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Electronic Supporting Information

Bismuth(III) benzohydroxamates: powerful anti-bacterial activity against *Helicobacter pylori* and hydrolysis to a unique Bi_{34} oxido-cluster $[Bi_{34}O_{22}(BHA)_{22}(H\text{-}BHA)_{14}(DMSO)_6]$

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General Information: Benzohydroxamic acid was purchased from Sigma-Aldrich Chemical Co. and used without further purification. $BiPh_3$ and $Bi(O^tBu)_3$ was prepared according to a literature procedure [1, 2]. THF and toluene used during reaction was obtained from solvent purification system. Ethanol was distilled from magnesium turnings prior to use and stored over 3Å MS under N_2. All molecular sieves were dried at 120 °C and allowed to cool under vacuum before use. ^{1}H and 13 C NMR spectra were recorded using either a Bruker DPX 300 and 400 MHz spectrometer as solutions in d_6-DMSO. Multiplicities are denoted as singlet (s) and broad singlet (bs). Infrared Spectra (IR) as pure solid were recorded on a Agilent Technologies Cary 630 FTIR. IR absorptions (ν_{max}) are reported in units of wavenumbers (cm^{-1}). Elemental Analysis was performed by the Chemical & MicroAnalytical Services Pty Ltd, Belmont, Victoria, Australia. Melting points are uncalibrated using a Bibby Stuart Scientific Melting Point Apparatus SMP3. Mass spectra were recorded on a Micromass Platform Electrospray mass spectrometer at cone voltages as specified using a DMSO/methanol or methanol solution as the mobile phase. The ion peaks (m/z) and their assignments are listed.

Crystallographic data: Crystallographic data of compound **4** was collected at the MX1 beamline at the Australian Synchrotron, Melbourne, Victoria, Australia (λ = 0.71070 Å). All data was collected at 100 K, maintained using an open flow of nitrogen. The software used for data collection and reduction of the data were BluIce[1] and XDS.[2] Compounds 2 was solved and refined with SHELX-97.[3] All non-hydrogen atoms were refined with anisotropic thermal parameters unless otherwise indicated and hydrogen atoms were placed in calculated positions using a riding model with C-H = 0.95-0.98 Å and $U_{iso}(H)=xU_{iso}(C)$, x = 1.2 or 1.5. CCDC number for compound **2** (1023760).

Sample collection: Several crystals were collected on the Oxford Bruker Excalibur machine and then subsequently at the Australian Synchotron MX1 beamline. In both cases after

multiple collections there was limited high angle reflections collected out to 0.81. The data used for refinement gave the best $R_{int}2$ value.

Structure solution and refinement: The Bi core was readily solved and refined fine. The periphery of the cluster- hydroximate ligands, DMSO and water molecules were found but refined poorly. The final refinement has only Bi, O, N, S and ipso C atoms refined as anisotropic. Residual electron density in the lattice was poorly resolved and could not be modelled. The associated residual electron density from the disordered DMSO and water molecules was compensated by application of the programme PLATON/SQUEEZE.[4] The void volume of 2564 $Å^3$ and calculated electron density account well for approximately 20 DMSO and 15-18 H_2O molecules which were found disordered in lattice of the cluster. Other analytical techniques, NMR, microanalysis and mass spec show these DMSO and water molecules not to be coordinated to the cluster, hence only present in the lattice.

Each of the phenyl rings of the hydroximate ligands was refined as a single hexagon with one thermal parameter per ring. Residual electron around the phenyl rings suggest rotational disorder, which could not be modelled successfully modelled. Two of the coordinated DMSO molecules were modelled as disordered over two positions. For some atoms where the two components overlap, these were restrained to have the same thermal parameters. The N-H protons belonging to the mono-deprotonated hydroximate ligands were put in calculated positions that made chemical sense according to the molecules C-o and C-N bond lengths and confirmed by NMR spectroscopy by integration values to belong to 7 of the ligands.

Bacterial Strains and culture conditions: H. pylori strains 251, B128 and 26695 were routinely cultured on HBA or in BHI, supplemented with either 7.5% (v/v) fresh horse blood or 10% (v/v) FCS, respectively.[4] Culture media were further supplemented with 155 mg L^{-1}

polymyxin B, 6.25 mg L^{-1} vancomycin, 3.125 mg L^{-1} trimethoprim, and 1.25 mg L^{-1} amphotericin B.

Determination of Minimum Inhibitory Concentration (MIC): The MIC of the bismuth complexes was determined by the agar dilution technique. For this, *H. pylori* cultures were incubated in BHI for 18 hours shaking at 140 rpm at 37°C under microaerobic conditions. Bacteria were pelleted, washed in phosphate buffered saline, then re-suspended in BHI.[5] Each suspension was adjusted to give an approximate density of 10^6 bacteria ml^{-1}. Aliquots (10 ml) of these suspensions were then streaked onto HBA plates containing doubling dilutions of the different concentrations of bismuth compounds, ranging in concentration from 100 μg mL^{-1} to 0.049 μg mL^{-1}. The compounds were tested alongside the benzohydroxamic acid, in comparable concentrations. The MICs were determined by examination of the plates after incubation for 3–5 days at 37 °C. All assays were conducted in duplicate.

NOTE: Benzohydroxamic acid = H_2-BHA = LH_2

Synthesis of $[Bi_2L_3]$ 1:

All the manipulations were carried out under nitrogen atmosphere with pre-dried solvents. Bismuth *tert*-butoxide (0.22 g, 0.5 mmol) was added to a clear solution of benzohydroxamic acid (0.103 g, 0.75 mmol) in THF (20 mL) at −80 °C and stirred overnight. THF was removed under reduced pressure and solid residue was washed with ether to purify the crude product. Yield: 0.27 g, 66%. Melting point: >233 °C (Dec.). ^{1}H NMR (300 MHz, d_6-DMSO): δ 7.33 (bs, 3H, aromatic-CH), 7.80 (bs, 2H, aromatic-CH). ^{13}C NMR (100 MHz, d_6-DMSO): 126.3 (aromatic-C), 128.2 (aromatic-C), 128.6 (aromatic-C), 134.4 (aromatic-qC), 166.5 (carbonyl-C). FT-IR (cm^{-1}): 3053 (brd, O-H), 1597 (m, C=N), 1558 (m, C=O), 776 (m, C-H-out of plane bend), 687 (Vs, ring in plane bend). Elemental analysis; ($C_{21}H_{15}Bi_2N_3O_6$), Calc

(Found): C 30.64 (30.27), H 1.84 (2.27), N 5.10 (5.42) %. Mass spectrum, (ESI^+): 481.0 $[Bi(LH)(L)+H]^+$, 503.0 $[Bi(LH)(L)+Na]^+$, 541.0 $[Bi(LH)(L)+Li\ (3H_2O)]^+$, ($ESI^-$): 479.0 $[BiL_2]^-$; (where $LH_2 = C_7H_7O_2N$).

Synthesis of $[BiL_3]$ 2:

Synthetic Route 1: In a Schlenk flask and under inert conditions, a mixture of triphenyl bismuth (0.22 g, 0.5 mmol) and benzohydroxamic acid (0.206 g, 1.5 mmol); (1:3 equivalent) in toluene (10 mL) was heated at 110 °C to reflux for 24 hours. This mixture was then cooled to room temperature before the precipitate was filtrated. Excess triphenyl bismuth was removed by washing the precipitate with small amounts of ethanol. The precipitate was then dried by vacuum.

Synthetic Route 2: In a Schlenk flask and under inert conditions, a mixture of triphenyl bismuth (0.22 g, 0.5 mmol) and benzohydroxamic acid (0.206 g, 1.5 mmol); (1:3 equivalent) in ethanol (10mL) at 80 °C was heated to reflux for 24 hours. This mixture was then cooled to room temperature before the precipitate was filtrated. Excess triphenyl bismuth was removed by washing the precipitate with small amounts of toluene. The precipitate was then dried by vacuum.

Synthetic Route 3: In a Schlenk flask and under inert conditions, a mixture of triphenyl bismuth (0.22 g, 0.5 mmol) and benzohydroxamic acid (0.206 g, 1.5 mmol); (1:3 equivalent) was heated at 60 °C for 4 hours. This mixture was then cooled to room temperature before the precipitate was filtrated. Excess triphenyl bismuth was removed by washing the precipitate with small amounts of ethanol and toulene. The precipitate was then dried by vacuum. Yield: 0.18 g, 58% (SR1-toulene), 0.17g, 55% (SR2-ethanol), 0.20 g, 65% (SR3-SF). Melting point: >242 °C (Dec.). FT-IR (cm^{-1}): 3161/3058 (brd, NH/OH), 1597 (m, C=N), 1560 (m, C=O), 781 (m, C-H-out of plane bend), 691 (Vs, ring in plane bend). ^1H NMR (300

MHz, d_6-DMSO): δ 7.40 (bs, 3H, aromatic-CH), 7.78 (bs, 2H, aromatic-CH), 11.14 (s, 0.52H, NH), 9.02 (s, 0.52H, OH). ^{13}C NMR (100 MHz, d_6-DMSO): 126.5 (aromatic-C), 128.4 (aromatic-C), 130.0 (aromatic-C), 132.9 (aromatic-qC), 164.6 (carbonyl-C). Elemental analysis; ($C_{21}H_{18}BiN_3O_6$), Calc (Found): C 40.86 (40.41), H 2.94 (2.56), N 6.81 (7.05). Mass spectrum, (ESI$^+$): 481.1 [Bi(LH)(L)+H]$^+$, 503.0 [Bi(LH)(L)+Na]$^+$, 639.0 [BiL_3+Na]$^+$, (ESI$^-$): 478.9.0 [BiL_2]$^-$; (where LH = $C_7H_7O_2N$).

Synthesis of [Bi(LH)L] 3: All the manipulations were carried out under nitrogen atmosphere with predried solvents. Bismuth *tert*-butoxide (0.21 g, 0.5 mmol) was added to a clear solution of benzohydroxamic acid (0.20 g, 1.5 mmol) in THF (20 mL) at −80 °C and stirred overnight. Vacuum was used to remove solvents, leaving behind a cream precipitate, which was washed with ethanol to purify the crude product. Yield: 0.18 g, 75%. Melting point: 215-217°C (decomp.). FT-IR (cm^{-1}): 3057 (brd, O-H), 1595 (m, C=N), 1561 (m, C=O), 775 (m, C-H-out of plane bend), 689 (Vs, ring in plane bend). ^{1}H NMR (300 MHz, d_6-DMSO): δ 7.39 (m, 3H, aromatic-CH), 7.80 (dd, 2H, aromatic-CH), 12.48 (s, OH). ^{13}C NMR (100 MHz, d_6-DMSO): 126.4 (aromatic-C), 128.4 (aromatic-C), 129.6 (aromatic-C), 133.3 (aromatic-C), 165.3 (carbonyl-C). Elemental analysis; ($C_{14}H_{11}O_3N_2Bi$), Calc (Found): C 36.22 (36.55), H 2.39 (2.85), N 6.03 (5.90) %. Mass spectrum, (ESI$^+$): 191.2 [L+Na(Methanol)]$^+$, 481.2 [Bi(LH)(L)+H]$^+$, 503.3 [Bi(LH)(L)+Na]$^+$, (ESI$^-$): 136.2 [L]$^-$, 478.9 [BiL_2]$^-$; (where LH = $C_7H_7O_2N$).

Synthesis of [$Bi_{34}O_{22}(L)_{22}(LH)_{14}(DMSO)_6$] 4:

[Bi_2L_3] **1** (20.0 mg, 24.29 μmol) was dissolved in DMSO (2.0 mL) layered with (1.0 mL) toluene. After leaving the solution at room temperature under ambient conditions, in the presence of moisture for 1 month, gave light yellow crystals of title cluster compound in

(10.0 mg, 0.78 μmol) by slow evaporation of the solvent. Melting point: > 227 °C (Dec.). ^{1}H NMR (400 MHz, d6-DMSO): δ 7.34 (bs, 3H, aromatic-CH), 7.81 (bs, 2H, aromatic-CH), 13.67 (s, OH). ^{13}C NMR (100 MHz, d6-DMSO): 126.3 (aromatic-C), 128.3 (aromatic-C), not visible (aromatic-qC), not visible (carbonyl-C). FT-IR (cm^{-1}): 1596 (m, C=N), 1558 (m, C=O), 779 (m, C-H-out of plane bend), 677 (Vs, ring in plane bend). Elemental analysis; ($C_{264}H_{230}Bi_{34}N_{36}O_{100}S_{6}$) Calc (Found): C 24.76 (26.25), H 1.81 (2.28), N 3.94 (4.20) % .

Table S1: Summary of X-ray diffraction data for **4**

Compound	4
Chemical formula	$C_{264}H_{230}Bi_{34}N_{36}O_{100}S_6$
Formula Mass	12804.52
Crystal system	Triclinic
a/Å	19.637(4)
b/Å	23.849(5)
c/Å	24.126(5)
α/°	115.19(3)
β/°	91.86(3)
γ/°	108.84(3)
Unit cell volume/Å^3	9484(3)
Temperature/K	100(2)
Space group	*P*-1
No. of formula units per unit cell, *Z*	1
No. of reflections measured	161178
No. of independent reflections	41070
R_{int}	0.0785
Final R_1 values ($I > 2\sigma(I)$)	0.0630
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1677
Final R_1 values (all data)	0.0914
Final $wR(F^2)$ values (all data)	0.1810

Selected Bond lengths and Angles of Compound $[Bi_{34}O_{22}(BHA)_{22}(H\text{-}BHA)_{14}(DMSO)_6]$ 4

Table S2 Bi-O^{2-} bond lengths in Bi_{24} Core

Bond	Length Å	Bond	Length Å
Bi(1)-O(5)	2.307(9)	Bi(5)-O(1)#1	2.239(8)
Bi(1)-O(1)#1	2.344(8)	Bi(5)-O(4)	2.482(8)
Bi(1)-O(1)	2.354(9)	Bi(6)-O(5)	2.134(8)
Bi(1)-O(3)#1	2.472(8)	Bi(6)-O(7)	2.209(10)
Bi(1)-O(4)	2.510(8)	Bi(6)-O(11)	2.229(8)
Bi(1)-O(2)#1	2.602(8)	Bi(7)-O(8)	2.115(8)
Bi(1)-O(11)	2.711(9)	Bi(8)-O(8)	2.210(9)
Bi(1)-O(14)	2.746(9)	Bi(8)-O(9)	2.237(9)
Bi(2)-O(2)	2.308(8)	Bi(9)-O(14)#1	2.147(9)
Bi(2)-O(1)	2.353(8)	Bi(9)-O(9)	2.276(9)
Bi(2)-O(5)	2.375(9)	Bi(9)-O(2)	2.585(8)
Bi(2)-O(8)	2.463(9)	Bi(10)-O(3)#1	2.110(8)
Bi(3)-O(2)	2.094(8)	Bi(10)-O(7)	2.209(10)
Bi(3)-O(6)	2.192(9)	Bi(10)-O(11)	2.216(10)
Bi(3)-O(3)	2.413(8)	Bi(11)-O(11)	2.128(10)
Bi(4)-O(4)	2.151(8)	Bi(11)-O(14)	2.162(9)
Bi(4)-O(6)	2.216(9)	Bi(11)-O(10)	2.511(10)
Bi(4)-O(5)	2.579(9)	Bi(12)-O(9)#1	2.125(10)
Bi(5)-O(6)	2.167(8)	Bi(12)-O(4)	2.155(8)
Bi(5)-O(3)	2.222(8)	Bi(12)-O(14)	2.338(9)

Table S3 Bi-O hydroximate ligand lengths

Bond	Length Å	Bond	Length Å
Bi(2)-O(16)	2.429(9)	Bi(13)-O(36)	2.239(15)

Bi(2)-O(15)	2.519(9)	Bi(13)-O(34)	2.405(14)
Bi(2)-O(22)	2.618(10)	Bi(13)-O(12)	2.731(11)
Bi(3)-O(18)	2.753(9)	Bi(14)-O(17)	2.145(11)
Bi(3)-O(24)	2.658(9)	Bi(14)-O(42)	2.284(11)
Bi(4)-O(19)	2.237(9)	Bi(14)-O(43)	2.369(11)
Bi(4)-O(40)	2.397(10)	Bi(14)-O(16)	2.397(10)
Bi(5)-O(18)	2.751(8)	Bi(14)-O(49)	2.407(11)
Bi(6)-O(15)	2.578(10)	Bi(14)-O(15)	2.416(9)
Bi(6)-O(17)	2.639(9)	Bi(15)-O(47)	2.146(9)
Bi(7)-O(23)	2.362(9)	Bi(15)-O(45)	2.254(10)
Bi(7)-O(33)	2.709(12)	Bi(15)-O(18)	2.274(9)
Bi(8)-O(22)	2.244(10)	Bi(15)-O(46)	2.279(10)
Bi(8)-O(48)	2.368(11)	Bi(15)-O(19)	2.548(9)
Bi(8)-O(20)	2.662(11)	Bi(16)-O(20)	2.170(12)
Bi(9)-O(21)	2.303(10)	Bi(16)-O(29)	2.182(16)
Bi(9)-O(41)	2.382(10)	Bi(16)-O(31)	2.187(11)
Bi(10)-O(23)	2.555(10)	Bi(16)-O(21)	2.451(11)
Bi(11)-O(10)	2.511(10)	Bi(16)-O(30)	2.519(12)
Bi(11)-O(37)	2.561(13)	Bi(17)-O(27)	2.165(10)
Bi(11)-O(13)	2.580(11)	Bi(17)-O(25)	2.237(11)
Bi(11)-O(12)	2.700(10)	Bi(17)-O(24)	2.281(9)
Bi(12)-O(39)	2.353(9)	Bi(17)-O(26)	2.315(10)
Bi(13)-O(13)	2.182(11)	Bi(17)-O(28)	2.606(10)
Bi(13)-O(35)	2.187(15)		

Table S4 Bi(1)-(12) core O-Bi-O angles

Bond	**Angle °**	**Bond**	**Angle °**
O(5)-Bi(1)-O(1)#1	110.0(3)	O(5)-Bi(1)-O(1)	75.3(3)

O(1)#1-Bi(1)-O(1)	72.3(3)	O(5)-Bi(1)-O(3)#1	102.0(3)
O(1)#1-Bi(1)-O(3)#1	119.8(3)	O(1)-Bi(1)-O(3)#1	68.5(3)
O(5)-Bi(1)-O(4)	75.3(3)	O(1)#1-Bi(1)-O(4)	71.7(3)
O(1)-Bi(1)-O(4)	121.0(3)	O(3)#1-Bi(1)-O(4)	168.0(3)
O(5)-Bi(1)-O(2)#1	174.1(3)	O(1)#1-Bi(1)-O(2)#1	75.4(3)
O(1)-Bi(1)-O(2)#1	104.8(3)	O(3)#1-Bi(1)-O(2)#1	72.8(3)
O(4)-Bi(1)-O(2)#1	109.2(3)	O(5)-Bi(1)-O(11)	68.1(3)
O(1)#1-Bi(1)-O(11)	175.3(3)	O(1)-Bi(1)-O(11)	110.8(3)
O(3)#1-Bi(1)-O(11)	64.9(3)	O(4)-Bi(1)-O(11)	103.6(3)
O(2)#1-Bi(1)-O(11)	106.7(3)	O(5)-Bi(1)-O(14)	105.2(3)
O(1)#1-Bi(1)-O(14)	114.0(3)	O(1)-Bi(1)-O(14)	172.6(3)
O(3)#1-Bi(1)-O(14)	104.3(3)	O(4)-Bi(1)-O(14)	65.8(3)
O(2)#1-Bi(1)-O(14)	74.0(3)	O(11)-Bi(1)-O(14)	63.3(3)
O(2)-Bi(2)-O(1)	81.2(3)	O(2)-Bi(2)-O(5)	114.7(3)
O(1)-Bi(2)-O(5)	74.0(3)	O(2)-Bi(2)-O(16)	81.8(3)
O(1)-Bi(2)-O(16)	141.6(3)	O(5)-Bi(2)-O(16)	82.4(3)
O(2)-Bi(2)-O(8)	122.8(3)	O(1)-Bi(2)-O(8)	76.4(3)
O(5)-Bi(2)-O(8)	108.4(3)	O(16)-Bi(2)-O(8)	140.9(3)
O(2)-Bi(2)-O(15)	145.0(3)	O(1)-Bi(2)-O(15)	130.7(3)
O(5)-Bi(2)-O(15)	70.2(3)	O(16)-Bi(2)-O(15)	64.1(3)
O(8)-Bi(2)-O(15)	83.9(3)	O(2)-Bi(2)-O(22)	82.7(3)
O(1)-Bi(2)-O(22)	124.4(3)	O(5)-Bi(2)-O(22)	157.8(3)
O(16)-Bi(2)-O(22)	87.0(3)	O(8)-Bi(2)-O(22)	69.0(3)
O(15)-Bi(2)-O(22)	87.6(3)	O(2)-Bi(3)-O(3)	83.5(3)
O(2)-Bi(3)-O(6)	83.7(3)	O(6)-Bi(3)-O(24)	144.8(3)
O(6)-Bi(3)-O(3)	69.7(3)	N(9)-Bi(3)-O(24)	75.3(4)
O(2)-Bi(3)-O(24)	76.5(3)	O(6)-Bi(3)-O(18)	73.2(3)
O(3)-Bi(3)-O(24)	134.7(3)	N(9)-Bi(3)-O(18)	109.2(4)
O(2)-Bi(3)-O(18)	146.5(3)	O(4)-Bi(4)-O(6)	73.9(3)

O(3)-Bi(3)-O(18)	66.0(3)	O(6)-Bi(4)-O(19)	74.7(3)
O(24)-Bi(3)-O(18)	135.1(3)	O(6)-Bi(4)-O(40)	135.8(4)
O(4)-Bi(4)-O(19)	85.8(3)	O(4)-Bi(4)-O(5)	76.4(3)
O(4)-Bi(4)-O(40)	79.6(3)	O(19)-Bi(4)-O(5)	150.4(3)
O(19)-Bi(4)-O(40)	68.6(4)	O(6)-Bi(5)-O(1)#1	85.1(3)
O(6)-Bi(4)-O(5)	77.7(3)	O(6)-Bi(5)-O(4)	68.4(3)
O(40)-Bi(4)-O(5)	129.2(3)	O(1)#1-Bi(5)-O(4)	73.9(3)
O(6)-Bi(5)-O(3)	73.9(3)	O(3)-Bi(5)-O(18)	68.4(3)
O(3)-Bi(5)-O(1)#1	75.1(3)	O(4)-Bi(5)-O(18)	123.9(3)
O(3)-Bi(5)-O(4)	132.5(3)	O(5)-Bi(6)-O(7)	90.6(3)
O(6)-Bi(5)-O(18)	73.6(3)	O(7)-Bi(6)-O(11)	69.5(4)
O(1)#1-Bi(5)-O(18)	141.5(3)	O(7)-Bi(6)-O(10)	136.2(3)
O(5)-Bi(6)-O(11)	80.8(3)	O(5)-Bi(6)-O(15)	72.8(3)
O(5)-Bi(6)-O(10)	79.2(4)	O(11)-Bi(6)-O(15)	138.6(3)
O(11)-Bi(6)-O(10)	66.8(3)	O(5)-Bi(6)-O(17)	78.8(3)
O(7)-Bi(6)-O(15)	79.3(3)	O(11)-Bi(6)-O(17)	141.6(3)
O(10)-Bi(6)-O(15)	135.0(3)	O(15)-Bi(6)-O(17)	62.9(3)
O(7)-Bi(6)-O(17)	142.2(3)	O(8)-Bi(7)-O(23)	81.3(3)
O(10)-Bi(6)-O(17)	77.7(3)	O(7)-Bi(7)-O(33)	146.0(3)
O(8)-Bi(7)-O(7)	87.0(3)	O(8)-Bi(8)-O(9)	85.5(3)
O(7)-Bi(7)-O(23)	70.8(3)	O(9)-Bi(8)-O(22)	72.8(3)
O(8)-Bi(7)-O(33)	75.2(3)	O(9)-Bi(8)-O(48)	141.8(3)
O(23)-Bi(7)-O(33)	78.0(3)	O(8)-Bi(8)-O(20)	159.2(3)
O(8)-Bi(8)-O(22)	80.5(4)	O(22)-Bi(8)-O(20)	79.1(4)
O(8)-Bi(8)-O(48)	80.2(4)	O(14)#1-Bi(9)-O(21)	82.3(4)
O(22)-Bi(8)-O(48)	70.0(3)	O(14)#1-Bi(9)-O(41)	76.4(4)
O(9)-Bi(8)-O(20)	84.7(3)	O(21)-Bi(9)-O(41)	67.0(4)
O(48)-Bi(8)-O(20)	96.5(4)	O(9)-Bi(9)-O(2)	77.1(3)
O(14)#1-Bi(9)-O(9)	72.7(3)	O(41)-Bi(9)-O(2)	135.1(3)

O(9)-Bi(9)-O(21)	73.7(4)	O(3)#1-Bi(10)-O(7)	89.5(3)
O(9)-Bi(9)-O(41)	132.4(3)	O(7)-Bi(10)-O(11)	69.8(3)
O(14)#1-Bi(9)-O(2)	85.2(3)	O(7)-Bi(10)-O(23)	66.0(3)
O(21)-Bi(9)-O(2)	150.5(3)	O(11)-Bi(11)-O(14)	83.7(3)
O(3)#1-Bi(10)-O(11)	80.2(3)	O(14)-Bi(11)-O(10)	78.3(3)
O(3)#1-Bi(10)-O(23)	79.3(3)	O(14)-Bi(11)-O(37)	97.0(6)
O(11)-Bi(10)-O(23)	131.0(3)	O(11)-Bi(11)-O(13)	76.6(4)
O(7)-Bi(10)-Bi(6)	35.2(3)	O(10)-Bi(11)-O(13)	86.6(4)
O(11)-Bi(11)-O(10)	67.7(3)	O(11)-Bi(11)-O(12)	86.7(4)
O(11)-Bi(11)-O(37)	128.9(4)	O(10)-Bi(11)-O(12)	143.7(3)
O(10)-Bi(11)-O(37)	62.6(4)	O(13)-Bi(11)-O(12)	61.9(4)
O(14)-Bi(11)-O(13)	158.7(4)	O(9)#1-Bi(12)-O(14)	71.8(3)
O(37)-Bi(11)-O(13)	89.0(6)	O(9)#1-Bi(12)-O(39)	75.8(3)
O(14)-Bi(11)-O(12)	125.7(3)	O(14)-Bi(12)-O(39)	141.5(3)
O(37)-Bi(11)-O(12)	128.9(5)	O(4)-Bi(12)-O(14)	79.1(3)
O(9)#1-Bi(12)-O(4)	87.0(3)	O(4)-Bi(12)-O(39)	79.1(3)

Table S5 Bi(13)-(17) O-Bi-O bond angles

Bond	**Angle °**	**Bond**	**Angle °**
O(13)-Bi(13)-O(35)	82.4(5)	O(13)-Bi(13)-O(36)	72.6(4)
O(35)-Bi(13)-O(36)	88.2(5)	O(13)-Bi(13)-O(34)	142.1(5)
O(35)-Bi(13)-O(34)	69.8(5)	O(36)-Bi(13)-O(34)	81.1(5)
O(35)-Bi(13)-O(12)	83.1(4)	O(13)-Bi(13)-O(12)	66.1(4)
O(34)-Bi(13)-O(12)	131.8(4)	O(36)-Bi(13)-O(12)	138.5(4)
O(17)-Bi(14)-O(43)	82.7(4)	O(17)-Bi(14)-O(42)	71.9(4)
O(17)-Bi(14)-O(16)	86.5(3)	O(42)-Bi(14)-O(43)	74.8(4)
O(43)-Bi(14)-O(16)	65.4(3)	O(42)-Bi(14)-O(16)	136.8(4)
O(42)-Bi(14)-O(49)	86.0(5)	O(17)-Bi(14)-O(49)	88.7(4)
O(16)-Bi(14)-O(49)	131.5(3)	O(43)-Bi(14)-O(49)	160.6(4)

O(42)-Bi(14)-O(15)	135.3(4)	O(17)-Bi(14)-O(15)	73.0(3)
O(16)-Bi(14)-O(15)	66.1(3)	O(43)-Bi(14)-O(15)	126.5(3)
O(47)-Bi(15)-O(45)	93.5(4)	O(49)-Bi(14)-O(15)	66.3(3)
O(45)-Bi(15)-O(18)	71.2(3)	O(47)-Bi(15)-O(18)	80.2(3)
O(45)-Bi(15)-O(46)	85.5(4)	O(47)-Bi(15)-O(46)	72.2(3)
O(47)-Bi(15)-O(19)	85.3(3)	O(18)-Bi(15)-O(46)	142.5(4)
O(18)-Bi(15)-O(19)	74.1(3)	O(45)-Bi(15)-O(19)	144.9(3)
O(47)-Bi(15)-N(15)	78.9(4)	O(46)-Bi(15)-O(19)	126.7(4)
O(18)-Bi(15)-N(15)	102.8(3)	O(45)-Bi(15)-N(15)	171.1(4)
O(19)-Bi(15)-N(15)	30.9(3)	O(46)-Bi(15)-N(15)	96.4(4)
O(20)-Bi(16)-O(31)	78.5(5)	O(20)-Bi(16)-O(29)	72.6(6)
O(20)-Bi(16)-O(21)	75.3(4)	O(29)-Bi(16)-O(31)	93.5(6)
O(31)-Bi(16)-O(21)	87.2(4)	O(29)-Bi(16)-O(21)	147.1(5)
O(29)-Bi(16)-O(30)	83.2(5)	O(20)-Bi(16)-O(30)	137.5(4)
O(21)-Bi(16)-O(30)	126.9(4)	O(31)-Bi(16)-O(30)	68.5(4)
O(27)-Bi(17)-O(24)	71.7(3)	O(27)-Bi(17)-O(25)	91.4(4)
O(27)-Bi(17)-O(26)	78.5(4)	O(25)-Bi(17)-O(24)	75.6(4)
O(24)-Bi(17)-O(26)	134.1(4)	O(25)-Bi(17)-O(26)	70.9(4)
O(25)-Bi(17)-O(28)	147.4(3)	O(27)-Bi(17)-O(28)	78.1(3)
O(26)-Bi(17)-O(28)	76.7(4)	O(24)-Bi(17)-O(28)	127.7(3)
O(25)-Bi(17)-N(4)	83.9(4)	O(27)-Bi(17)-N(4)	155.2(3)
O(26)-Bi(17)-N(4)	76.9(4)	O(24)-Bi(17)-N(4)	129.8(3)
		O(28)-Bi(17)-N(4)	92.8(4)

Table S6 Bi-O-Bi bond angles

Bond	Angle °	Bond	Angle°
Bi(5)#1-O(1)-Bi(1)#1	112.6(4)	Bi(5)#1-O(1)-Bi(2)	117.4(3)
Bi(1)#1-O(1)-Bi(2)	104.9(3)	Bi(5)#1-O(1)-Bi(1)	108.9(3)
Bi(1)#1-O(1)-Bi(1)	107.7(3)	Bi(2)-O(1)-Bi(1)	104.7(3)
Bi(3)-O(2)-Bi(2)	121.5(4)	Bi(3)-O(2)-Bi(9)	114.6(3)
Bi(2)-O(2)-Bi(9)	115.2(3)	Bi(3)-O(2)-Bi(1)#1	104.4(3)
Bi(2)-O(2)-Bi(1)#1	98.5(3)	Bi(9)-O(2)-Bi(1)#1	96.5(3)
Bi(10)#1-O(3)-Bi(5)	120.9(4)	Bi(10)#1-O(3)-Bi(3)	116.9(3)
Bi(5)-O(3)-Bi(3)	98.2(3)	Bi(10)#1-O(3)-Bi(1)#1	113.1(4)
Bi(5)-O(3)-Bi(1)#1	105.4(3)	Bi(3)-O(3)-Bi(1)#1	99.3(3)
Bi(4)-O(4)-Bi(12)	122.5(4)	Bi(4)-O(4)-Bi(5)	97.4(3)
Bi(12)-O(4)-Bi(5)	115.1(3)	Bi(4)-O(4)-Bi(1)	107.3(3)
Bi(12)-O(4)-Bi(1)	111.9(3)	Bi(5)-O(4)-Bi(1)	99.6(3)
Bi(6)-O(5)-Bi(1)	113.8(4)	Bi(6)-O(5)-Bi(2)	112.6(4)
Bi(1)-O(5)-Bi(2)	105.5(4)	Bi(6)-O(5)-Bi(4)	110.8(4)
Bi(1)-O(5)-Bi(4)	100.5(3)	Bi(2)-O(5)-Bi(4)	113.0(3)
Bi(5)-O(6)-Bi(3)	107.1(4)	Bi(5)-O(6)-Bi(4)	105.4(4)
Bi(3)-O(6)-Bi(4)	138.3(4)	Bi(7)-O(7)-Bi(6)	129.9(5)
Bi(7)-O(7)-Bi(10)	120.2(4)	Bi(6)-O(7)-Bi(10)	109.5(4)
Bi(7)-O(8)-Bi(8)	113.9(3)	Bi(7)-O(8)-Bi(2)	118.0(4)
Bi(8)-O(8)-Bi(2)	104.4(3)	Bi(12)#1-O(9)-Bi(8)	117.1(4)
Bi(12)#1-O(9)-Bi(9)	101.2(4)	Bi(8)-O(9)-Bi(9)	127.2(4)
N(14)-O(10)-Bi(6)	115.2(9)	N(14)-O(10)-Bi(11)	113.2(8)
Bi(6)-O(10)-Bi(11)	96.3(4)	Bi(11)-O(11)-Bi(10)	120.5(4)
Bi(11)-O(11)-Bi(6)	117.5(4)	Bi(10)-O(11)-Bi(6)	108.5(4)
Bi(11)-O(11)-Bi(1)	107.6(3)	Bi(10)-O(11)-Bi(1)	101.5(3)
Bi(6)-O(11)-Bi(1)	97.3(3)	C(85)-O(12)-Bi(11)	113.8(9)
Bi(13)-O(13)-Bi(11)	127.1(5)	Bi(11)-O(12)-Bi(13)	103.6(4)

Bi(9)#1-O(14)-Bi(12)	98.6(4)	Bi(9)#1-O(14)-Bi(11)	117.9(4)
Bi(9)#1-O(14)-Bi(1)	103.9(4)	Bi(11)-O(14)-Bi(12)	128.5(4)
Bi(12)-O(14)-Bi(1)	98.8(3)	Bi(11)-O(14)-Bi(1)	105.4(3)
Bi(2)-O(15)-Bi(6)	94.9(3)	Bi(14)-O(15)-Bi(2)	112.9(3)
Bi(14)-O(17)-Bi(6)	114.8(4)	Bi(14)-O(15)-Bi(6)	107.9(4)
Bi(5)-O(18)-Bi(3)	79.1(2)	Bi(14)-O(16)-Bi(2)	116.9(3)
Bi(8)-O(22)-Bi(2)	98.7(3)	Bi(15)-O(18)-Bi(5)	114.7(4)
Bi(17)-O(24)-Bi(3)	111.5(4)	Bi(15)-O(18)-Bi(3)	126.4(4)
Bi(7)-O(23)-Bi(10)	99.9(4)	Bi(4)-O(19)-Bi(15)	152.1(4)
		Bi(9)-O(21)-Bi(16)	140.0(5)

Table S7 Ligand pertinent bond lengths and angles

Ligand	C-N distance (Å)	C-O distance (Å)	Bi-O-N (°)	C-N-O (°)
1	N(1)-C(1) 1.30(2)	C(1)-O(29) 1.33(4)	Bi(16)-O(20)-N(1), 115.9(10)	C(1)-N(1)-O(20), 112.2(18)
2	N(2)-C(8) 1.34(2)	C(8)-O(30) 1.19(3)	Bi(16)-O(31)-N(2), 114.4(9)	C(8)-N(2)-O(31), 121.15(15)
3	N(3)-C(15) 1.26(2)	C(15)-O(41) 1.26(4)	Bi(9)-O(21)-N(3), 118.3(9)	C(15)-N(3)-O(21), 114.4(15)
4	N(4)-C(22) 1.257(22)	C(22)-O(48) 1.31(3)	Bi(8)-O(22)-N(4), 115.2(7)	C(22)-N(4)-O(22), 114.3(12)
5	N(5)-C(29) 1.29(2)	C(29)-O(26) 1.29(3)	Bi(17)-O(25)-N(5), 111.4(9)	C(29)-N(5)-O(25), 120.5(14)
6	N(6)-C(36) 1.296(19)	C(36)-O(27) 1.30(3)	Bi(17)-O(24)-N(6), 115.0(7)	C(36)-N(6)-O(24), 110.0(12)
7	N(7)-C(43) 1.30(2)	C(43)-O(49) 1.29(4)	Bi(14)-O(15)-N(7), 115.7(6)	C(43)-N(7)-O(15),112.2(13)
8	N(8)-C(50) 1.335(17)	C(50)-O(42) 1.27(3)	Bi(14)-O(17)-N(8), 116.7(7)	C(50)-N(8)-O(17), 111.5(7)
9	N(9)-C(57) 1.318(18)	C(57)-O(43) 1.31(3)	Bi(14)-O(16)-N(9), 117.8(7)	C(57)-N(9)-O(16), 112.1(11)

10	N(10)-C(64) 1.249(17)	C(64)-O(32) 1.27(3)	Bi(7)-O(23)-N(10), 113.8(6)	C(64)-N(10)-O(23), 117.9(12)
11	N(11)-C(71) 1.27(2)	C(71)-O(34) 1.24(4)	Bi(13)-O(35)-N(11), 113.3(11)	C(71-N(11)-O(35), 123.3(18)
12	N(12)-C(78) 1.29(2)	C(78)-O(36) 1.32(3)	Bi(13)-O(13)-N(12), 117.2(9)	C(78)-N(12)-O(13),111.5(14)
13	N(13)-C(85) 1.268(16)	C(85)-O(12) 1.25(3)	Bi(10)-O(44)-N(13), 108.6(11)	C(85)-N(13)-O(44), 119.3(19)
14	N(14)-C(92) 1.33(2)	C(92)-O(37) 1.22(4)	Bi(11)-O(10)-N(14), 113.2(8)	C(82)-N(14)-O(10), 120.2(15)
15	N(15)-C(106) 1.27(2)	C(106)-O(40) 1.26(3)	Bi(4)-O(19)-N(15), 116.9(8)	C(106)-N(15)-O(19), 112.9(13)
16	N(16)-C(113) 1.22(2)	C(113)-O(46) 1.31(3)	Bi(15)-O(47)-N(16), 116.9(7)	C(113)-N(16)-o(47), 113.1(12)
17	N(17)-C(120) 1.314(16)	C(120)-O(45) 1.33(3)	Bi(15)-O(18)-N(17), 116.(6)	C(120)-N(17)-O(18), 113.5(11)
18	N(18)-C(99) 1.304(18)	C(99)-O(38) 1.26(3)	Bi(12)-O(39)-N(18), 114.1(7)	C(99)-N(18)-O(39), 121.1(10)

Bi_{22}, Bi_{24} and Bi_{38} core comparisons

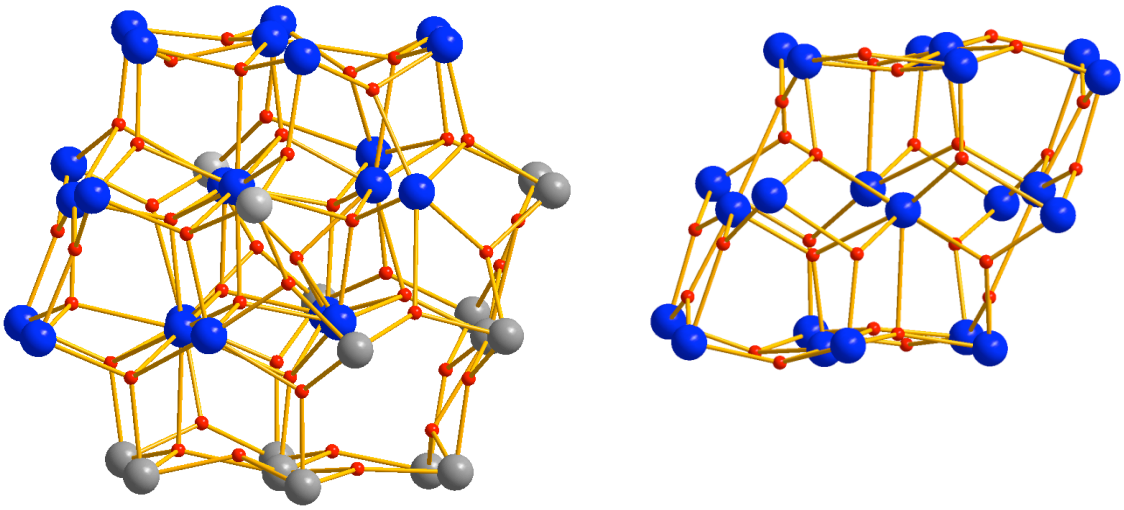

Figure S1. Comparison of the Bi_{38}-oxido core as reported for $[Bi_{38}O_{45}(OMc)_{24}(DMSO)_9]\cdot 2DMSO\cdot 7H_2O$ (OMc = methacrylate, left) and the Bi_{22}-oxido core as reported for $[Bi_{22}O_{26}(OSiMe_2tBu)_{14}]$ (right).[7,8] Bismuth atoms which occur in similar positions of the clusters are represented in blue

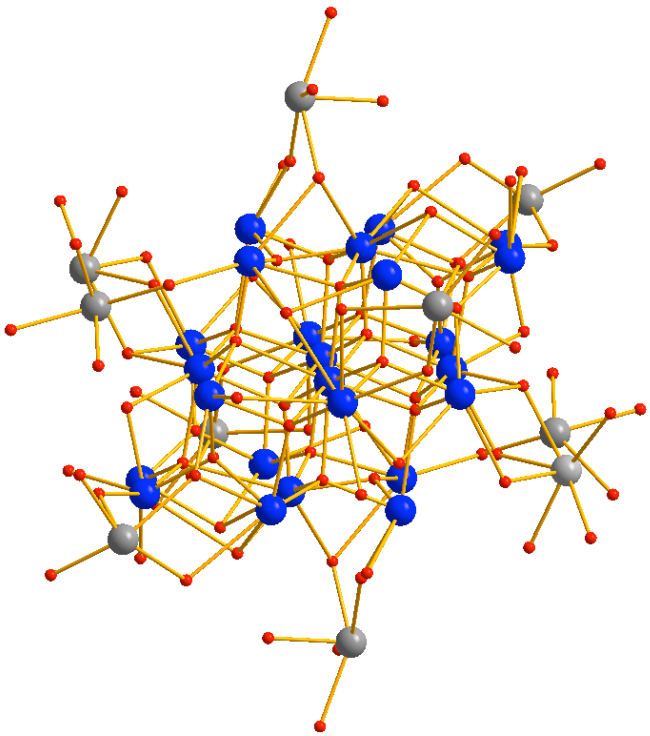

Figure S2. Bismuth oxido core structure of compound **4**. The 24 bismuth atoms $\{Bi_{24}\}$ which correspond to a cut out of the molecular structure in $[Bi_{38}O_{45}(OMc)_{24}(DMSO)_9]\cdot 2DMSO\cdot 7H_2O$ (OMc = methacrylate) are represented in blue.

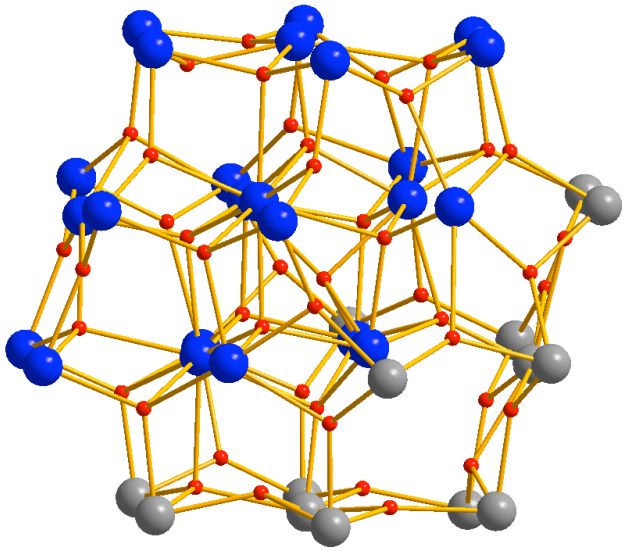

Figure S3. Bismuth oxido core structure of $[Bi_{38}O_{45}(OMc)_{24}(DMSO)_9]\cdot 2DMSO\cdot 7H_2O$ (OMc = methacrylate). The 24 bismuth atoms $\{Bi_{24}\}$ which correspond to the bismuth atom positions in compound **4** are represented in blue.

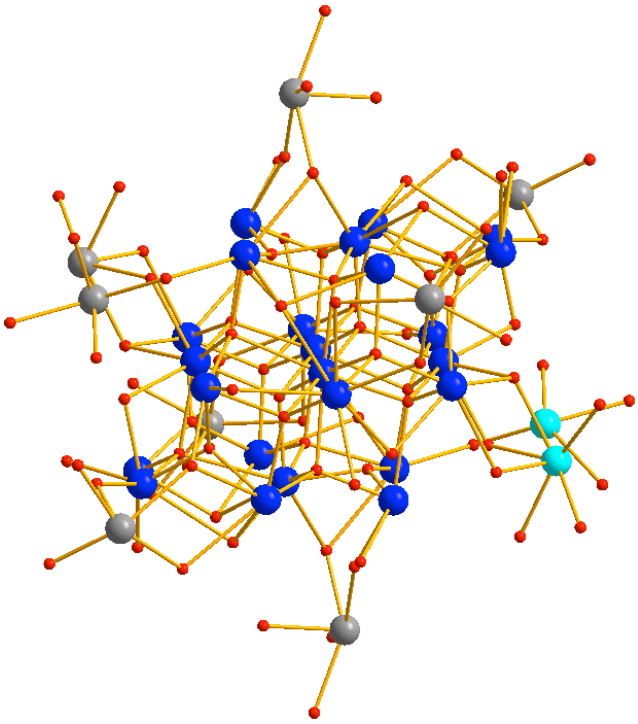

Figure S4. Bismuth oxido core structure of compound **4**. In addition to the 24 bismuth atoms $\{Bi_{24}\}$ represented in blue - which correspond to a cut out of the molecular structure in $[Bi_{38}O_{45}(OMc)_{24}(DMSO)_9]\cdot 2DMSO\cdot 7H_2O$ (OMc = methacrylate) – two bismuth atoms are represented in cyan which might easily attach to one of the blue layers upon hydrolysis/condensation. This arrangement might be regarded as a snapshot on the way to enlarge one of the blue layers to give the final size of the layers as observed in $\{Bi_{38}\}$-oxido clusters.

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NMR and Mass Spectral Data

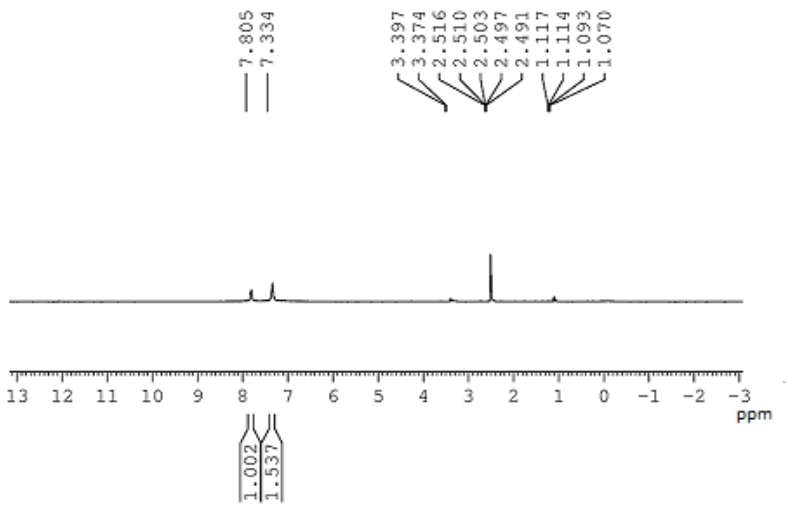

Figure S5: ^{1}H NMR (300 MHz, d_6-DMSO) spectrum of complex **1** [Bi_2L_3]

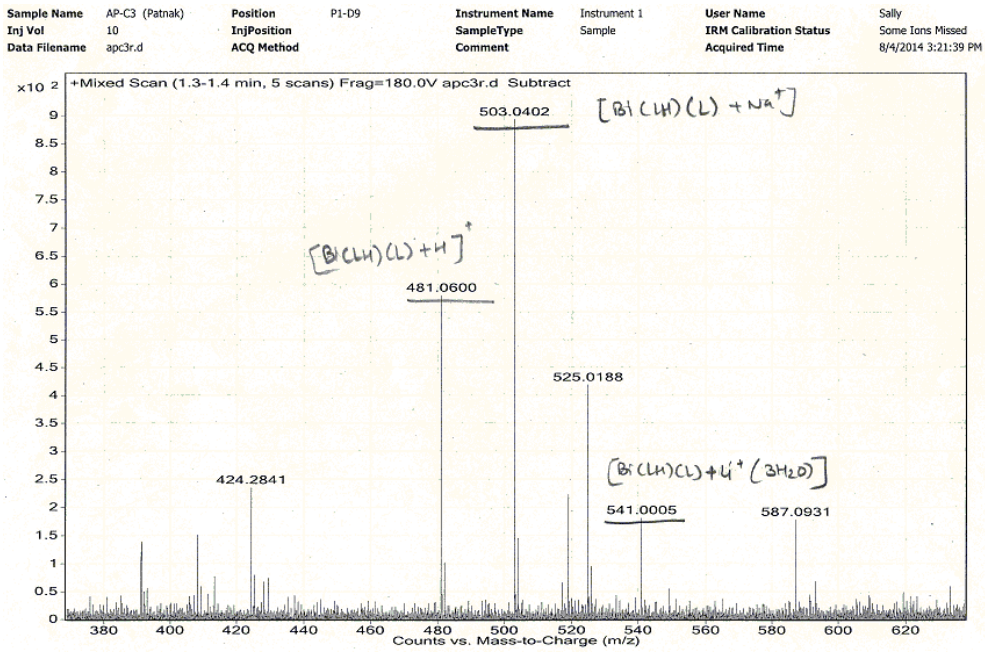

Figure S6: Mass-spectrum (ESI^{+}) of complex **1** [Bi_2L_3]

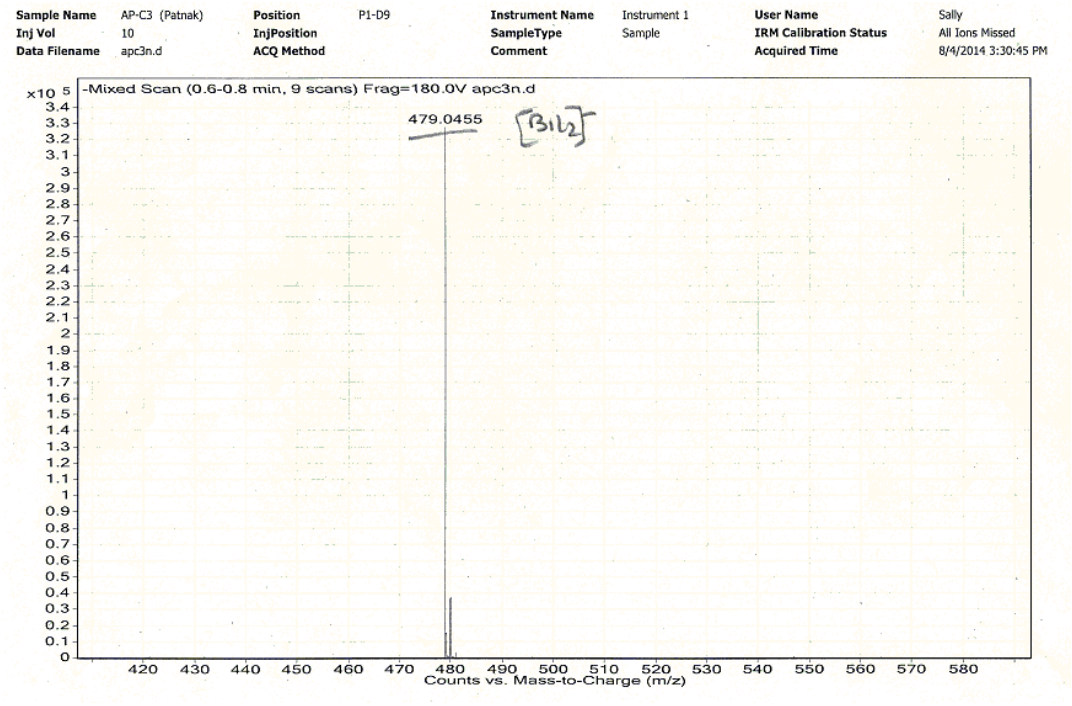

Figure S7: Mass-spectrum (ESI$^-$) of complex **1** [Bi_2L_3]

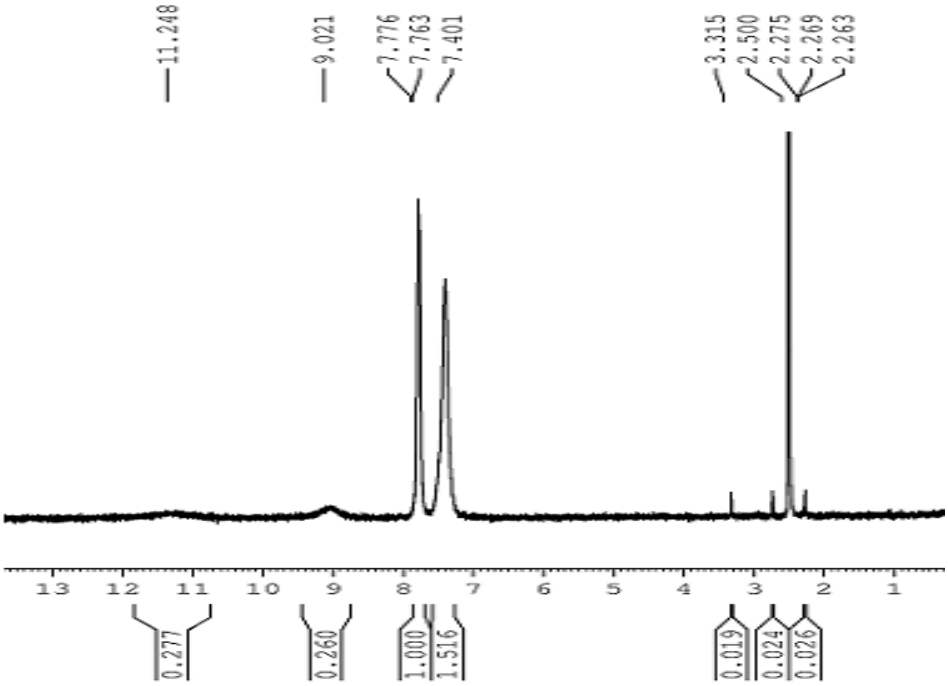

Figure S8: ^{1}H NMR (300 MHz, d_6-DMSO) spectrum of complex **2** [BiL_3].

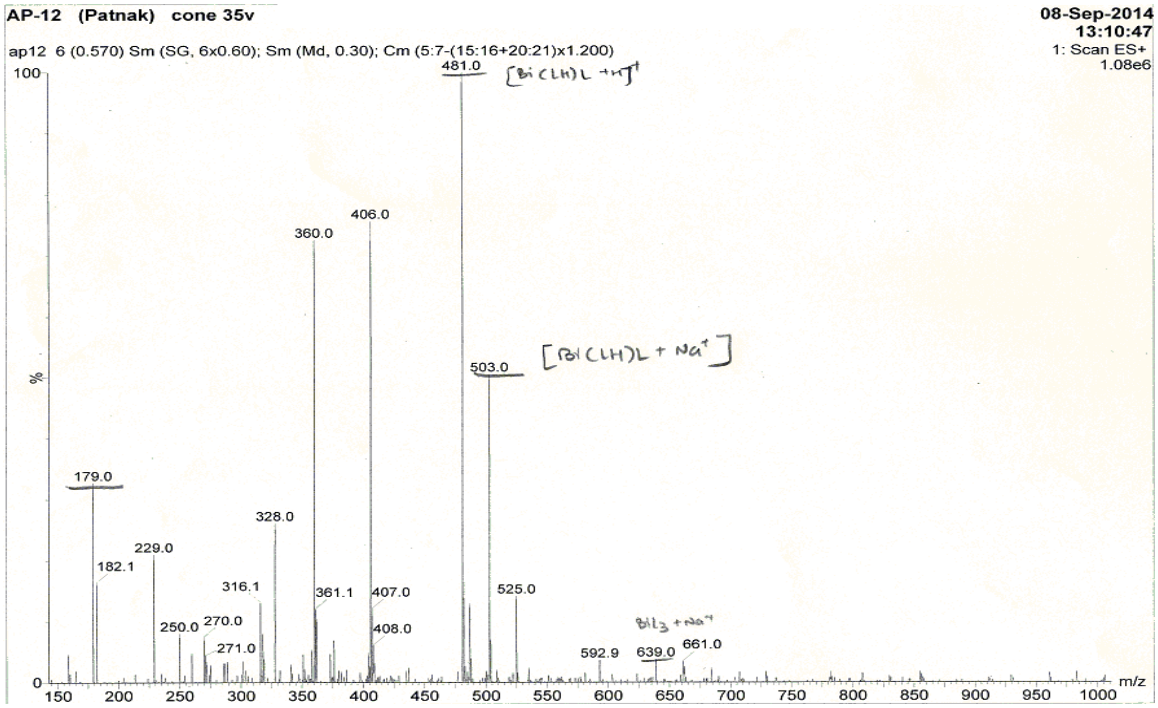

Figure S9: Mass-spectrum (ESI^+) of complex **2** [BiL_3]

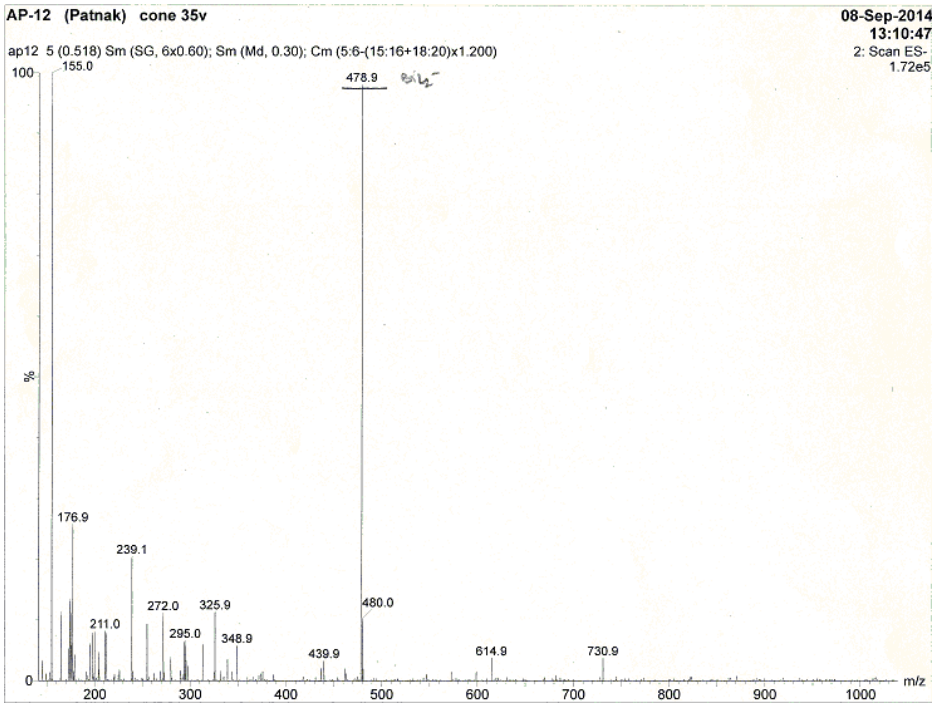

Figure S10: Mass-spectrum (ESI^-) of complex **2** [BiL_3]

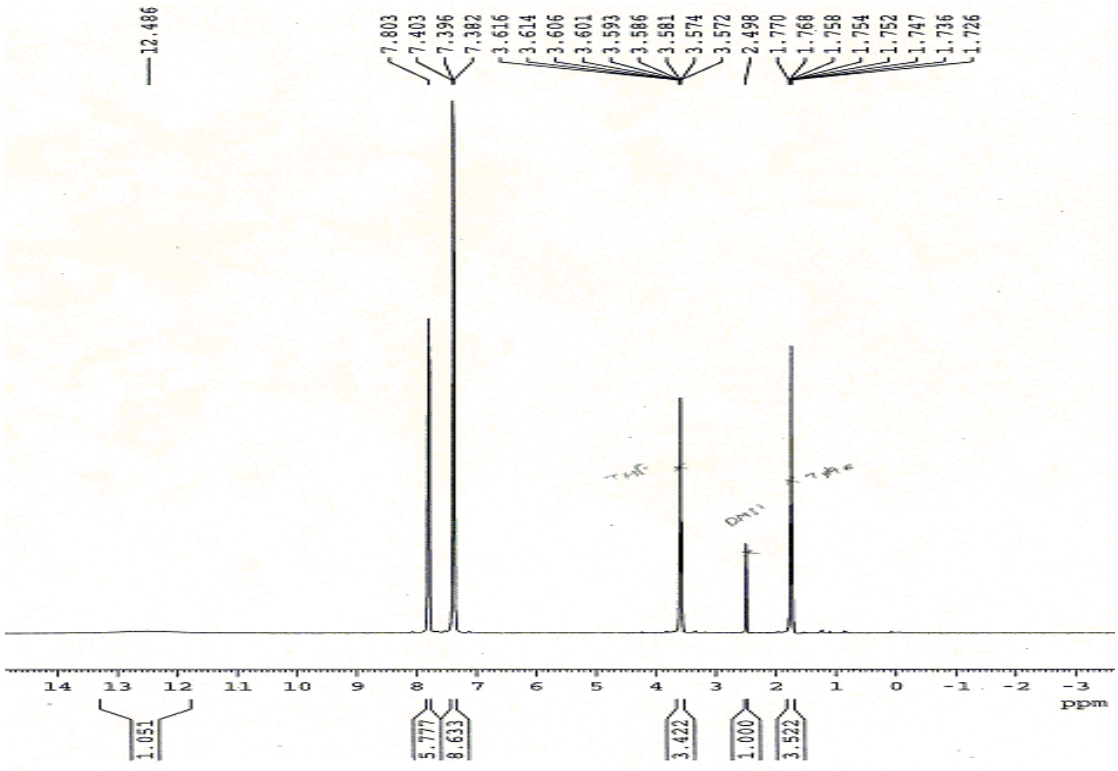

Figure S11: ^{1}H NMR (300 MHz, d_6-DMSO) spectrum of complex **3** [Bi(LH)L]

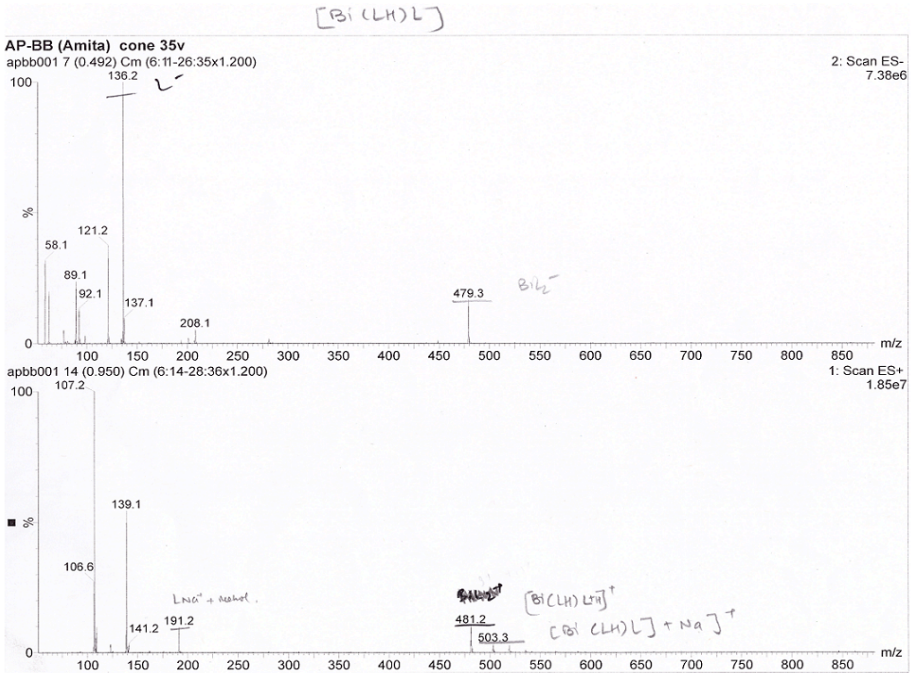

Figure S12: Mass-spectrum of complex **3** [Bi(LH)L]

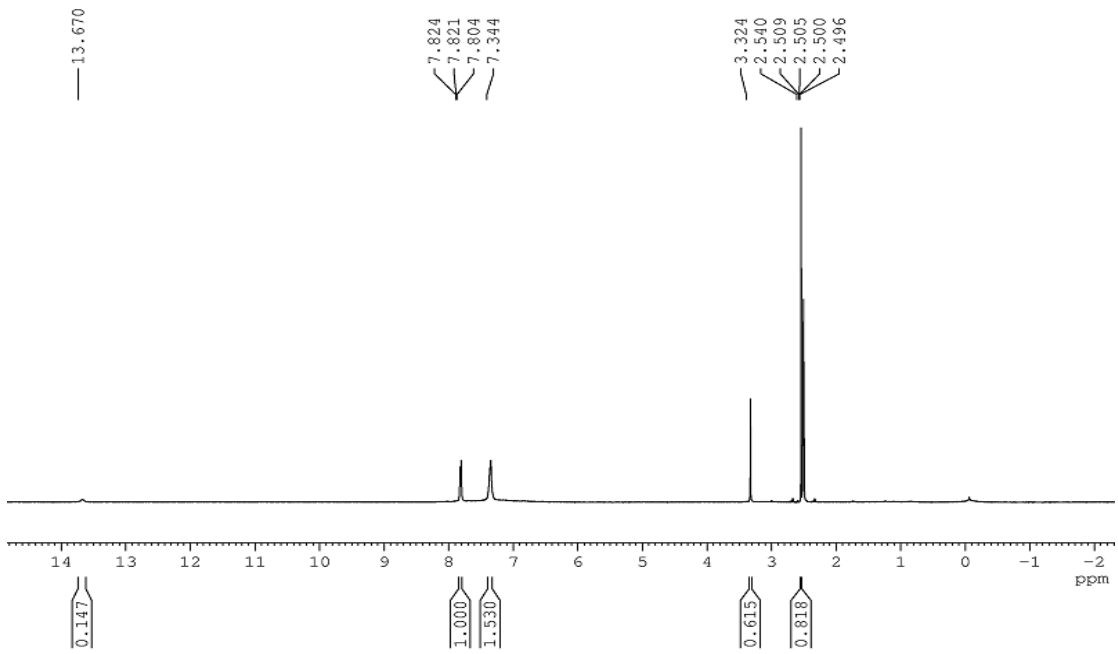

Figure S13: ^{1}H NMR (400 MHz, d_6-DMSO) spectrum of complex **4**

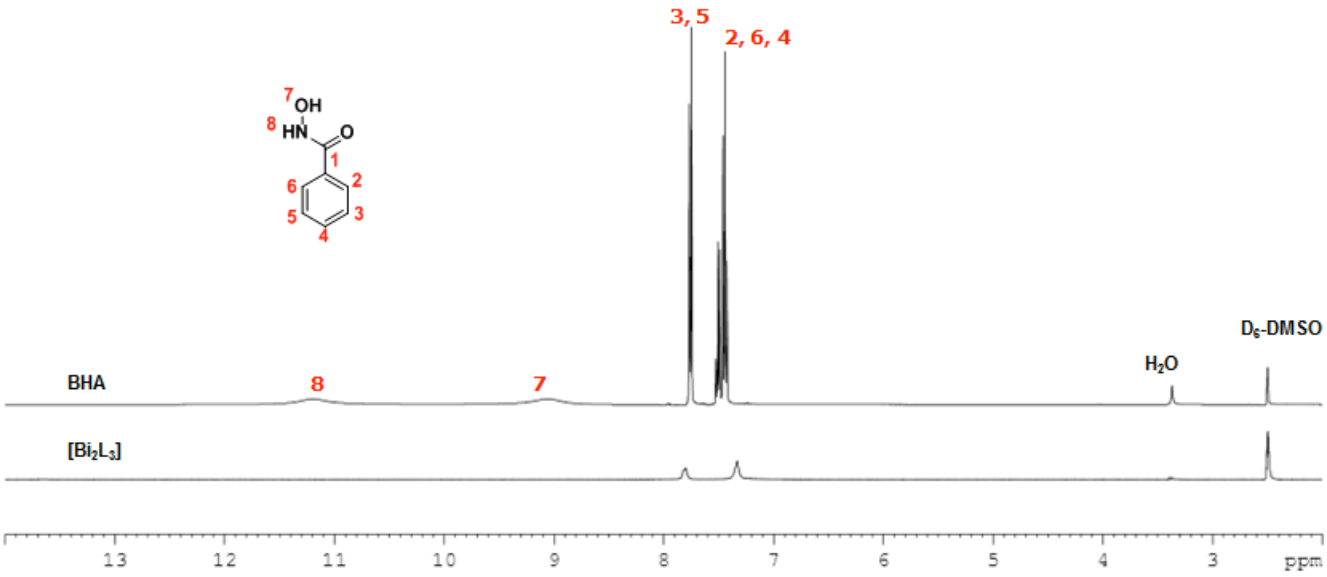

Figure S14: ^{1}H NMR (400 MHz, d_6-DMSO) comparison of H_2-BHA (top) and $[Bi_2L_3]$ (bottom s).