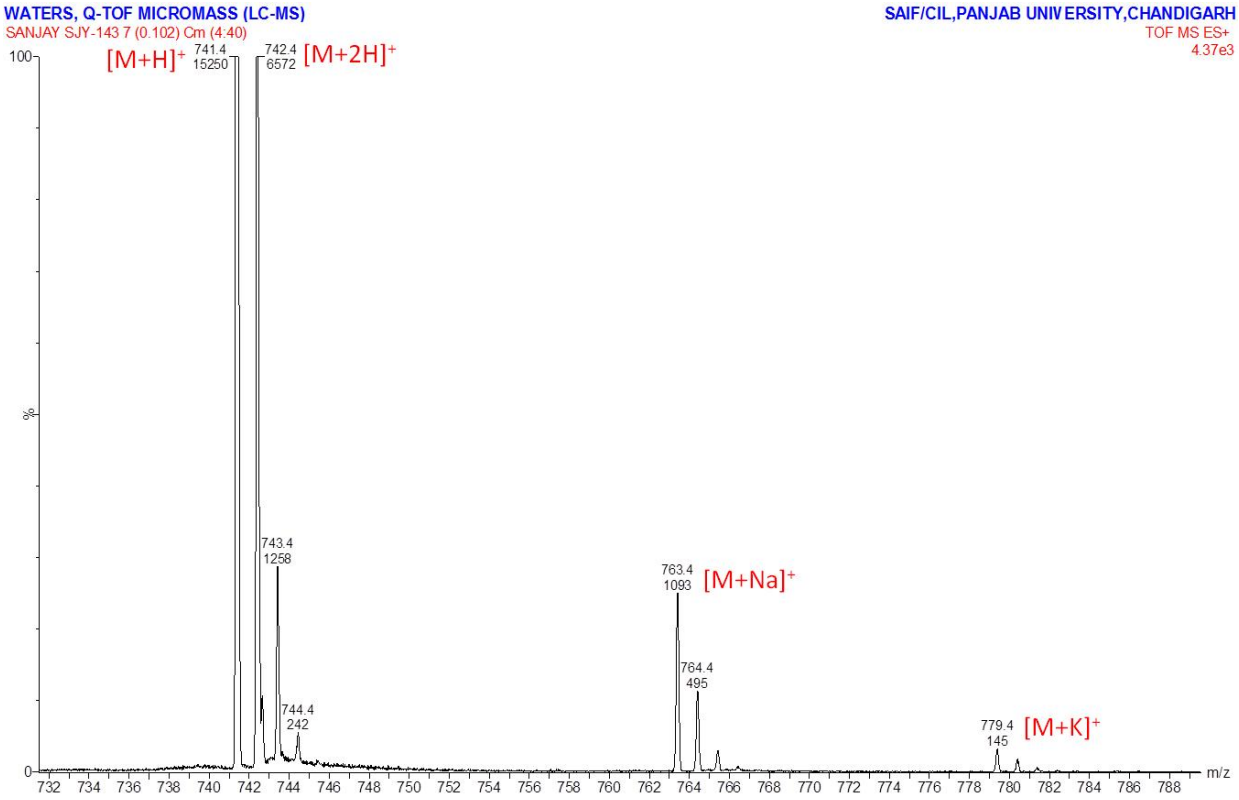

Figure S5: LC-MS of tripodal ligand L^1

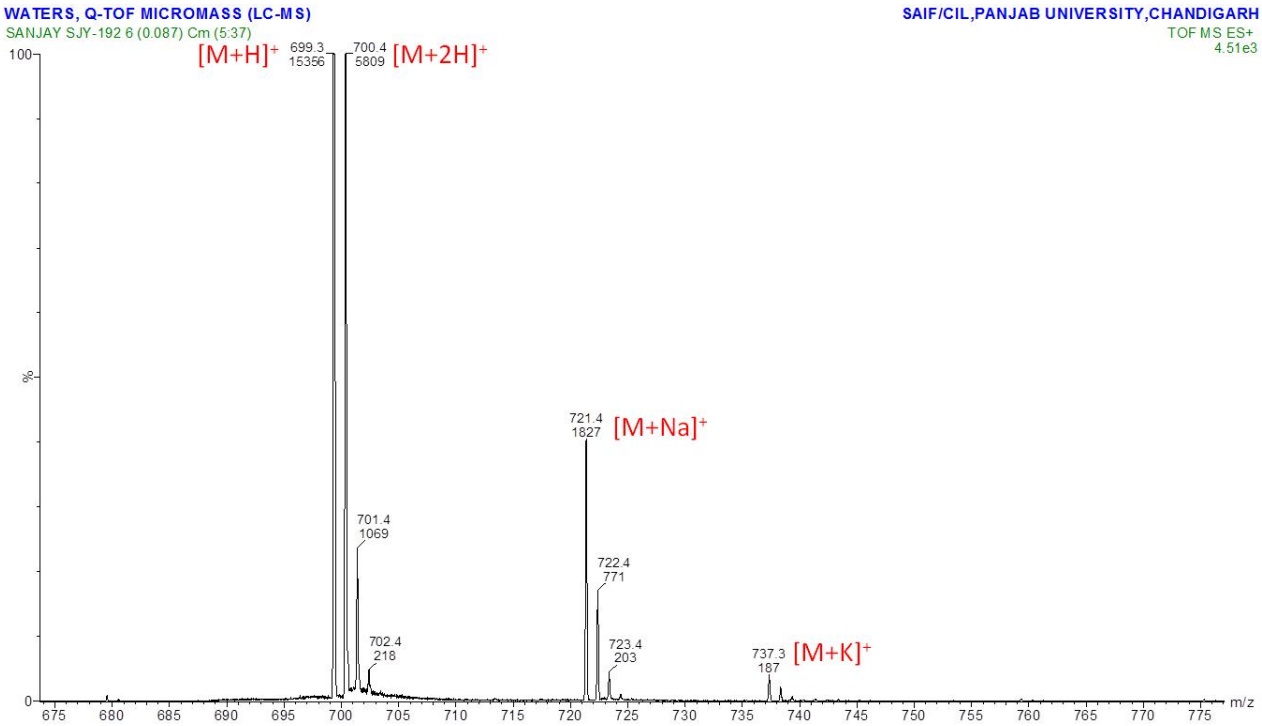

Figure S6: LC-MS of tripodal ligand L^2

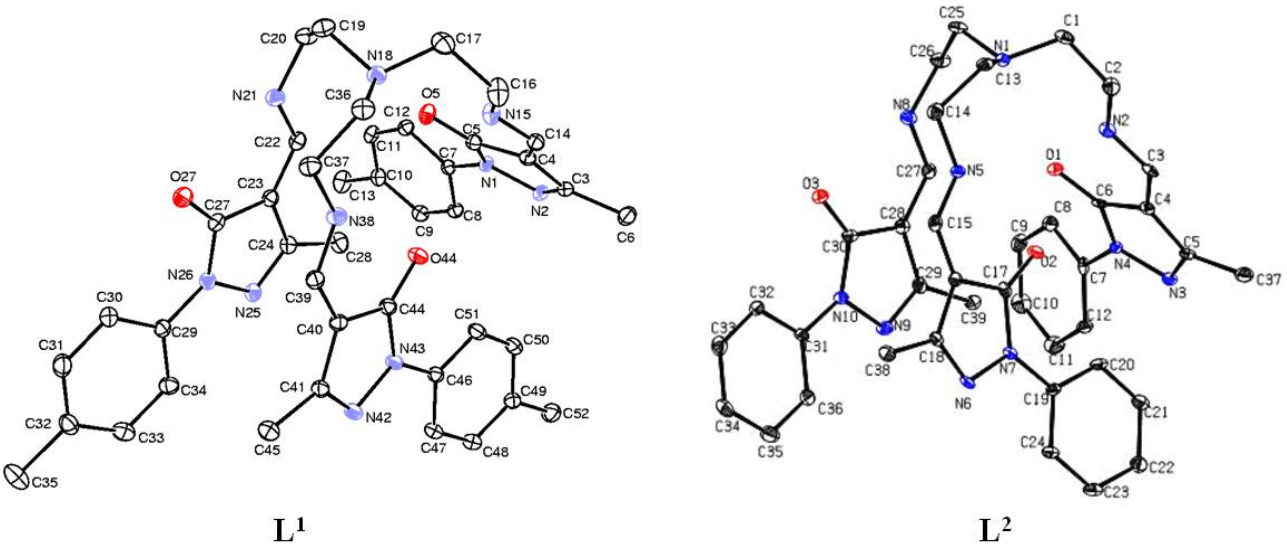

Figure S7: ORTEP view of tripodal ligands L^1 and L^2.

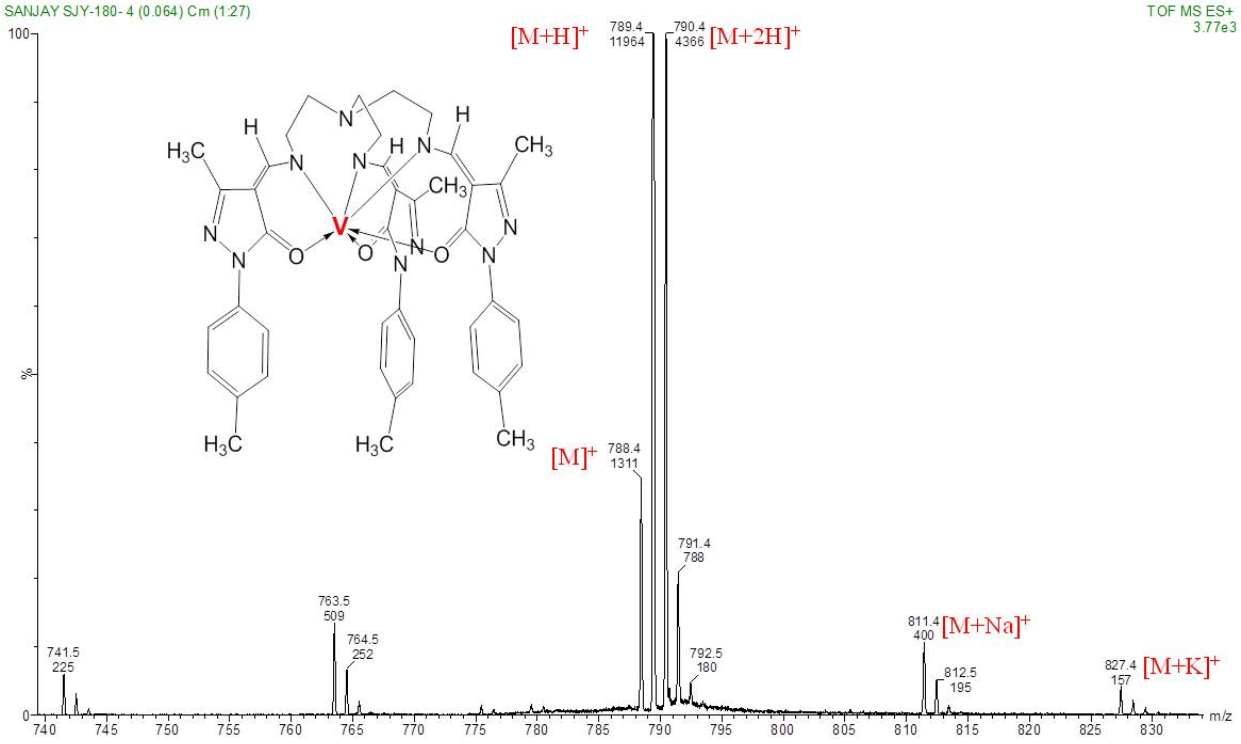

Figure S8: LC-MS of [VL^1]

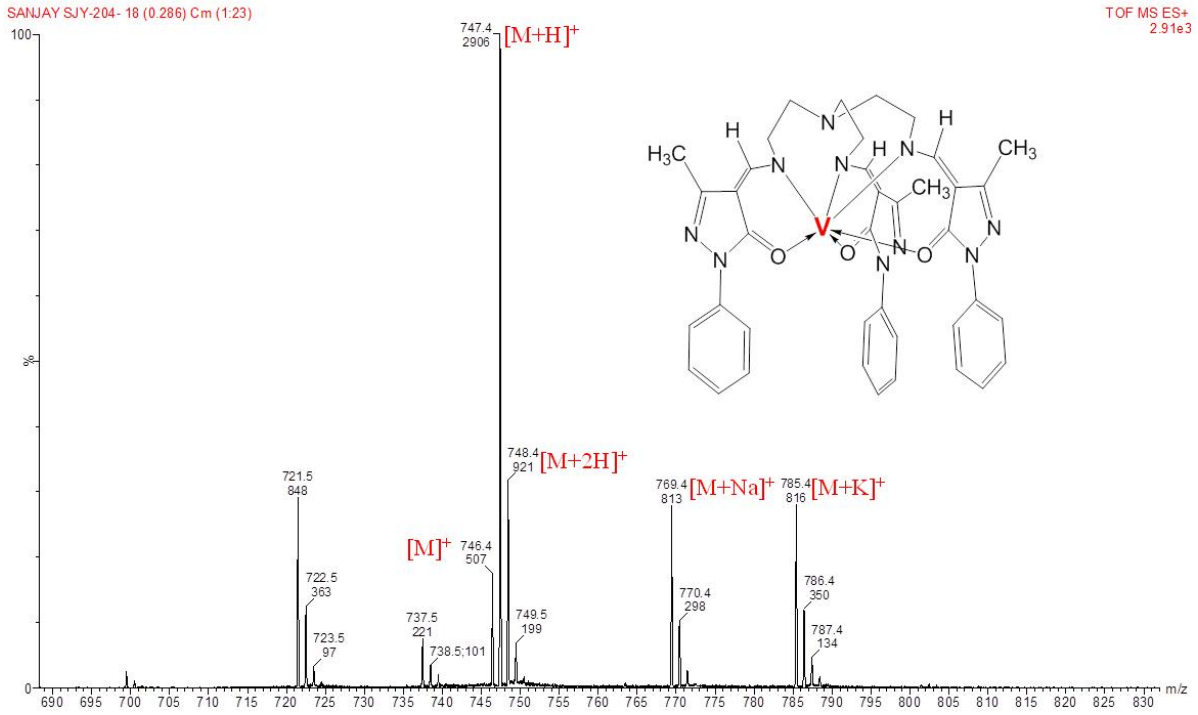

Figure S9: LC-MS of [VL^2]

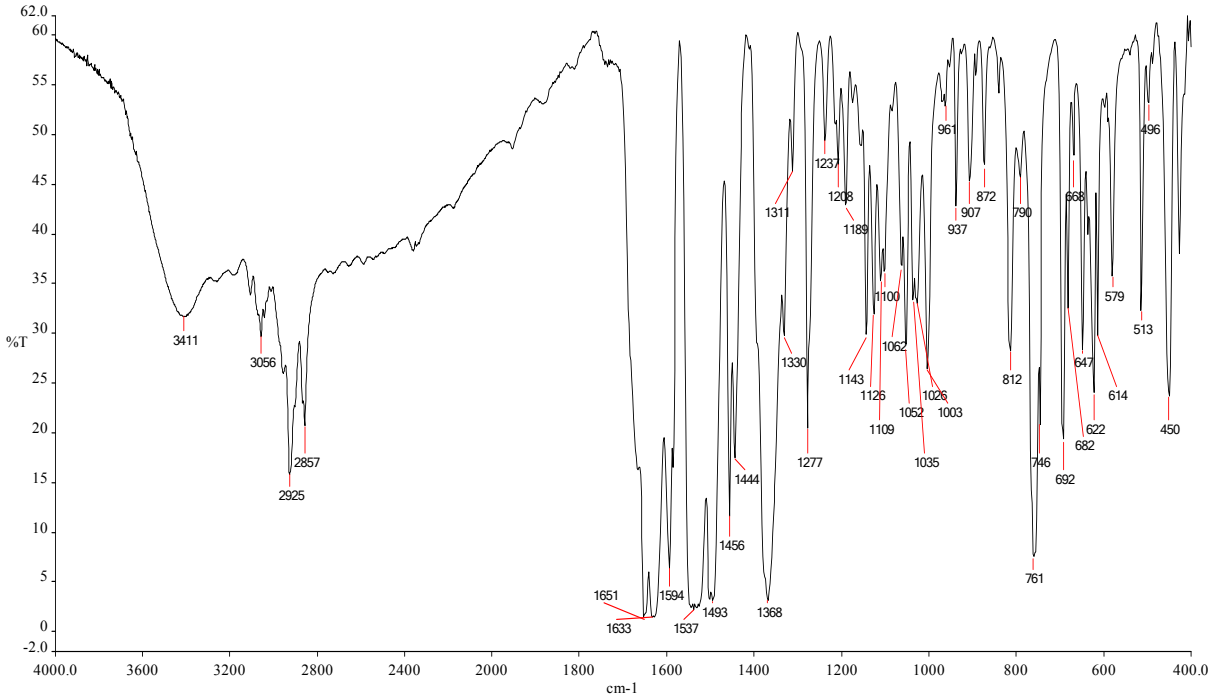

Figure S10: FT-IR spectrum of [VL^1].

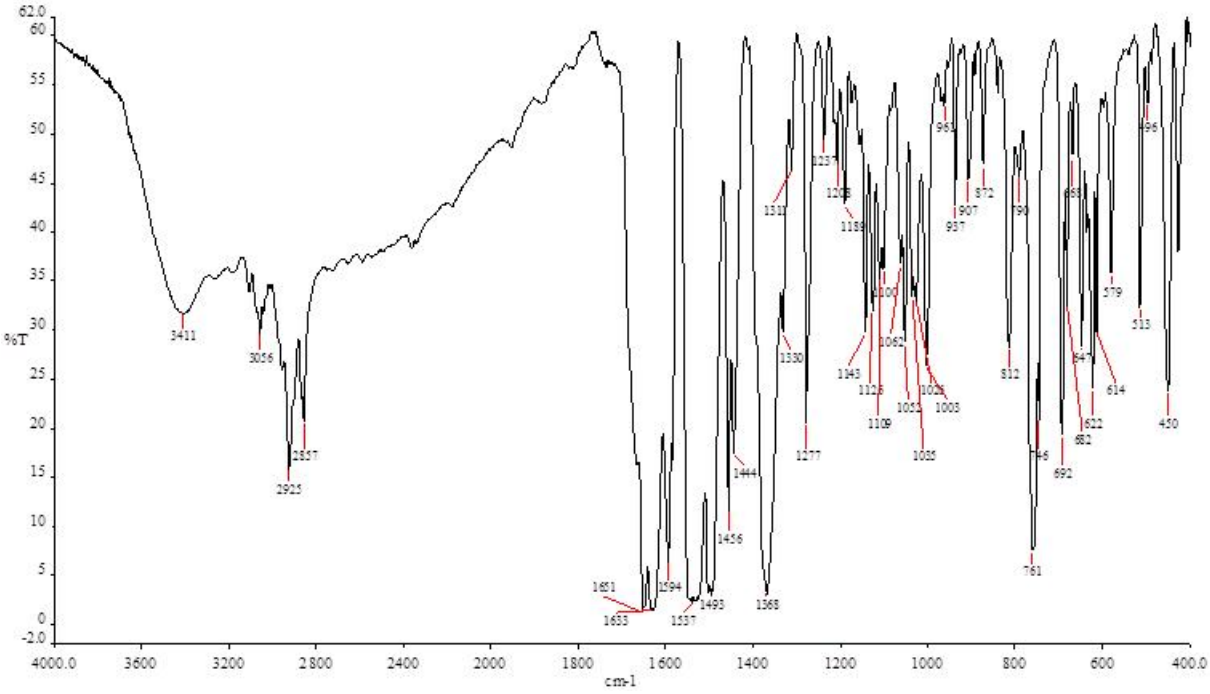

Figure S11: FT-IR spectrum of [VL^2].

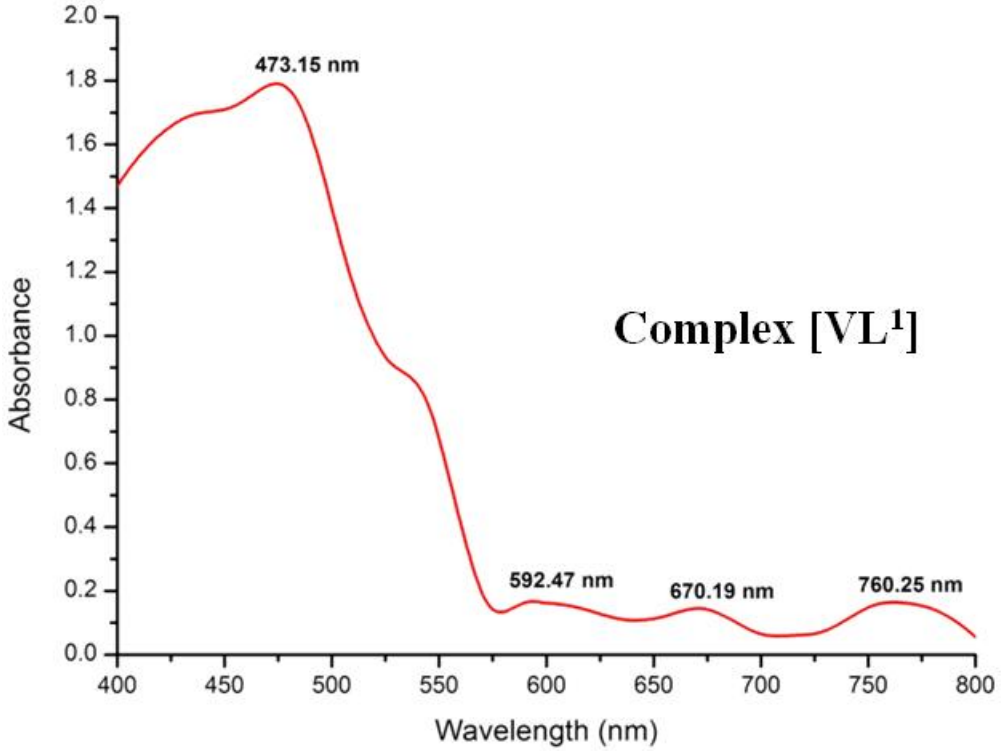

Figure S12: Electronic spectrum of [VL^1].