Supplementary Information

Sulfonato-encapsulated bismuth(III) oxido-clusters from Bi_2O_3 in water under mild conditions

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Contains:

General Information:

All sulfonic acids and Bi_2O_3 were purchased from Aldrich Chemical Co. Infrared spectra were obtained on a Perkin Elmer 1600 FT-IR. NMR spectra were obtained with Bruker AV300, or AV400 spectrometers with chemical shifts referenced to D6-DMSO. Mass spectrometry (ES) was performed on Micromass Platform Electrospray Mass Spectrometer. Elemental analysis was carried out by the Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago, and Dunedin, New Zealand. Melting points are uncalibrated using a Bibby Stuart Scientific Melting Point Apparatus SMP3.

General Experimental Procedure:

A suspension of sulfonic acid RSO_3H (6 mmol, 6 eq) and Bi_2O_3 (1 mmol, 1 eq) in water was sonicated. A colour change from yellow to colourless indicated the completeness of the reaction. Then the reaction mixture was heated to 90 °C and filtered hot. The filtrate was allowed to cool slowly to room temperature and was left for crystallisation.

Compound 1: $[Bi_{18}O_{12}(OH)_{12}(O_3SC)_{18}(H_2O)_2]\cdot 13H_2O$

The general procedure was carried out using *S*-(+)-10-camphorsulfonic acid (CSO_3H) (1.394 g, 6 mmol, 6 eq) and Bi_2O_3 (0.466 g, 1 mmol, 1 eq) with an overall reaction time of 4 h. Within 1-2 days colourless prismatic crystals were observed in quantitative yield (according to the bismuth present) which were suitable for X-ray crystallography.

M.p. = > 240 °C (Dec.). ^{1}H NMR (300 MHz, D_6-DMSO, 30°C): δ = 2.95 (1H, d, ^3J = 15.01 Hz, H^{10a}), 2.70-2.63 (2H, m, H^{6a}, H^{10b}), 2.29 (1H, dt, ^2J = 6.00 Hz, ^3J = 18.01 Hz, H^{3a}), 1.98 (1H, t, ^3J = 6.00 Hz, H^4), 1.92-1.80 (2H, m, H^{3b}, H^{5a}), 1.43-1.26 (2H, m, H^{5b}, H^{6b}), 1.05 (3H, s, H^8), 0.77 (3H, s, H^9). ^{13}C NMR (100 MHz, D_6-DMSO, 30°C): δ = 216.11 (C^2), 58.24 (C^1), 47.43 (C^7), 47.22 (C^{10}), 42.35 (C^4), 42.22 (C^3), 26.50 (C^5), 24.45 (C^6), 20.03 (C^8), 19.62 (C^9). FT IR (Nujol, cm^{-1}): **ῡ** = 3404m, 1729s, 1687m, 1655m, 1639m, 1561m, 1546m, 1509m, 1414m, 1284m, 1237s, 1197s, 1175s, 1143s, 1026s, 786w, 618w, 583w. FT IR (KBr, cm^{-1}): **ῡ** = 3448s, 2956s, 1739s, 1686m, 1654m, 1637m, 1560m, 1542m, 1508m, 1457s,

1414s, 1393s, 1374s, 1284s, 1233s, 1191s, 1046s, 966m, 937m, 853m, 790s, 686m, 619s. Elemental Analysis: $C_{180}H_{308}O_{111}S_{18}Bi_{18}$ (8591.013): calcd. C 25.16, H 3.61; found C 25.27, H 3.52.

Compound 2: $[Bi_6O_4(OH)_4(O_3SNH_2)_6]\cdot(H_2O)$

To a suspension of Bi_2O_3 (0.466g, 1 mmol, 1 eq) in water was added an aqueous solution of sulfamic acid (HSO_3NH_2) (0.583g, 6 mmol, 6 eq). This reaction mixture was sonicated for 2 h. The colourless precipitate was filtered and dried to yield 0.515 g (78%) of **2**. Upon dissolving the colourless precipitate in hot water (90 °C), colourless block-shaped crystals suitable for X-ray crystallography were obtained after two weeks.

M.P. = > 350 °C (Dec.). FT IR (Nujol, cm^{-}): **ῡ** = 3437w, 3277w, 3272w, 1628w, 1564w, 1226m, 1163m, 1096w, 1042m, 801w. ES^{+}: *m/z* = 267.27 (20%, $[Bi_4O_3(OH)L(H_2O)_4]^{4+}$); 313.27 (15%, $[Bi_4O_2L_4]^{4+}$); 341.30 (35%, $[Bi_4O_2(OH)L_3(MeOH)_6]^{4+}$); 381.30 (80%, $[Bi_4O_3(OH)L_2(MeOH)(H_2O)]^{3+}$); 415.21 (50%, $[Bi_3OL_4(MeOH)_4(H_2O)_5]^{3+}$); 437.19 (100%, $[Bi_4O_2(OH)_3L_2(MeOH)_4(H_2O)_4]^{3+}$); 531.27 (6%, $[Bi_4O_3(OH)_3L(MeOH)]^{2+}$); 551.50 (10%, $[Bi_4O_3(OH)_3L(H_2O)_4]^{2+}$); 579.53 (38%, $[Bi_4O_3(OH)_3L(MeOH)_4]^{2+}$); 607.57 (40%, $[Bi_3O(OH)_2L_3(MeOH)_5(H_2O)_5]^{2+}$); 647.56 (28%, $[Bi_4O_3(OH)_3L(MeOH)_6(H_2O)_4]^{2+}$); 663.53 (10%, $[Bi_4O_3(OH)_3L(MeOH)_7(H_2O)_4]^{2+}$); 678.48 (6%, $[Bi_4O_2(OH)_3L_3(MeOH)_3(H_2O)_3]^{2+}$); 711.57 (8%, $[Bi_4O_3(OH)L_3(H_2O)_{13}]^{2+}$); 739.60 (12%, $[Bi_4O(OH)_3L_5(MeOH)_3]^{2+}$); 949.80 (5%, $[Bi_6O_4(OH)_3L_5(MeOH)(H_2O)]^{2+}$); 977.83 (10%, $[Bi_6O_4(OH)_4L_4(MeOH)_3(H_2O)_5]^{2+}$). ES^{-}: *m/z* = 214.94 (50%, $[Bi_2O_2(OH)L_3(MeOH)(H_2O)_4]^{4-}$); 327.89 (100%, $[Bi_3O_3(OH)_2L_5(MeOH)_4(H_2O)_5]^{4-}$); 378.92 (7%, $[Bi_3O_3(OH)_2L_5(MeOH)_4(H_2O)_{11}]^{4-}$); 398.92 (9%, $[Bi_4O_4(OH)_3L_5(MeOH)_4(H_2O)_2]^{4-}$); 446.85 (10%, $[Bi_4O_4(OH)_3L_5(MeOH)_{10}(H_2O)_6]^{4-}$); 469.94 (5%, $[Bi_4O_4(OH)_3L_4(MeOH)_2(H_2O)_5]^{3-}$); 495.90 (6%, $[Bi_3O_2(OH)_2L_6(MeOH)_4(H_2O)_5]^{3-}$); 520.91 (8%, $[Bi_4O_4(OH)_4L_3(MeOH)_9(H_2O)]^{3-}$); 559.80 (12%, $[Bi_4O_4(OH)L_6(MeOH)_3(H_2O)_5]^{3-}$); 603.96 (5%, $[Bi_4O_4(OH)L_6(MeOH)_6(H_2O)_7]^{3-}$); 684.79 (6%, $[Bi_3O_2(OH)_2L_5(MeOH)_5(H_2O)_2]^{2-}$); 805.98 (15%, $[Bi_4O_4(OH)L_5(MeOH)_5(H_2O)_3]^{2-}$); 1033.99 (12%, $[Bi_3O_3(OH)_3L(MeOH)(H_2O)_{10}]^{-}$); 1340.99 (6%, $[Bi_4O_4(OH)_3L_2(H_2O)_{11}]^{-}$). Elemental analysis: $Bi_6O_{27}H_{18}S_6N_6$ (1980.435): calcd. H 0.91, N 4.20, S 9.69; found H 1.10, N 3.98, S 9.12.

Compound 3: $[Bi_{38}O_{45}(O_3SM)_{24}(H_2O)_{14}]\cdot(m\text{-xylene})$

2,4,6-Mesitylenesulfonic acid (MSO_3H) (1.418 g, 6 mmol, 6 eq) and Bi_2O_3 (0.466 g, 1 mmol, 1 eq) were applied to the general procedure. After sonication of 4 h, the reaction mixture was stirred at room temperature for further 24 h. The colourless precipitate was filtered off and 100 mg dissolved in warm *m*-xylene and filtered warm. This was left for crystallisation and after about two weeks colourless prismatic crystals suitable for X-ray crystallography were obtained. These crystals were isolated and identified as **3**. Overall yield: 52 mg (58 % based on Bi content).

M.p. = > 290 °C (Dec.). ^{1}H NMR (300 MHz, D_6-DMSO, 30°C): δ = 6.79 (2H, s, H^3, H^5); 2.52 (6H, s, H^7, H^9); 2.19 (3H, s, H^8). ^{13}C NMR (100 MHz, D_6-DMSO, 30°C): δ = 141.55 (C^1), 137.19 (C^4), 136.10 (C^2, C^6), 130.10 (C^3, C^5), 22.78 (C^7, C^9), 20.34 (C^8). FTR IR (Nujol, cm^{-1}): **ῡ** = 3370m, 1187s, 1165s, 1090s, 1015s, 848m, 687m. FTR IR (KBr, cm^{-1}): **ῡ** = 3422m, 2943m, 1606m, 1560m, 1474m, 1452s, 1406m, 1242m, 1209s, 1186s, 1093s, 1021s, 845s, 684s, 618m. Elemental Analysis: $C_{232}H_{312}O_{131}S_{24}Bi_{38}$ (13907.506): calcd. C 20.03, H 2.26; found C 21.24, H 2.66.

Crystallographic Details

Single crystals of **1** and **3** were mounted on a magnetic pin with a nylon loop in viscous hydrocarbon oil. Crystal data were collected at the MX1 (**3**) and MX2 (**1**) beamline at the Australian Synchrotron, Melbourne, Victoria, Australia with silicon monochromated $Mo_{K\alpha}$ radiation (λ = 0.71070 Å). All data were 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] Structural solution and refinements were carried out using SHELXL-97[3] suite of programs utilising the graphical interface X-Seed.[4] The refinements were carried out by using full-matrix least-squares techniques on F^2, minimizing the function $(F_o\text{-}F_c)^2$, where the weight is defined as $4F_0^2/2F_o^2$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-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.

A representative colourless prismatic crystal of **2** was mounted on an OXFORD Gemini Ultra CCD diffractometer equipped with an OXFORD Cryosystems 700 Cryostream and cooled to 123(1) K. Data were collected with monochromatic (graphite) $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) and processed using the CrysAlisProv1.171.34.36 software;[5] Lorentz, polarization and absorption corrections (multi-scan) were applied. The structure was solved and refined with SHELX-97[3] suite of programs utilising the graphical interface X-Seed.[4] The refinements were carried out by using full-matrix least-squares techniques on F^2, minimizing the function $(F_o\text{-}F_c)^2$, where the weight is defined as $4F_0^2/2F_o^2$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-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.

Crystallographic data of **1**: $C_{180}H_{340}O_{125}S_{18}Bi_{18}$, M= 8843.24, 0.02 x 0.01 x 0.01 mm, monoclinic, space group $C2$, a = 30.797(6), b = 19.123(4), c = 22.706(5) Å, β = 102.00(3)°, V = 13080(5) Å^3, Z = 2, ρ_{calc} = 2.245 g cm^{-3}, μ = 12.299 mm^{-1}, F_{000} = 8404, T = 100(2) K, $2\theta_{max}$ = 53.24°, 48107 reflections collected, 25425 unique (R_{int} = 0.0420). Flack χ = 0.017(3), Final GooF = 1.053, R_1 = 0.0304 for observed data, wR_2 = 0.0805 for all data, 1637 parameters, 79 restraints.

Crystallographic data of **2**: $H_{18}N_6O_{27}S_6Bi_6$, M= 1980.44, 0.02 x 0.02 x 0.01 mm, hexagonal, space group R-3, a = 14.7996(2), b = 14.7996(2), c = 11.1737(3) Å, γ = 120.00°, V = 2119.47(7) Å^3, Z = 3, ρ_{calc} = 4.655 g cm^{-3}, μ = 37.792 mm^{-1}, F_{000} = 2610, T = 123(2) K, $2\theta_{max}$ = 63.30°, 5444 reflections collected, 1455 unique (R_{int} = 0.0285). Final GooF = 1.170, R_1 = 0.0286 for observed data, wR_2 = 0.0482 for all data, 89 parameters, 28 restraints.

Crystallographic data of **3**: $C_{224}H_{274}O_{131}S_{24}Bi_{38}$, M= 13773.11, 0.02 x 0.02 x 0.01 mm, monoclinic, space group $P21/n$, a = 22.5150(12), b = 24.2440(4), c = 31.4000(6) Å, β = 91.452(2)°, V = 17134.31(10) Å^3, Z = 2, ρ_{calc} = 2.670 g cm^{-3}, μ = 19.658 mm^{-1}, F_{000} = 12408, T = 100(2) K, $2\theta_{max}$ = 52.80°, 122277 reflections collected, 33883 unique (R_{int} = 0.0431). Final GooF = 1.018, R_1 = 0.0553 for observed data, wR_2 = 0.1347 for all data,

1922 parameters, 178 restraints.

Variata

Compound 1: The O atom O(1) lies on an inversion centre. The oxygen atoms O(11), O(54)-O(60) and O(62)-O(66) are water molecules which are either located on the cluster core or are positioned within the crystal lattice. Therefore, the short inter D···A contact is probably due to hydrogen bonding.

Compound 2: As modelled in the space group *R*-3, the ASU comprised the Bi atom, the sulphonamide ligand, two O/OH sites and an O atom of a water molecule. One of the O/OH sites O(4)/O(5) lies on a three-fold axis and the water O atom O(8) lies at a site with crystallographically-imposed-3-$\bar{3}$ symmetry. The structure was refined with each of the O/OH sites modelled as disordered with occupancies fixed as 0.5 oxide:0.5 hydroxide (based on Bi-O bond distances). The anisotropic refinement of O(5) and O(8) was restrained. The hydrogen atoms of the amine group were located in the difference Fourier map and were refined with restrained N-H distances; the hydroxide hydrogen atoms were placed in calculated positions. Hydrogen atoms on the water molecule were not modelled due to the high symmetry of the water O atom site O(8). The disorder modelling of the O/OH sites is similar to that for the analogous NTf_2 cluster reported recently.[6]

Compound 3: The sulfate oxygen atom O(60) is located on the disordered ligand S11, in which only the mesityl moiety is disordered – a trial modelling of the sulphate group, and therefore, the oxygen atom O(60) as disordered was not successful. The oxygen atom O(28) is a coordinated water molecule located in the vicinity of the disordered ligand S10. It shows elongated thermal ellipsoids suggesting disorder. However, the disorder could not be modelled. A void was located centred at 010 and contains presumably a xylene molecule, but this could not be modelled.

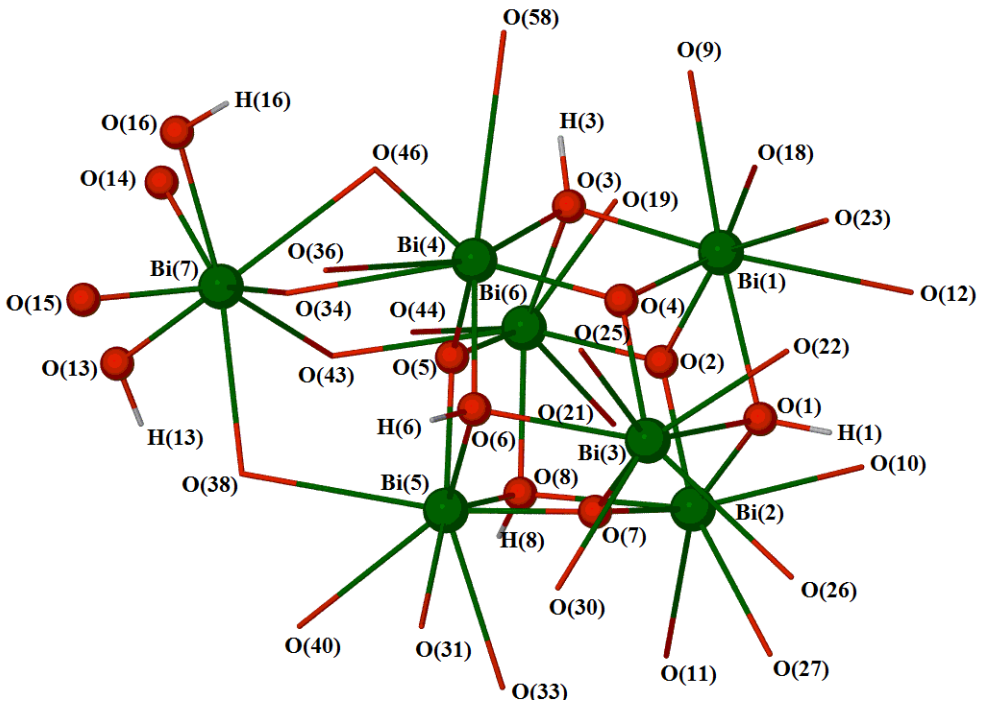

Figure 1 Detailed and labelled cluster core showing the coordination environment of each Bi atom of one cluster core and the linkage to the next cluster core of compound **1** (green = Bi atoms and red = O atoms). Non-highlighted O atoms are from the CSO_3 ligands or water molecules. Hydrogen atoms of the hydroxide O atoms are shown.

Table 1 Selected Bi-O bond lengths [Å] and Bi-O-Bi bond angles [°] of **1**. Other Bi-O bond lengths include Bi-OH_2 [O(9), O(10), O(11), O(12) and O(58)] and Bi-O_3SC bond lengths.

Bi-O [Å]		**Bi-OH [Å]**		**other Bi-O [Å]**	
Bi(1)-O(2)	2.225(5)	Bi(1)-O(1)	2.486(5)	Bi(1)-O(9)	2.659(6)
Bi(1)-O(4)	2.197(5)	Bi(1)-O(3)	2.299(5)	Bi(1)-O(12)	2.831(5)
Bi(2)-O(2)	2.133(5)	Bi(2)-O(1)	2.316(5)	Bi(1)-O(18)	2.639(6)
Bi(2)-O(7)	2.162(5)	Bi(2)-O(8)	2.549(5)	Bi(1)-O(23)	2.707(6)
Bi(3)-O(4)	2.176(5)	Bi(3)-O(1)	2.380(5)	Bi(2)-O(10)	2.586(6)
Bi(3)-O(7)	2.178(5)	Bi(3)-O(6)	2.464(5)	Bi(2)-O(11)	2.928(14)
Bi(4)-O(4)	2.141(5)	Bi(4)-O(3)	2.422(5)	Bi(2)-O(27)	2.654(6)
Bi(4)-O(5)	2.091(5)	Bi(4)-O(6)	2.278(5)	Bi(3)-O(22)	2.639(5)
Bi(5)-O(5)	2.199(4)	Bi(5)-O(6)	2.482(5)	Bi(3)-O(25)	2.663(6)
Bi(5)-O(7)	2.127(5)	Bi(5)-O(8)	2.291(5)	Bi(3)-O(26)	2.754(6)
Bi(6)-O(2)	2.144(5)	Bi(6)-O(3)	2.354(5)	Bi(3)-O(30)	2.676(6)
Bi(6)-O(5)	2.209(5)	Bi(6)-O(8)	2.299(5)	Bi(4)-O(34)	2.642(5)
Bi(7)-O(14)	2.170(5)	Bi(7)-O(13)	2.341(5)	Bi(4)-O(36)	3.224(5)
Bi(7)-O(15)	2.170(5)	Bi(7)-O(16)	2.521(5)	Bi(4)-O(46)	3.096(5)
				Bi(4)-O(58)	3.226(8)
av. Bi-O	**2.166**	**av. Bi-OH**	**2.442**	Bi(5)-O(31)	2.600(6)
				Bi(5)-O(33)	2.699(6)
Bi-O-Bi [°]		**Bi-O-Bi [°]**		Bi(5)-O(40)	2.981(6)
				Bi(6)-O(19)	2.587(5)
O(2)-Bi(1)-O(1)	67.5(2)	O(5)-Bi(4)-O(4)	94.6(2)	Bi(6)-O(21)	2.644(6)
O(2)-Bi(1)-O(3)	71.7(2)	O(5)-Bi(4)-O(6)	74.0(2)	Bi(6)-O(43)	2.819(6)
O(3)-Bi(1)-O(1)	122.9(2)	O(6)-Bi(4)-O(3)	127.6(2)	Bi(6)-O(44)	3.286(6)
O(4)-Bi(1)-O(1)	69.9(2)	O(5)-Bi(5)-O(6)	68.2(2)	Bi(7)-O(34)	2.594(5)
O(4)-Bi(1)-O(2)	90.1(2)	O(5)-Bi(5)-O(8)	71.6(2)	Bi(7)-O(38)	2.698(5)
O(4)-Bi(1)-O(3)	72.3(2)	O(7)-Bi(5)-O(5)	91.3(2)	Bi(7)-O(43)	2.695(6)
O(1)-Bi(2)-O(8)	125.0(2)	O(7)-Bi(5)-O(6)	71.3(2)	Bi(7)-O(46)	2.713(5)
O(2)-Bi(2)-O(1)	72.3(2)	O(7)-Bi(5)-O(8)	75.6(2)		
O(2)-Bi(2)-O(7)	91.4(2)	O(8)-Bi(5)-O(6)	125.9(2)		
O(2)-Bi(2)-O(8)	70.9(2)	O(2)-Bi(6)-O(3)	70.7(2)		
O(7)-Bi(2)-O(1)	72.5(2)	O(2)-Bi(6)-O(5)	91.7(2)		
O(7)-Bi(2)-O(8)	69.7(2)	O(2)-Bi(6)-O(8)	74.7(2)		
O(1)-Bi(3)-O(6)	123.6(2)	O(5)-Bi(6)-O(3)	70.9(2)		
O(4)-Bi(3)-O(1)	72.4(2)	O(5)-Bi(6)-O(8)	70.2(2)		
O(4)-Bi(3)-O(6)	68.8(2)	O(8)-Bi(6)-O(3)	125.9(2)		
O(4)-Bi(3)-O(7)	91.1(2)	O(13)-Bi(7)-O(16)	122.6(2)		
O(7)-Bi(3)-O(1)	70.9(2)	O(14)-Bi(7)-O(13)	70.9(2)		
O(7)-Bi(3)-O(6)	70.9(2)	O(14)-Bi(7)-O(16)	68.3(2)		
O(4)-Bi(4)-O(3)	70.8(2)	O(15)-Bi(7)-O(13)	73.1(2)		
O(4)-Bi(4)-O(6)	73.1(2)	O(15)-Bi(7)-O(14)	90.9(2)		
O(5)-Bi(4)-O(3)	72.7(2)	O(15)-Bi(7)-O(16)	69.4(2)		

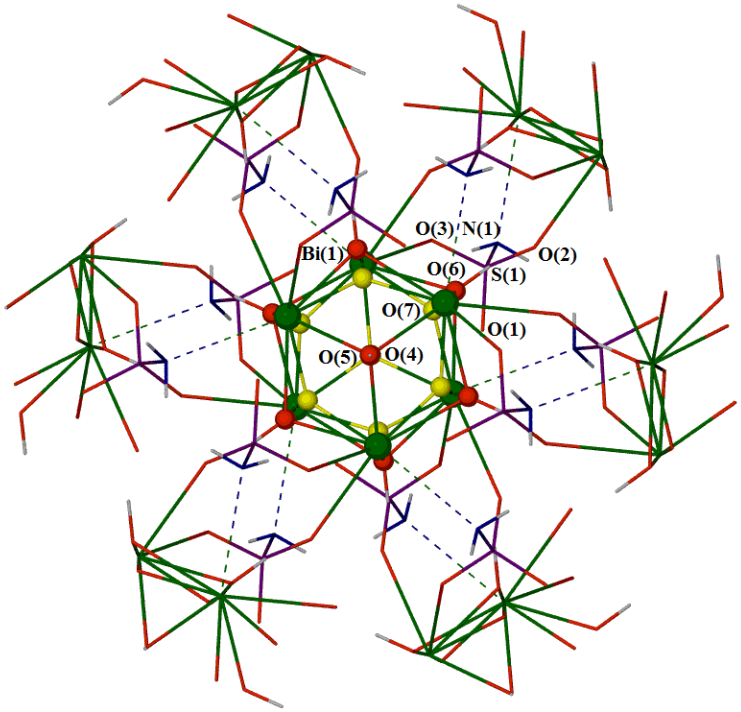

Figure 2 Environment of the O_3SNH_2 ligands which bridge the individual Bi_6 units through Bi-O and Bi···N Interactions in compound **2** (green = Bi atoms, red = O atoms, yellow = disordered O atoms, blue = N atoms and white = H atoms). Perspective shown is down the crystallographic *c*-axis.

Table 2 Selected Bi-O/Bi-N bond lengths [Å] and Bi-O-Bi bond angles of **2**. Symmetry transformations used to generate equivalent atoms: * = -x+y+1,-x+2,z; # = y,-x+y+1,-z; $ = -x+5/3,-y+4/3,-z+1/3; ‘ = -y+4/3,x-y+2/3,z-1/3; “ -y+2,x-y+1,z; & = x-y+1,x,-z.

Bi-O [Å]		Bi-O-Bi [°]	
Bi(1)-O(7)	2.105(7)	Bi(1)-O(4)-Bi(1)*	117.9(2)
Bi(1)-O(4)	2.147(2)	Bi(1)-O(4)-Bi(1)”	117.9(2)
Bi(1)-O(7)*	2.152(7)	Bi(1)*-O(4)-Bi(1)”	117.9(2)
Bi(1)-O(7)#	2.258(7)	Bi(1)-O(5)-Bi(1)*	97.91(3)
Bi(1)-O(6)#	2.323(7)	Bi(1)-O(5)-Bi(1)”	97.91(3)
Bi(1)-O(6)	2.357(8)	Bi(1)*-O(5)-Bi(1)”	97.91(3)
Bi(1)-O(5)	2.4361(5)	Bi(1)&-O(6)-Bi(1)	104.0(3)
Bi(1)-O(6)*	2.502(8)	Bi(1)&-O(6)-Bi(1)”	99.7(3)
Bi(1)-O(3)	2.576(4)	Bi(1)-O(5)-Bi(1)”	98.2(3)
Bi(1)-O(2)$	2.794(5)	Bi(1)-O(7)-Bi(1)”	119.3(3)
Bi(1)-O(1)*	2.821(4)	Bi(1)-O(7)-Bi(1)&	115.4(3)
Bi(1)-N(1)’	3.012(5)	Bi(1)”-O(7)-Bi(1)&	113.5(3)

Table 3 Hydrogen bond lengths [Å] and bond angles [°] of **2**. Symmetry transformations used to generate equivalent atoms: * = y,-x+y+1,-z+1; # = -y+5/3,x-y+1/3,z+1/3

D-H···A	D-H [Å]	H···A [Å]	D···A [Å]	D-H···A [°]
N(1)-H(2)···O(1)*	0.87(2)	2.10(3)	2.951(7)	165(7)
N(1)-H(1)···O(2)#	0.87(2)	2.12(5)	2.915(7)	151(8)
O(5)-H(5)···O(8)	1.00	1.88	2.8803(10)	180.0

Table 4-Selected Bi-O bond lengths [Å] of **3**. Symmetry transformation used to generate equivalent atoms: * -x, -y, -z

Bi-O [Å]		Bi-O [Å]		Bi-O [Å]		Bi-O [Å]	
Bi(1)-O(1)	2.6569(7)	Bi(4)-O(2)	2.083(6)	Bi(10)-O(10)	2.116(7)	Bi(16)-O(17)	2.131(7)
Bi(1)-O(2)*	2.477(7)	Bi(4)-O(5)	2.422(7)	Bi(10)-O(13)	2.154(7)	Bi(16)-O(18)	2.170(7)
Bi(1)-O(3)	2.369(7)	Bi(4)-O(6)	2.182(7)	Bi(11)-O(13)	2.320(7)	Bi(16)-O(19)	2.137(7)
Bi(1)-O(4)*	2.399(7)	Bi(4)-O(7)	2.389(8)	Bi(11)-O(14)	2.236(6)	Bi(17)-O(19)	2.206(7)
Bi(1)-O(8)	2.668(8)	Bi(5)-O(5)	2.144(7)	Bi(11)-O(15)	2.568(7)	Bi(17)-O(20)	2.161(7)
Bi(1)-O(16)*	2.624(7)	Bi(5)-O(6)	2.114(7)	Bi(11)-O(22)	2.086(7)	Bi(18)-O(5)	2.131(7)
Bi(1)-O(22)*	2.579(8)	Bi(5)-O(20)	2.157(7)	Bi(12)-O(12)	2.120(7)	Bi(18)-O(18)	2.145(7)
Bi(2)-O(1)	2.536(5)	Bi(6)-O(6)	2.146(7)	Bi(12)-O(13)	2.155(6)	Bi(18)-O(21)	2.143(7)
Bi(2)-O(2)	2.272(7)	Bi(6)-O(7)	2.153(7)	Bi(12)-O(14)	2.143(7)	Bi(19)-O(11)	2.161(7)
Bi(2)-O(3)	2.424(6)	Bi(6)-O(15)*	2.122(7)	Bi(13)-O(14)	2.099(7)	Bi(19)-O(12)	2.143(7)
Bi(2)-O(4)	2.313(7)	Bi(7)-O(7)	2.192(7)	Bi(13)-O(15)	2.144(7)	Bi(19)-O(21)	2.108(7)
Bi(2)-O(11)	2.627(7)	Bi(7)-O(8)	2.158(8)	Bi(13)-O(16)	2.143(7)	Bi(20)-O(3)	2.114(6)
Bi(2)-O(22)	2.464(7)	Bi(7)-O(9)	2.083(9)	Bi(14)-O(8)*	2.210(7)	Bi(20)-O(10)	2.295(7)
Bi(3)-O(1)	2.5883(6)	Bi(8)-O(3)	2.164(6)	Bi(14)-O(16)	2.127(7)	Bi(20)-O(19)*	2.319(7)
Bi(3)-O(2)	2.535(7)	Bi(8)-O(8)	2.382(8)	Bi(14)-O(17)	2.101(7)		
Bi(3)-O(3)*	2.336(7)	Bi(8)-O(9)	2.434(13)	Bi(15)-O(4)	2.082(6)	**shortest Bi-O**	**2.082(6)**
Bi(3)-O(4)	2.503(6)	Bi(8)-O(10)	2.300(7)	Bi(15)-O(12)	2.600(7)		
Bi(3)-O(19)	2.641(7)	Bi(9)-O(9)	2.135(9)	Bi(15)-O(17)	2.429(7)	**longest Bi-O**	**2.668(8)**
Bi(3)-O(20)	2.595(7)	Bi(9)-O(10)	2.235(7)	Bi(15)-O(18)	2.286(7)		
Bi(3)-O(22)*	2.260(7)	Bi(9)-O(11)	2.157(7)	Bi(15)-O(21)	2.307(8)	**av. Bi-O**	**2.281**

Table 5 Selected Bi-O-Bi bond angles [°] of **3**. Symmetry transformation used to generate equivalent atoms: * -x, -y, -z.

Bi-O-Bi [°]		Bi-O-Bi [°]		Bi-O-Bi [°]		Bi-O-Bi [°]	
Bi(1)*-O(1)-Bi(1)	**180.0**	Bi(5)-O(6)-Bi(4)	112.6(3)	Bi(10)-O(13)-Bi(12)	131.8(3)	Bi(16)-O(19)-Bi(20)*	114.8(3)
Bi(1)-O(3)-Bi(2)	98.3(2)	Bi(5)-O(6)-Bi(6)	131.5(3)	Bi(10)-O(10)-Bi(20)	103.8(3)	Bi(17)-O(19)-Bi(3)	101.2(3)
Bi(1)-O(2)-Bi(3)	97.0(2)	Bi(5)-O(20)-Bi(17)	125.3(3)	Bi(11)-O(22)-Bi(1)*	117.4(3)	Bi(17)-O(20)-Bi(3)	103.9(3)
Bi(1)*-O(4)-Bi(3)	96.8(2)	Bi(6)-O(6)-Bi(4)	108.9(3)	Bi(11)-O(22)-Bi(2)	117.4(3)	Bi(17)-O(19)-Bi(20)*	108.1(3)
Bi(2)-O(1)-Bi(1)	**88.560(14)**	Bi(6)-O(7)-Bi(4)	101.6(3)	Bi(11)-O(22)-Bi(3)*	121.5(3)	Bi(18)-O(5)-Bi(4)	127.9(3)
Bi(2)*-O(1)-Bi(1)	**91.440(14)**	Bi(6)-O(7)-Bi(7)	129.3(4)	Bi(12)-O(13)-Bi(11)	103.6(3)	Bi(18)-O(5)-Bi(5)	125.9(3)
Bi(2)-O(2)-Bi(1)	99.5(2)	Bi(6)*-O(15)-Bi(11)	129.2(3)	Bi(12)-O(14)-Bi(11)	106.9(3)	Bi(18)-O(18)-Bi(15)	105.6(3)
Bi(2)-O(4)-Bi(1)*	104.2(2)	Bi(6)*-O(15)-Bi(13)	124.2(3)	Bi(12)-O(12)-Bi(15)	128.8(3)	Bi(18)-O(21)-Bi(15)	104.9(3)
Bi(2)-O(22)-Bi(1)*	95.0(2)	Bi(7)-O(8)-Bi(1)	109.2(3)	Bi(12)-O(12)-Bi(19)	123.3(3)	Bi(18)-O(18)-Bi(16)	133.3(3)
Bi(2)*-O(1)-Bi(2)	**180.0**	Bi(7)-O(7)-Bi(4)	116.4(3)	Bi(13)-O(16)-Bi(1)*	110.0(3)	Bi(19)-O(11)-Bi(2)	106.0(3)
Bi(2)-O(1)-Bi(3)	**90.686(14)**	Bi(7)-O(8)-Bi(8)	96.1(3)	Bi(13)-O(14)-Bi(11)	113.3(3)	Bi(19)-O(12)-Bi(15)	100.2(3)
Bi(2)*-O(1)-Bi(3)	**89.314(14)**	Bi(7)-O(9)-Bi(8)	96.5(5)	Bi(13)-O(15)-Bi(11)	100.1(3)	Bi(19)-O(21)-Bi(15)	111.4(3)
Bi(2)-O(2)-Bi(3)	98.5(2)	Bi(7)-O(9)-Bi(9)	136.6(5)	Bi(13)-O(14)-Bi(12)	133.1(3)	Bi(19)-O(21)-Bi(18)	132.1(4)
Bi(2)-O(4)-Bi(3)	98.3(2)	Bi(7)-O(8)-Bi(14)*	127.4(4)	Bi(14)*-O(8)-Bi(1)	100.6(3)	Bi(20)-O(3)-Bi(1)	127.3(3)
Bi(3)-O(1)-Bi(1)	**91.355(14)**	Bi(8)-O(3)-Bi(1)	110.9(3)	Bi(14)-O(16)-Bi(1)*	104.3(3)	Bi(20)-O(3)-Bi(2)	116.9(3)
Bi(3)*-O(1)-Bi(1)	**88.644(14)**	Bi(8)-O(8)-Bi(1)	95.2(3)	Bi(14)*-O(8)-Bi(8)	123.7(3)	Bi(20)-O(3)-Bi(3)*	109.3(3)
Bi(3)*-O(3)-Bi(1)	102.3(3)	Bi(8)-O(3)-Bi(2)	115.4(3)	Bi(14)-O(16)-Bi(13)	127.4(3)	Bi(20)*-O(19)-Bi(3)	93.9(2)
Bi(3)*-O(22)-Bi(1)	101.5(3)	Bi(8)-O(3)-Bi(3)*	127.2(3)	Bi(14)-O(17)-Bi(15)	110.5(3)		
Bi(3)*-O(3)-Bi(2)	98.3(2)	Bi(9)-O(11)-Bi(2)	110.5(3)	Bi(14)-O(17)-Bi(16)	131.6(3)		
Bi(3)*-O(22)-Bi(2)	99.3(3)	Bi(9)-O(9)-Bi(8)	103.8(5)	Bi(15)-O(4)-Bi(1)*	120.3(3)	**acute$_{min}$ angle**	**88.560(14)**
Bi(3)*-O(1)-Bi(3)	**180.0**	Bi(9)-O(10)-Bi(8)	105.1(3)	Bi(15)-O(4)-Bi(2)	120.5(3)		
Bi(4)-O(2)-Bi(1)	114.1(3)	Bi(9)-O(11)-Bi(19)	127.2(3)	Bi(15)-O(4)-Bi(3)	112.3(3)	**obtuse$_{max}$ angle**	**136.6(5)**
Bi(4)-O(2)-Bi(2)	123.4(3)	Bi(9)-O(10)-Bi(20)	123.2(3)	Bi(16)-O(19)-Bi(3)	110.9(3)		
Bi(4)-O(2)-Bi(3)	119.5(3)	Bi(10)-O(10)-Bi(8)	120.7(3)	Bi(16)-O(17)-Bi(15)	105.2(3)	**straight angle**	**180.0**
Bi(5)-O(20)-Bi(3)	114.0(3)	Bi(10)-O(10)-Bi(9)	127.1(3)	Bi(16)-O(18)-Bi(15)	109.0(3)		
Bi(5)-O(5)-Bi(4)	102.9(3)	Bi(10)-O(13)-Bi(11)	113.8(3)	Bi(16)-O(19)-Bi(17)	123.2(3)		

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