Supporting Information

Formation of Nitrate Zipped Dimeric Capsule and Un-Zipping by Chloride Doping

M. Arunachalam and Pradyut Ghosh*

Department of Inorganic Chemistry, Indian Association for the CultiVation of Science,
2A & 2B Raja S. C. Mullick Road, Kolkata 700032, India.

E-mail: icpg@iacs.res.in

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Experimental Section

^{1}H NMR and ^{13}C NMR spectra for complexes **1**, **2** and **3** were recorded on Bruker 600 MHz FT-NMR spectrometer (model: DPX-600). ^{1}H NMR and ^{13}C NMR spectra for complex **4** were recorded on Bruker 300 MHz FT-NMR spectrometer (model: DPX-300) in DMSO-*d*$_6$ at 25ºC. HRMS measurements were carried out on QTof-Micro YA 263 instruments. Tetraethylammonium chloride, tetrabutyammonium nitrate and tetrabutylammonium perchlorate were purchased from Sigma-Aldrich,USA and were used as received. Synthesis of **L** was according to the literature procedure·

$[H_3L(NO_3)_3(H_2O)]_2$, 1 : Complex **1** was obtained by adding 0.5mL of 69% Nitric acid to the aqueous suspension of **L** (511 mg, 1mmol). After the addition of acid, the suspension becomes clear and the solution was filtered and kept for crystallization at room temperature. Colorless crystals suitable for X-ray crystallography were obtained after 5 days. Yield of 1: 60-65%; ^{1}H NMR (DMSO-d$_6$, 600 MHz) δ 2.32 (s, 9H), 5.81 (s, 6H), 7.67-7.72 (m, 6H), 7.89 (d, 3H, *J* = 6Hz), 8.17 (d, 3H, *J* = 6Hz), 9.29 (d, 3H, *J* = 6Hz). ^{13}C NMR (75 MHz) δ 16.75, 46.89, 113.66, 116.08, 127.80, 128.27, 130.21, 132.37, 132.69, 140.24, 142.93. HRMS (ESI): m/z 1043.3956 $[2L+Na]^+$, 1022.4185 $[H_2(2L)]^+$, 1021.4061 $[H(2L)]^+$, 785.8361 $[(H_3L)(HNO_3)_4+Na]^+$, 549.2183 $[L+K]^+$, 533.2379 $[L+Na]^+$, 512.2410 $[H_2L]^+$, 511.2327 $[HL]^+$. Anal. Calcd for C33H35N9O10: C, 55.23; H, 4.92; N, 17.56. Found: C, 55.02; H, 4.75; N, 17.42.

$[H_3L(Cl)(NO_3)_2(H_2O)_8]$, 2 : Complex **2** was obtained by adding excess of tetraethylammonium chloride to the aqueous solution of complex **1** (45 mg). The resulting clear solution was kept for crystallization at room temperature. Colourless crystals of complex **2** were obtained after 4 days. Yield of **2**: 40%; ^{1}H NMR (DMSO-d$_6$, 300 MHz) δ 2.33 (s, 9H), 5.81 (s, 6H), 7.65-7.74 (m, 6H), 7.90 (d, 3H, *J* = 7.8Hz), 8.16 (d, 3H, *J* = 6.9Hz), 9.26 (s, 3H). ^{13}C NMR (75 MHz) δ 16.32, 45.53, 113.47, 115.05, 126.04, 126.65, 128.86, 131.52, 131.70, 140.94, 141.73.

[$H_3L(Cl)(NO_3)_2(H_2O)_8$], 2' : Complex **2'** was obtained by adding tetrabutylammonium chloride (417mg, 1.5mmol, 6eq) to the aqueous solution of **L** (127.5 mg, 0.25mmol, 1 eq) in 10mL water. 80μl of 69% nitric acid was added to the aqueous suspension. Warmed the resulting clear solution was filtered and kept for crystallization at room temperature. Colourless crystals of complex **2'** were obtained after 15 days. Yield of **2'**: 35%.

[$H_3L(Cl)_3(HCl)(H_2O)_8$], 3 : Complex **3** was obtained by adding 0.5mL of 37% Hydrochloric acid to the aqueous suspension of **L** (511 mg, 1mmol). After the addition of acid, the suspension becomes clear and the solution was filtered and kept for crystallization at room temperature. Colorless crystals suitable for X-ray crystallography were obtained after 3 weeks. Yield of 2: 55-58%; ^{1}H NMR (DMSO-d_6, 600 MHz) δ 2.31 (s, 9H), 5.80 (s, 6H), 7.64-7.70 (m, 6H), 7.89 (d, 3H, *J* = 12Hz), 8.18 (d, 3H, *J* = 6Hz), 9.88 (s, 3H). ^{13}C NMR (150 MHz) δ 16.31, 45.48, 113.44, 115.11, 125.91, 126.50, 128.90, 131.58, 141.02, 141.68. HRMS (ESI): m/z 1043.2969 [2L+Na]$^+$, 1022.3341 [H_2(2L)]$^+$, 1021.3216 [H(2L)]$^+$, 785.8361 [(H_3L)(HNO_3)$_4$+Na]$^+$, 549.1703 [L+K]$^+$, 533.1877 [L+Na]$^+$, 512.2123 [H_2L]$^+$, 511.2037 [HL]$^+$.

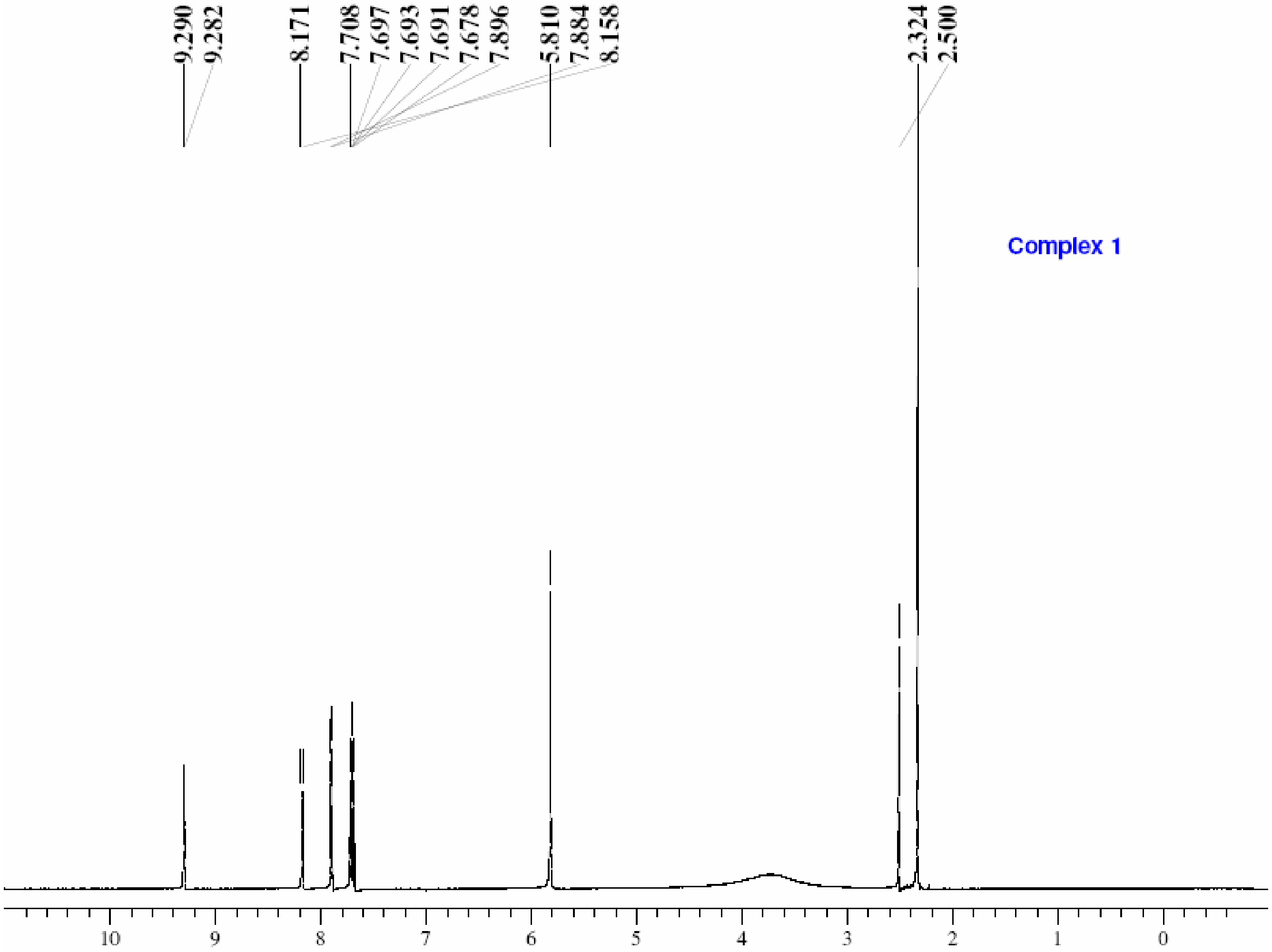

Figure S1. ^{1}H-NMR spectra of Complex 1 in DMSO-d_6

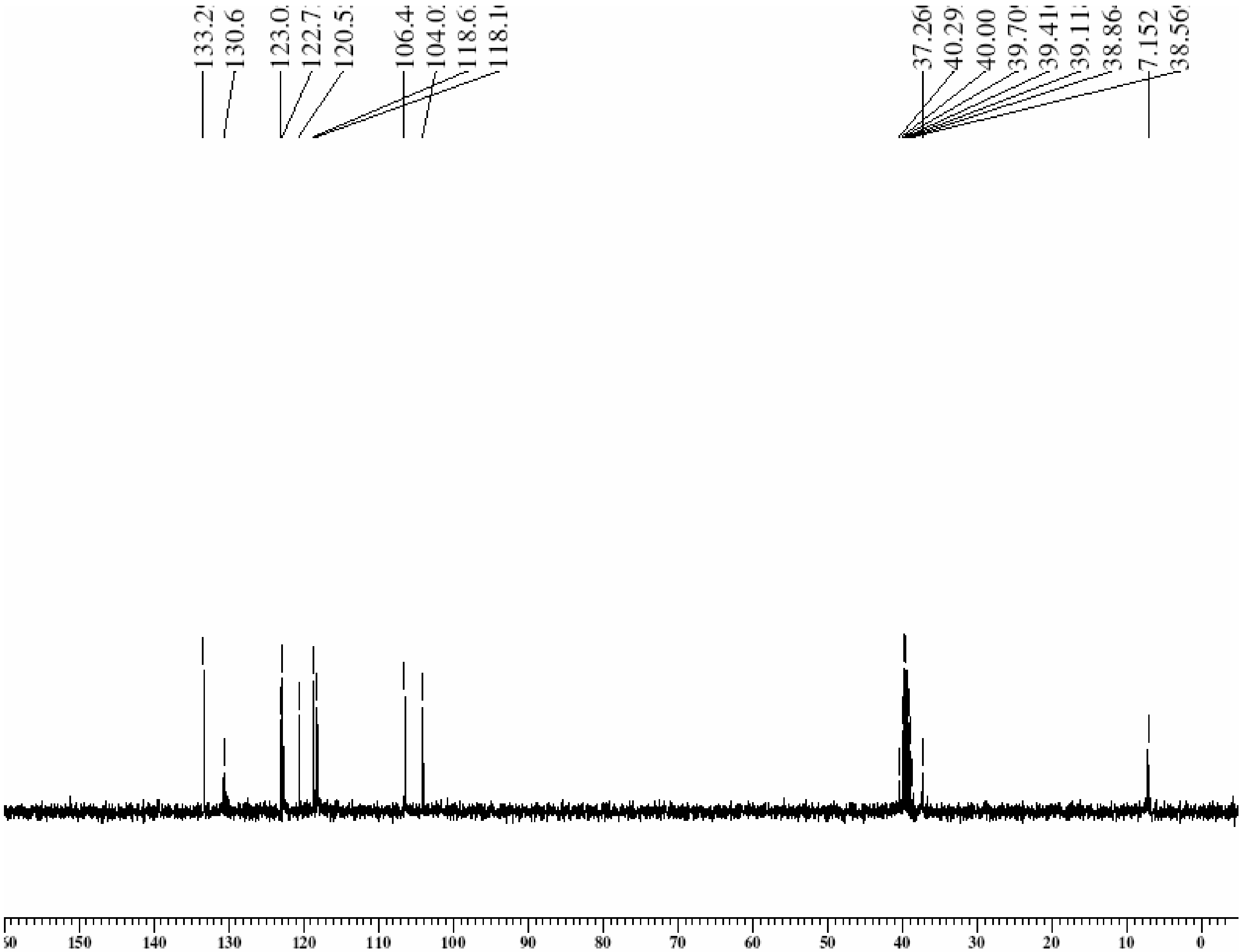

Figure S2. ^{13}C-NMR of Complex 1

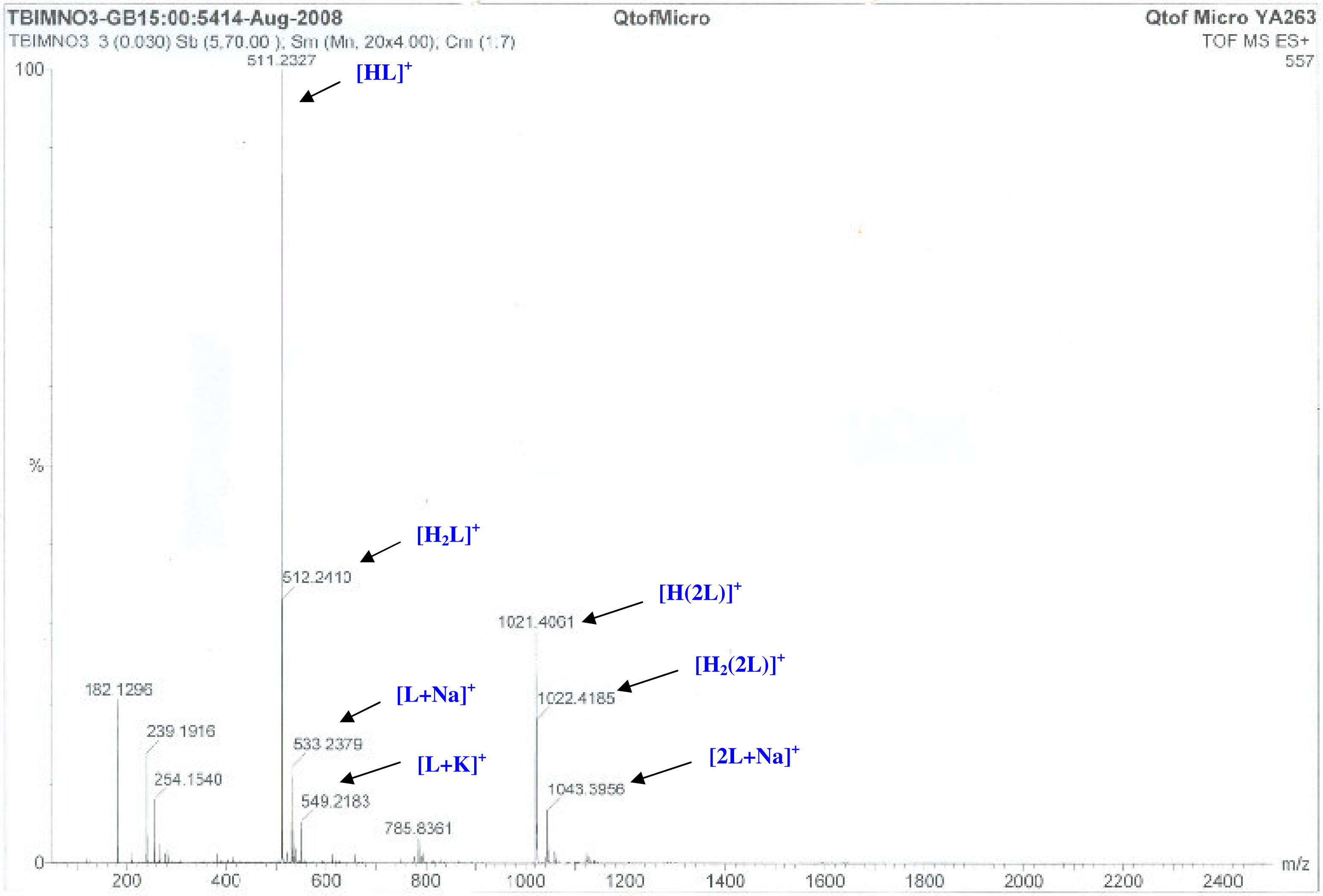

Figure S3. HRMS(ESI) spectrum of Complex 1

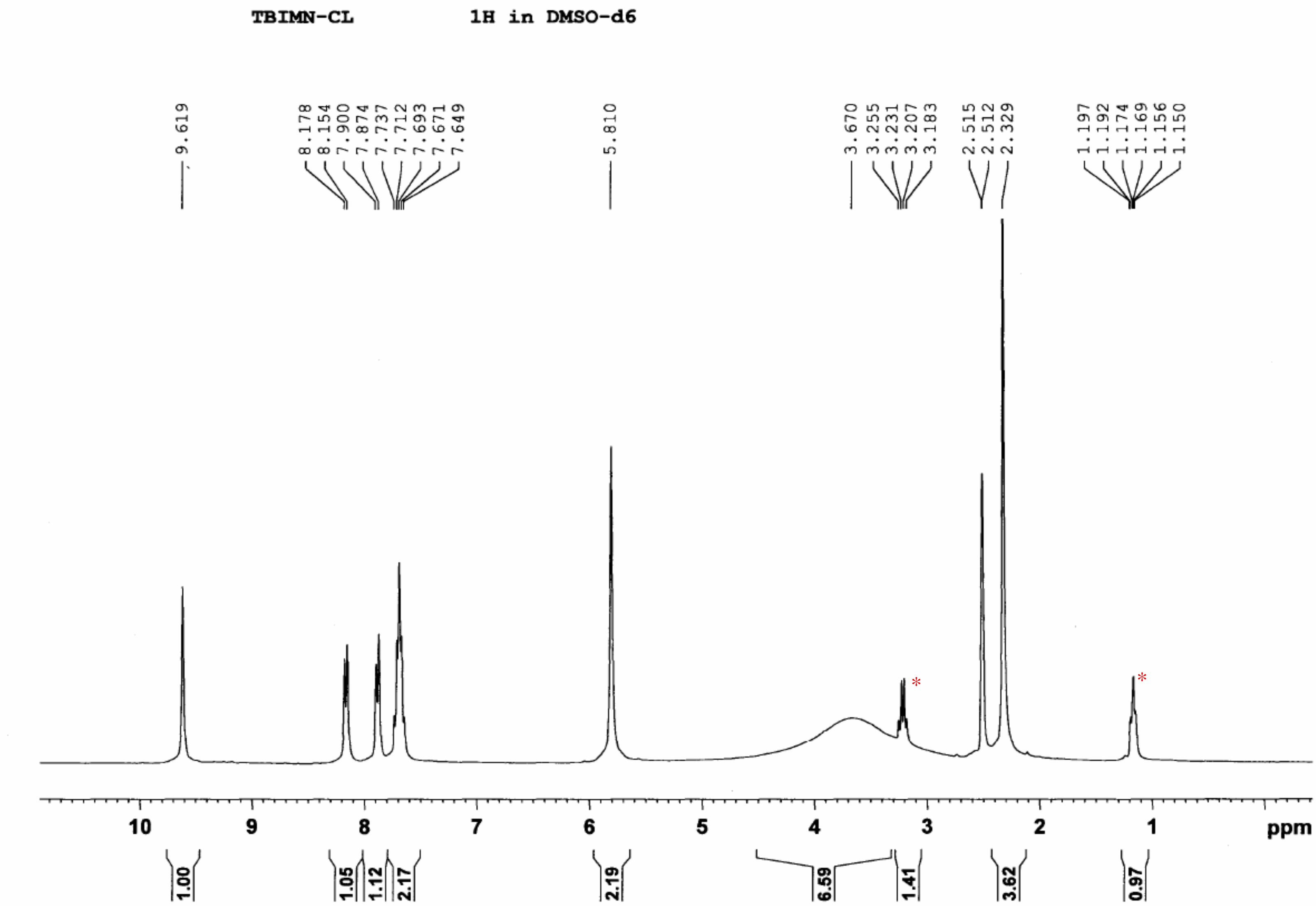

Figure S4.^{1}H-NMR spectrum of Complex 2

(*-represents the impurities peak corresponds to tetraethylammonium chloride added during preparation of complex 2)

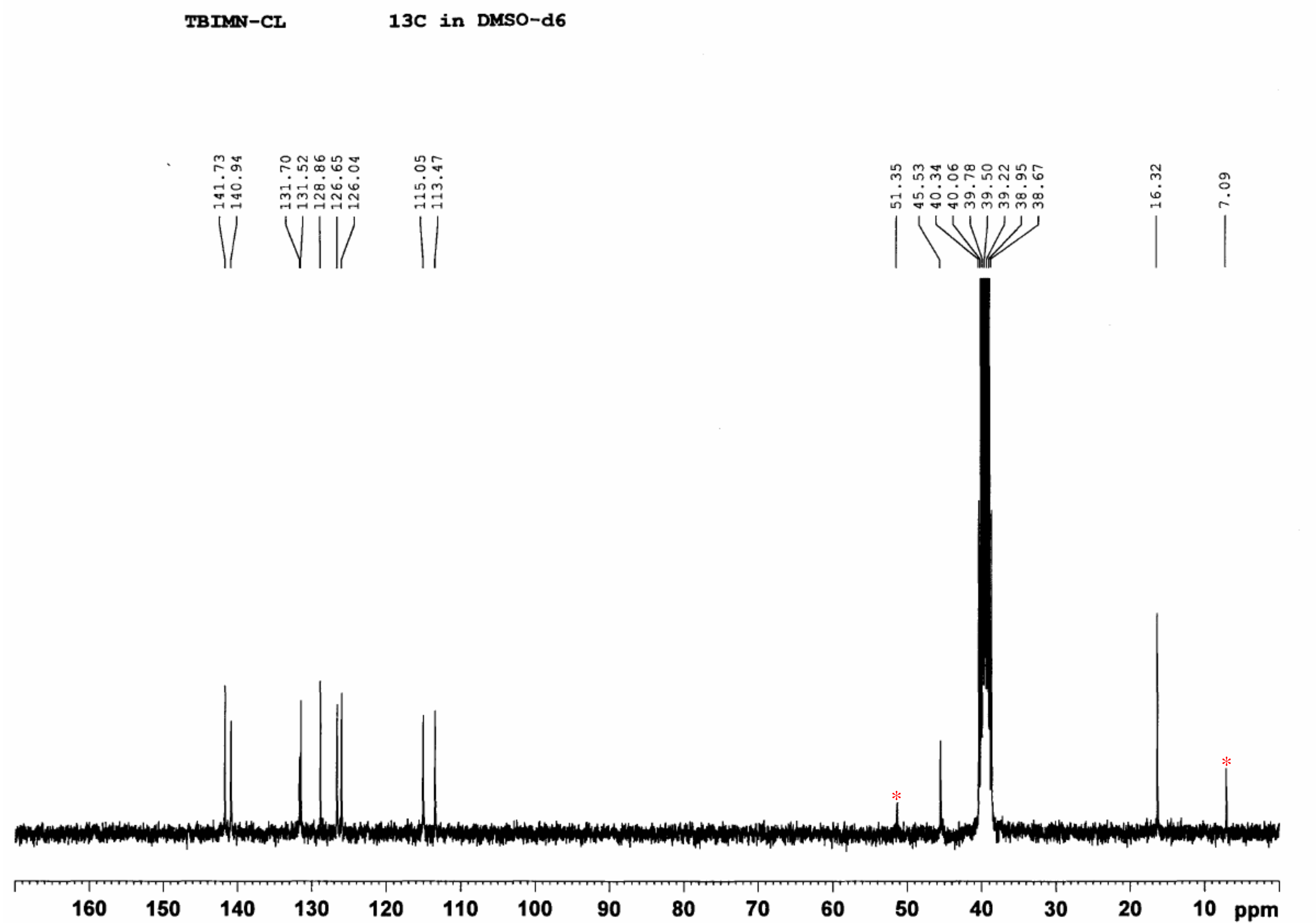

Figure S5. ^{13}C-NMR of Complex 2

(-represents the impurities peak corresponds to tetraethylammonium chloride added during preparation of complex 2)*

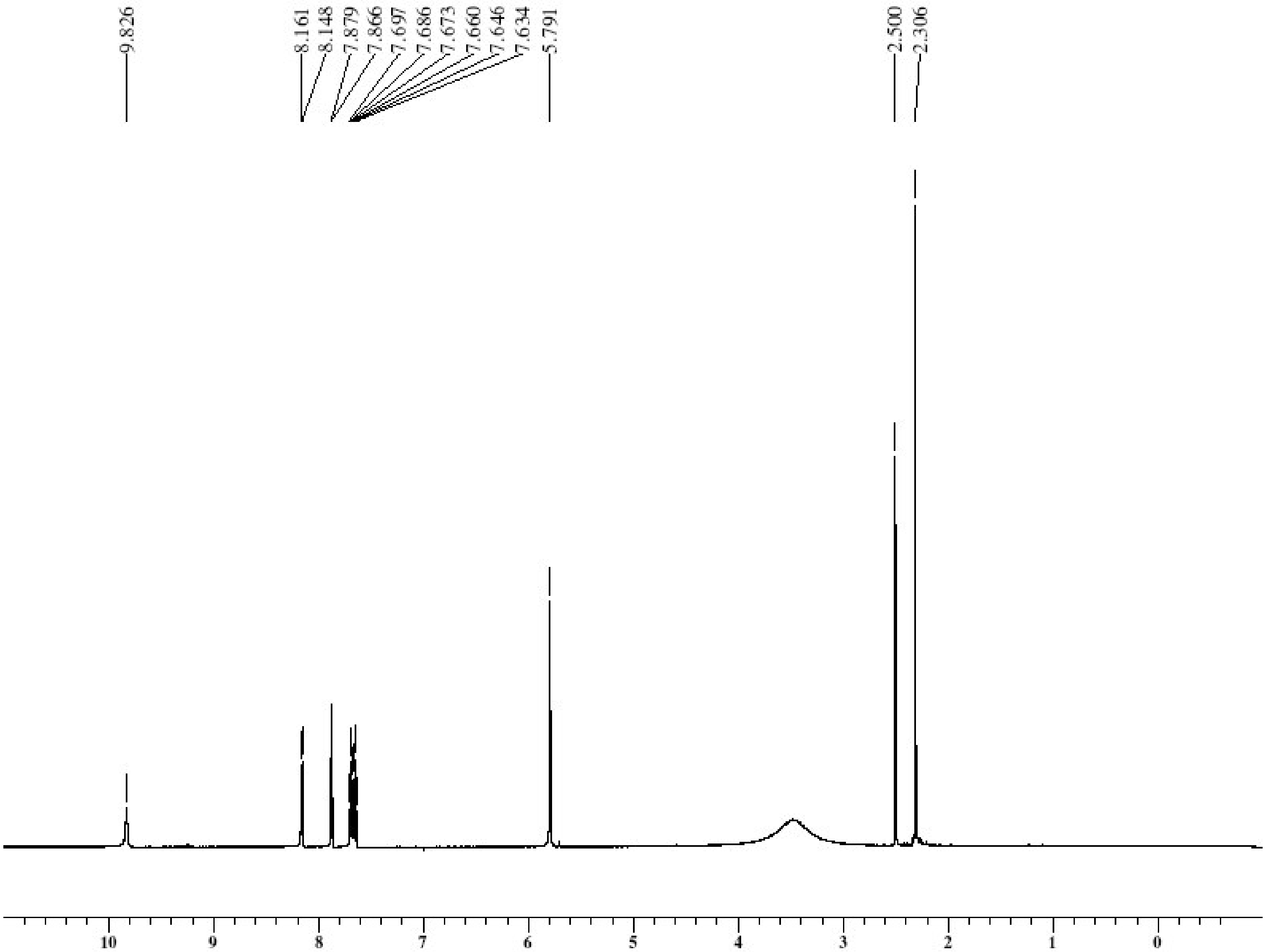

Figure S6. ^{1}H-NMR of Complex 3

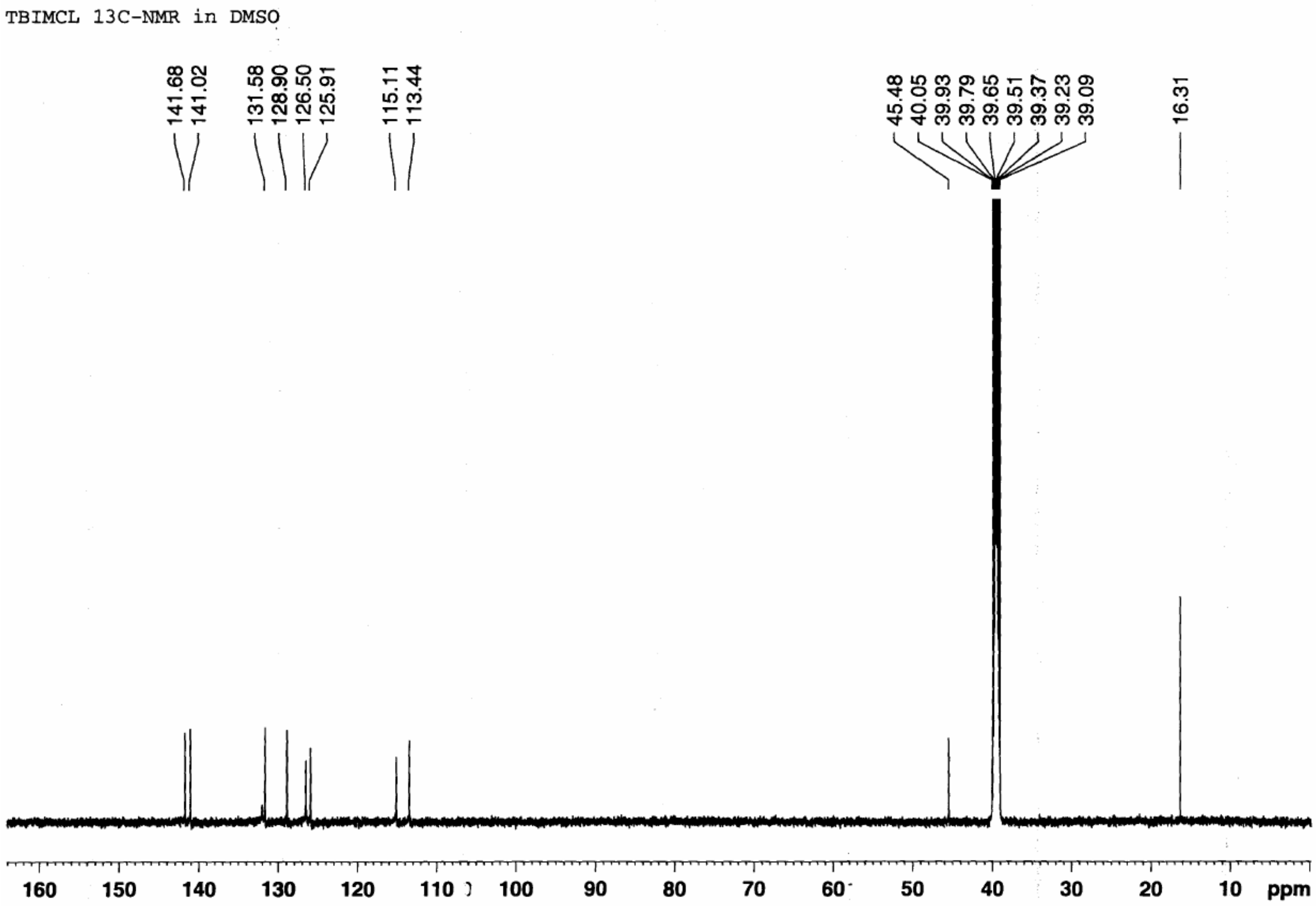

Figure S7. ^{13}**C-NMR of Complex 3**

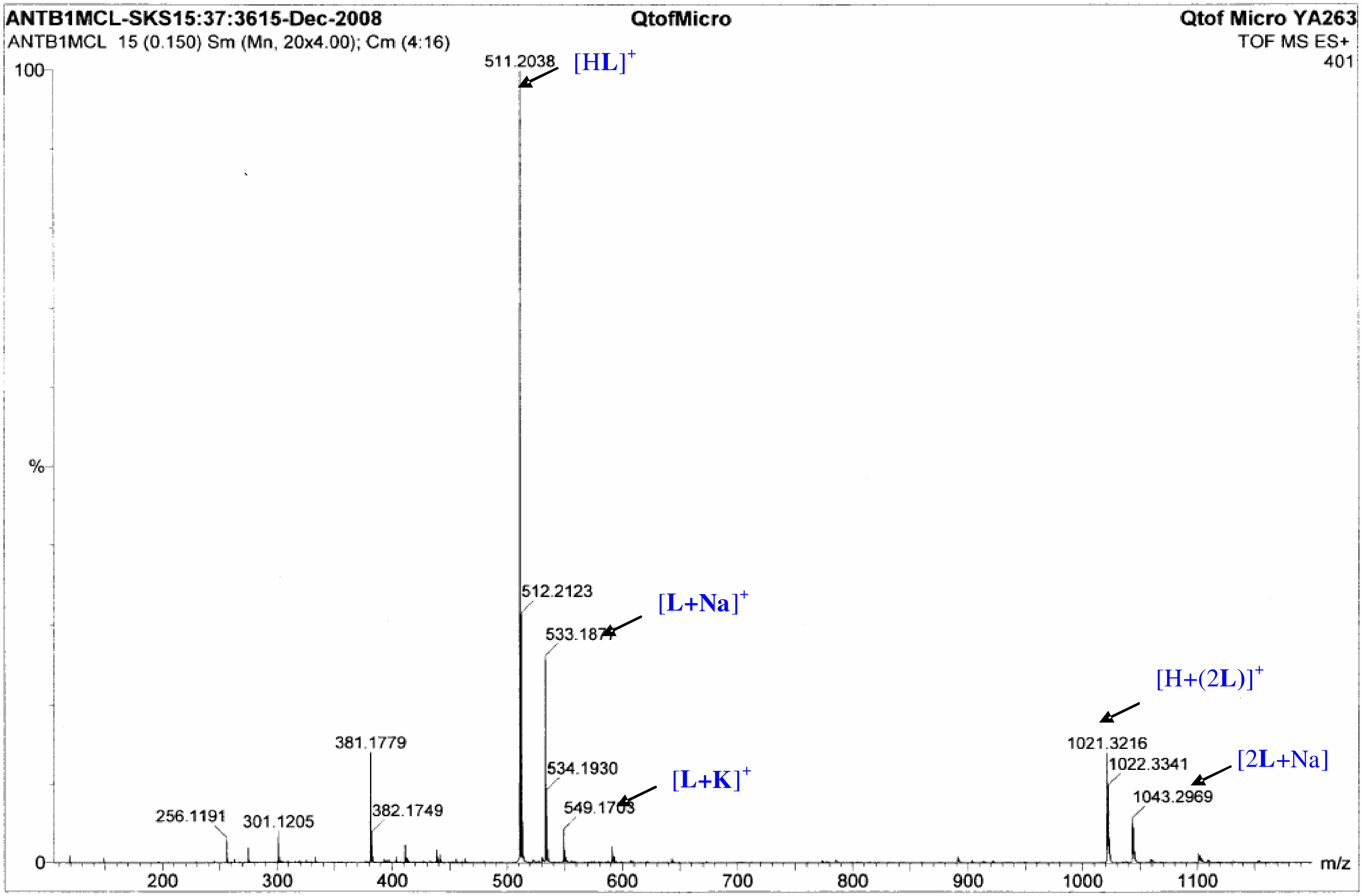

Figure S8. HRMS(ESI) spectrum of Complex 3

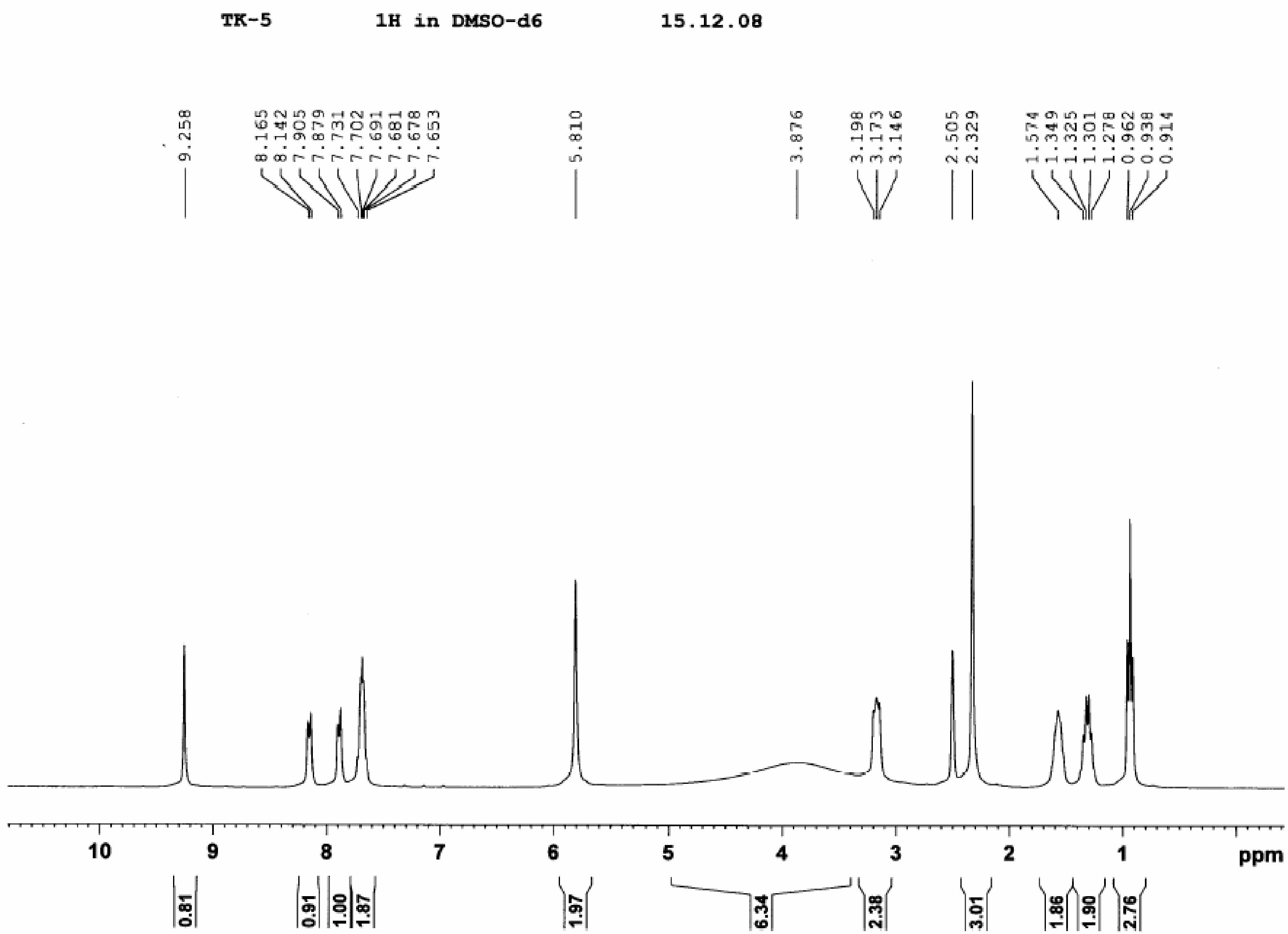

Figure S9. ^{1}H-NMR (300 MHz) of Complex 1 after the addition of n-$Bu_4N^+ClO_4^-$ at 25 °C in DMSO-$_{d6}$.

Crystallographic Refinement Details

The crystallographic data and details of data collection for **1**, **2**, **2’** and **3** are given in Table S1. In each case, a crystal of suitable size was selected from the mother liquor and immersed in partone oil, then mounted on the tip of a glass fiber and cemented using epoxy resin. Intensity data for all four crystals were collected using Mo K_{α} (λ = 0.7107 Å) radiation on a Bruker SMART APEX diffractometer equipped with CCD area detector at 100K. The data integration and reduction were processed with SAINT[1a] software. An empirical absorption correction was applied to the collected reflections with SADABS[1b]. The structures were solved by direct methods using SHELXTL[2] and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97[3] program package. Graphics are generated using PLATON[4] and MERCURY 1.3.[5] In all cases, non-hydrogen atoms are treated anisotropically except disordered water molecules (treated isotropically) in complexes **2**, **2’** and **3**. Whenever possible, the hydrogen atoms are located on a difference Fourier map and refined. In other cases, the hydrogen atoms are geometrically fixed. We were unable to locate the most of the hydrogen atoms of water molecules from the difference Fourier map.

One of the nitrate anions in complex **1** designated by N40O41O42O43, one oxygen atom (O43) and nitrate anion designated by N48O49O50O51, one oxygen atom (O49) and nitrogen center (N48) were disordered at two sites and the occupancy factor were refined using the FVAR command of the SHELXTL program. In case of nitrate anion N44O45O46O47, all three oxygen atoms were disordered at two positions and the occupancy factor were refined using the FVAR command and distance restraints DFIX and SADI were applied using SHELXTL program. All disordered atoms were refined only isotropically in the final cycles of refinement.

In complex **2,** water is the only solvent used in the crystallization process, therefore smeared electron density observed were treated as disordered water molecules (O34 and O35) and these water molecules were disordered at two sites and the occupancy factor were refined using the FVAR command of the SHELXTL program. Further, disordered water oxygen atoms O34A, O34B, O35A and O35B were situated at the plane of symmetry, and water oxygen O28 was located around an inversion center as well as on the plane of symmetry which resulted in strange connectivity of water molecules. Disordered oxygen atoms and O28 were refined only isotropically in the final cycles of refinement. The residual electron density (2.74, 2.34 and 2.13) were observed around Cl27 at distances 1.45, 1.18 and 1.13 Å respectively with the following coordinates : Q1 0.3688 0.0000 0.2144 , Q2 0.4068 0.0000 0.0867 and Q3 0.3095 0.0000 0.0699 .

In complex **2’,** due to the high thermal parameter all three water molecules were refined only isotropically in the final cycles of refinement. The residual electron density (1.32, 1.10 and 1.02) were observed around Cl31 at distances 1.42, 1.19 and 1.17Å respectively with the following coordinates : Q1 0.3674 0.0000 0.2117 , Q2 0.4056 0.0000 0.0818 and Q3 0.3080 0.0000 0.0643.

In addition to the three water molecules located for the complex **3** from difference Fourier map, number of diffused scattered peaks with electron density ranging from 10.35Å^{-3} to 1.36 Å^{-3} were observed, which can be attributed to disordered solvent present in this complex. Attempts to model these peaks were unsuccessful since residual electron density peaks obtained was diffused. PLATON/SQUEEZE[6] was used to refine the structure further. Total potential solvent accessible area volume of 271.7Å^3 and 69 electrons counts/ unit cell were found. This electron counts corresponds to tentatively seven water molecules present in the unit cell. Thus, the structure of the compound revealed that one molecule of $[H_3\mathbf{L}]^{3+}$**,** one HCl molecule, three Cl$^-$ ions, 3 lattice water molecules in the asymmetric unit along with tentatively 7 more molecules of disordered water in the lattice, whose contribution is removed by PLATON/SQUEEZE program. The residual electron density 1.34 and 1.80 were observed around Cl41 and Cl43 at distances 0.75 and 0.87 Å respectively with the following coordinates: Q2 0.2245 0.9940 0.4417 and Q1

0.3381 0.9791 0.0701 respectively. Further residual electron density 1.26 and 1.14 were observed around Cl42 at distances 2.01 and 0.86 Å with the following coordinates: Q3 0.7439 0.3890 0.2309 and Q4 0.6859 0.5492 0.1116.

References

(1) (a) SAINT and *XPREP*, 5.1 ed.; Siemens Industrial Automation Inc.: Madison, WI, 1995.Sheldrick, G. M. (b) *SADABS, empirical absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1997.

(2) Sheldrick, G. M. *SHELXTL Reference Manual:* V*ersion 5.1*; Bruker AXS: Madison, WI, 1997.

(3) Sheldrick, G. M. *SHELXL-97: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(4) Spek, A. L. *PLATON-97*; University of Utrecht: Utrecht, The Netherlands, 1997.

(5) Mercury 1.3 Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., 2003-2004.

(6) Spek, A. L. *PLATON for MS-Windows*, *J. Appl. Cryst*. 36, 7-13.

Table S1: Crystallographic Parameters for Complex 1, 2, 2' and 3

Crystal Data	**Complex 1**	**Complex 2**	**Complex 2'**	**Complex 3**
Empirical formula	$C_{33}H_{35}N_9O_{10}$	$C_{66}H_{82}Cl_2N_{16}O_{20}$	$C_{66}H_{82}Cl_2N_{16}O_{20}$	$C_{33}H_{33}Cl_4N_6O_3$
FW	717.70	1490.38	1490.38	709.5
Crystal size (mm)	0.40 x 0.28 x 0.12	0.50 x 0.40 x 0.20	0.50 x 0.30 x 0.15	0.30 x 0.20 x 0.20
Crystal description	BLOCK	BLOCK	BLOCK	BLOCK
Crystal system	MONOCLINIC	MONOCLINIC	MONOCLINIC	TRICLINIC
Space group	P21/c	C2/m	C2/m	P-1
a/Å	12.0912(15)	22.891(3)	22.8777(19)	10.2508(5)
b/Å	15.0534(19)	11.2053(12)	11.0220(9)	10.3104(5)
c /Å	19.735(3)	13.5851(15)	13.5118(11)	20.0734(10)
$\alpha/^0$	90.00	90.00	90.00	82.4230(10)
$\beta/^0$	90.931(2)	100.816(3)	100.711(2)	80.8690(10)
$\gamma/^0$	90.00	90.00	90.00	74.6420(10)
Volume / $Å^{-3}$	3591.6(8)	3422.7(6)	3347.7(5)	2010.86(17)
Z	4	2	2	2
$D_{calc.}/Mgm^{-3}$	1.327	1.436	1.479	1.172
F(000)	1504	1548	1408	742
μ MoK_α (mm^{-1})	0.101	0.183	0.187	0.331
Temperature (K)	100(2)	100(2)	100(2)	100(2)
2θ max (°)	22.54	26.45	24.86	31.95
Observed reflections[I>2 σ(I)]	27000	18071	19006	31194
Parameters refined	474	270	269	418
Goodness of fit	1.026	1.034	0.994	1.081
Final R_1 on observed data	0.0880	0.0979	0.0767	0.0647
Final wR_2 on observed data	0.2537	0.2927	0.2300	0.1772

Table S2. Hydrogen Boning Parameters for Complex **1**

D-H…A	**D-H (Å)**	**H···A (Å)**	**D···A (Å)**	**∠D-H···A (º)**
N12-H12···O50[1]	0.8600	1.9187	2.7748	173.47
N20-H20···O45A[2]	0.8600	2.0944	2.8503	146.33
N20-H20···O47A[2]	0.8600	2.2870	3.0634	150.24
N33-H33···O42[3]	0.8600	2.4747	3.1114	131.43
N33-H33···O43A[3]	0.8600	1.9088	2.7607	170.54
O52-H52A···O43A[4]	0.8877	1.9435	2.7850	157.65
C13-H13···O52[5]	0.9300	2.4513	3.1768	134.91
C19-H19···O52[5]	0.9300	2.5341	3.4065	156.36
C32-H32···O52[5]	0.9300	2.3281	3.0598	135.29
N12-H12···O49A[6]	0.8600	2.5991	3.1105	119.19
1 = 1-x, 1-y,1-z.; 2 = -x,1/2+y,1/2-z; 3 = -1+x,1/2-y,1/2+z; 4 = 1-x,1/2+y,1/2-z; 5 = x, y, z; 6 = x,1/2-y,1/2+z				

Table S3. Hydrogen Boning Parameters for Complex **2**

D-H…A	D-H (Å)	H···A (Å)	D···A (Å)	∠D-H···A (º)
N2-H2···Cl27^{1}	0.8600	2.2560	3.0736	158.81
N23-H23···O29^{2}	0.8600	1.8581	2.7180	179.16
N23-H23···O31^{2}	0.8600	2.4606	3.0029	121.69
C10-H10A···O30^{1}	0.9700	2.5138	3.3788	148.45
C10-H10B···O30^{3}	0.9700	2.5138	3.3788	148.45
C15-H15B···O30^{4}	0.9700	2.3557	3.3191	172.05
C24-H24···O31^{4}	0.9700	2.3516	3.2007	151.64
1 = x, y, z.; 2 = x,y,-1+z; 3 = x,-y,z; 4 = -x, y, -z				

Table S4. Hydrogen Boning Parameters for Complex **2’**

D-H…A	D-H (Å)	H···A (Å)	D···A (Å)	∠D-H···A (º)
N7-H7···O29^{1}	0.6745	2.4370	2.9867	138.60
N7-H7···O30^{1}	0.6745	2.0587	2.7103	162.77
N20-H20···Cl31^{2}	0.7654	2.2897	3.0198	159.85
C4-H4A···O28^{3}	0.9700	2.3398	3.3010	170.78
C6-H6···O29^{3}	0.9300	2.3379	3.1859	151.45
C9-H9···O30^{4}	0.9300	2.5796	3.3216	137.08
C15-H15A···O28^{2}	0.9600	2.5747	3.2351	126.13
C17-H17···O28^{2}	0.9838	2.5261	3.3748	144.38
1= x,y,-1+z; 2 = x, y, z; 3 = -x,y,-z; 4 = 1/2-x,1/2-y,-z				

Figure S10. View showing the C-H···O interactions of the anions with the C-H protons of the tripodal receptor in complex **2**.

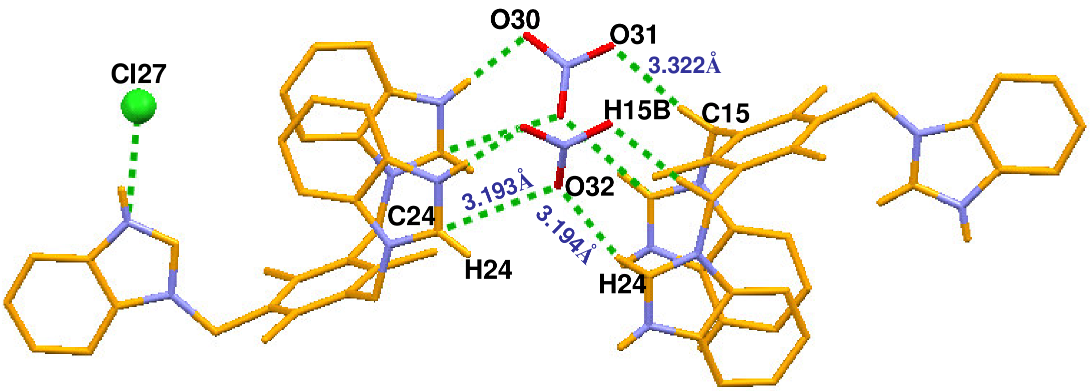

Table S5. Hydrogen Boning Parameters for Complex **3**

D-H…A	**D-H (Å)**	**H···A (Å)**	**D···A (Å)**	**∠D-H···A (º)**
N12-H12···Cl41[1]	0.8600	2.2612	3.1075	167.96
N25-H25···Cl43[1]	0.8600	2.2719	3.1187	168.22
N38-H38···Cl40[2]	0.8600	2.1237	2.9733	169.45
C13-H13···Cl40[3]	0.9300	2.4433	3.3655	171.28
C26-H26···Cl40[3]	0.9300	2.4562	3.3786	171.38
C39-H39···Cl(41)[4]	0.9300	2.6932	3.5722	157.94
1 = -x,1-y,1-z; 2 = 2-x,-y,1-z; 3 = 1-x,-y,1-z; 4 = 1-x,1-y,1-z				