Solvolytic routes to new nonabismuth hydroxy- and alkoxy-oxo complexes: synthesis, characterization and solid-state structures of novel nonabismuth polyoxo cations $Bi_9(\mu_3\text{-O})_8(\mu_3\text{-OR})_6{}^{5+}$ (R = H, Et)†

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Base hydrolysis of $BiO(ClO_4)$ yields $ClO_4{}^-$ salts of the novel nonabismuth polyoxo cation $Bi_9(\mu_3\text{-O})_8(\mu_3\text{-OH})_6{}^{5+}$ (**1**); ethanolysis converts **1** to the ethoxide $Bi_9(\mu_3\text{-O})_8(\mu_3\text{-OEt})_6{}^{5+}$ (**2**).

Polybismuth compounds (Bi_n) are potential molecular precursors to ceramics[1] and models for the structure and chemistry of bulk oxides[2-4] and poorly-understood pharmaceuticals.[5,6] Polyhedral polyoxo (Bi_n) complexes with organic moieties are attractive for their high bismuth density, organic solubility and reactivity. However, the synthesis of hybrid organic–inorganic complexes *via* microhydrolysis,[7] condensation, or aggregation of alkoxides,[1,8] carboxylates,[9] or siloxides[10] is not always trivial and frequently relies on hydrolytically unstable homoleptic precursors.

Main-group oxides have been converted into oxo-alkoxides *via* alcoholysis.[11] Polyhedral oxo-hydroxo Bi complexes, with similar surface functionality to oxides, could exhibit analogous reactivity and offer a new synthon for organic–inorganic hybrid complexes.

Despite solution evidence for polyoxo Bi_n complexes with nuclearities n = 2–9,[12-16] only octahedral $Bi_6(\mu_3\text{-O})_x(\mu_3\text{-OH})_{8-x}{}^{(10-x)+}$ salts have been isolated. Nonabismuth complexes are postulated hydrolysis products based on electrophoresis and tyndallometry.[12,13,16] The paucity of structural information stems from the high Lewis acidity of Bi(III), expandable coordination sphere, and low aqueous solubility of its salts.[17,18] Intractable oligomers are often obtained, and isolation conditions are not well established.[19] We report here the isolation of a nonabismuth compound, $[Bi_9(\mu_3\text{-O})_8(\mu_3\text{-OH})_6](ClO_4)_5$ (**1**), and its alcoholysis to $[Bi_9(\mu_3\text{-O})_8(\mu_3\text{-OEt})_6(HOEt)](ClO_4)_5\cdot 4HOEt$ (**2**).

Compound **1** is obtained in 70% yield *via* base (NaOH) hydrolysis of 0.1 M aqueous $BiO(ClO_4)$ containing 1,1,1-tris(hydroxymethyl)ethane (THME).‡ The Bi_9 formulation is consistent with analytical, spectroscopic and spectrometric data. Synthesis of **1** is not dependent upon THME, but the triol facilitates crystal growth (possibly by slowing crystallization). Relative yields of **1** with and without THME are comparable.

The solid-state structure of **1**, from single-crystal X-ray diffractometry,§ has nine Bi atoms adopting a D_{3h} tricapped trigonal prismatic geometry. While unknown for Bi complexes, the structure is similar to that of $Ga_9(\mu_3\text{-O})_9(C_6H_2Me_3\text{-}2,4,6)_9$[20] and $[Me_3CAl(\mu_3\text{-O})]_9$[21] and suggests a common structural motif for nonanuclear p-block polyoxos. The structure can be described as three edge-bridging $Bi_4(\mu_3\text{-O})_2(\mu\text{-OH})_4$ subunits around two

μ_3-oxos (Fig. 1), similar to other Bi_n complexes.[1,13,22–24] The three peripheral Bi atoms are tetracoordinate, similar to that in $[Bi_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]X_6$ (X = ClO_4, NO_3)[13,24,25] and $Bi_6(\mu_3\text{-O})_4(\mu_3\text{-}OC_6F_5)[\mu_3\text{-OBi}(OC_6F_5)_4]_3$.[1] The central Bi atoms are pentacoordinate, reminiscent of the low-temperature α and metastable β phases of Bi_2O_3.[26] The structural motifs in **1** are comparable to other high-nuclearity Bi complexes, including $[Bi_{22}O_{26}(OSiMe_2\text{-}CMe_3)_{14}]$,[10] $(NH_4)_{12}[Bi_{12}O_8(cit)_8](H_2O)_{10}$ (cit = citrate)[27] and $Bi_6(\mu_3\text{-O})_4(\mu_3\text{-}OC_6F_5)[\mu_3\text{-OBi}(OC_6F_5)_4]_3$.

It is noteworthy that **1** and the $Bi_9{}^{5+}$ Zintl ion possess D_{3h} symmetry structures. A similar correlation exists between O_h symmetry $[Bi_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]^{2+}$ and $Bi_6{}^{2+}$. There is considerable debate[28] about metal–metal interactions in polyoxo clusters of the heavy main-group elements. The Bi–Bi distances in **1** lie in the range 3.584(8)–3.964(9) Å, significantly less than twice the atomic van der Waals radius of Bi (2.4 Å).[9] While these distances are longer than typically identified as "bonding" in Bi clusters ($d_{Bi–Bi}$ = 3.0–3.1 Å), Bi–Bi bond lengths of 3.42 and 3.47 Å have been found in the heterometallic $[Ru_2Bi_{17}(\mu\text{-Br})_4]^{5+}$[29] and $[NEt_4]_2[Bi_4Fe_4(CO)_{13}]$,[30] respectively. Similarly, Bi–Bi bond lengths of 3.31 Å have been reported for the Zintl ion $Bi_5{}^{3+}$,[31] suggesting that there is considerable flexibility in the relative Bi spatial orientations in Bi_n polyoxo complexes. Whether the contraction between the Bi atoms in **1** is the result of partial covalent bonding, an artifact of the μ_3-oxo or μ_3-OH ligands, or nonbonding requirements, is unknown.
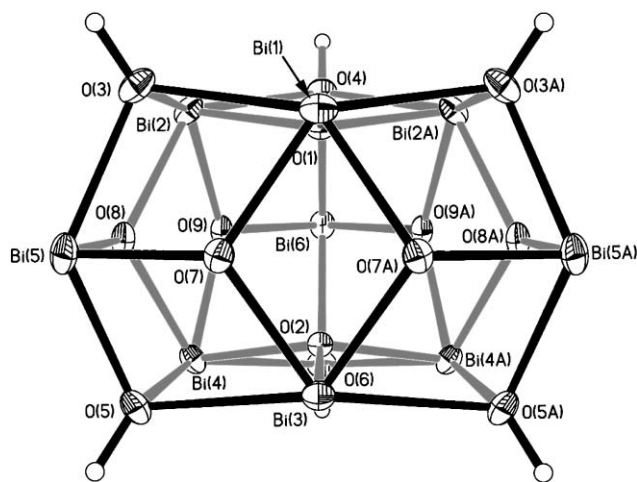
Fig. 1 Thermal ellipsoid plot of cationic core of **1** viewed along a C_2 axis; nearest $Bi_4(\mu_3\text{-O})_2(\mu\text{-OH})_4$ subunit has been emphasized for clarity. Atoms labeled with a number and a letter are generated by a crystallographic mirror plane.

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† Dedicated to Prof. Ian Rothwell, a leader in aryloxide and early transition metal chemistries.

Charge balance requires six μ_3-OH groups to be present in **1**. The locations of the hydrogens were assigned from displacement of each μ_3-oxygen above the plane of the three Bi atoms to which it is bound. The average distance of the μ_3-OH above the Bi_3 plane is 1.175(8) Å, *vs.* 0.418(7) Å for the external μ_3-oxos. The central oxos O(1) and O(2) are directed *into* the interior, and lie ~0.361 and 0.224 Å below the Bi_3 planes, respectively. The reason for the unusual concave orientation of the two oxos is unknown, but this orientation may allow the Bi atoms to approximate a close-packed structure. The assignment of hydroxide positions in the solid-state structure of **1** is supported by the isolation and characterization of the ethoxide derivative **2** (Fig. 2).

The μ_3-OH ligands in **1** are shared asymmetrically among the Bi atoms, with one Bi–O_{OH} bond ~0.2 Å shorter than the other two. These results suggest a localized bond between a μ_3-OH and one Bi and two predominantly dative interactions to the other Bi atoms, consistent with bonding modes in other polynuclear bismuth complexes including $[Bi(OEt)_3]_8 \cdot (7 + x)HOEt$[32] and $Bi_6(\mu_3\text{-}O)_4(\mu_3\text{-}OC_6F_5)\{\mu_3\text{-}OBi(OC_6F_5)_4\}_3$.[8]

Strong inter- and intramolecular hydrogen bonding in **1** precludes dissolution in all but strongly coordinating solvents, *e.g.* DMSO and DMF. Analysis of the structure using the program Mercury[33] suggests the presence of hydrogen bonding between the hydroxyl protons and the lattice water (average $d(O_{water} \cdots H)$ *ca.* 1.86 Å; $\angle O_{water} \cdots H\text{–}O_{hydroxide}$ *ca.* 172.7°). There are additional short contacts between the hydroxyl groups and perchlorates ($d(O_{perchlorate} \cdots O)$ *ca.* 3.02 Å) that may further stabilize the lattice. The coordination requirements of several Bi atoms in **1** are completed *via* weak interactions ($d(Bi \cdots O_{perchlorate})$ = 2.929(8)–3.202(10) Å) with perchlorates.

TOF-MALDI mass spectrometry showed a Bi_9 ion, $Bi_9O_{13}^+$, that underwent stepwise decomposition *via* loss of Bi_2O_3 to produce $Bi_7O_{10}^+$, $Bi_5O_7^+$ and $Bi_3O_4^+$. Electrospray mass spectrometry (positive ion mode) on a DMF–CH_3CN solution of **1** showed a mixture of $Bi_9O_{13}^+$, $Bi_6O_8(ClO_4)^+$ and $Bi_3O_4^+$, with the parent ion difficult to detect. MS/MS and MS/MS/MS experiments confirmed that the predominant species in solution under these conditions was $Bi_6O_8(ClO_4)^+$, which could be converted successively to $Bi_5O_7^+$ and then $Bi_3O_4^+$. However, the energy required to achieve these transformations is >3 times the usual electrospray ionization energy, so we conclude that **1** is in equilibrium with other Bi_n polyoxo species in DMF. A single solution NMR resonance is observed for each NMR-active nucleus (^1H: δ 5.9; ^{17}O: δ 167) at 20 °C in DMSO. The ^1H chemical shift is consistent with one report of polyoxo Bi_n in solution.[34] The ^{17}O resonance may be a composite of μ_3-OH and μ_3-O ligands, perhaps arising from dynamic proton exchange.

Ethanolysis of **1** with gentle heating produces the ethoxide **2** in quantitative yield.‡ The central Bi–O core of **1** remains intact in **2** (Fig. 2), suggesting that, in contrast to DMF, the less strongly coordinating ethanol does not compromise the core's structural integrity. The μ_3-OEt ligands are shared asymmetrically among the three Bi atoms. The ethoxide oxygens average 1.278(4) Å above each Bi_3 plane, whereas the μ_3-O's average 0.370(2) Å above their Bi_3 plane. The central μ_3-O's lie 0.252 and 0.254 Å below the Bi_3 planes. These distances suggest a distortion in the core, compared to that in **1**, driven possibly by ethoxide steric requirements. The bond distances, angles and orientation of the ligands in **1** and **2** are consistent with what has been observed in other polyoxo bismuth complexes including $[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$[10] and $[Bi(OEt)_3]_8 \cdot (7 + x)HOEt$.[32]

Compound **2** crystallizes with $\geqslant 8$ EtOH molecules per unit cell, four of which associate with Bi *via* weak dative interactions (d_{Bi-O} = 2.636–3.195 Å) (Fig. 3). The shortest contacts are slightly longer than some Bi–O_{OEt} distances in the core. Intermolecular H-bonding exists between the lattice solvent and ethanols
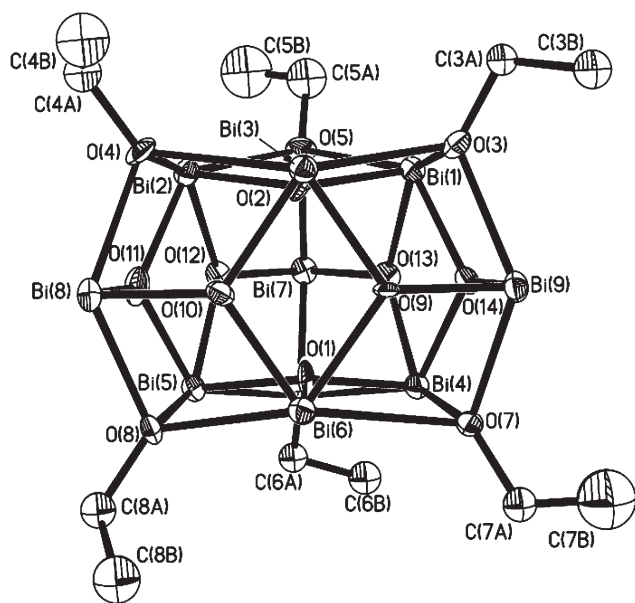
Fig. 2 Thermal ellipsoid plot of cationic core of **2**. Hydrogen atoms and coordinated solvent molecules have been omitted for clarity.
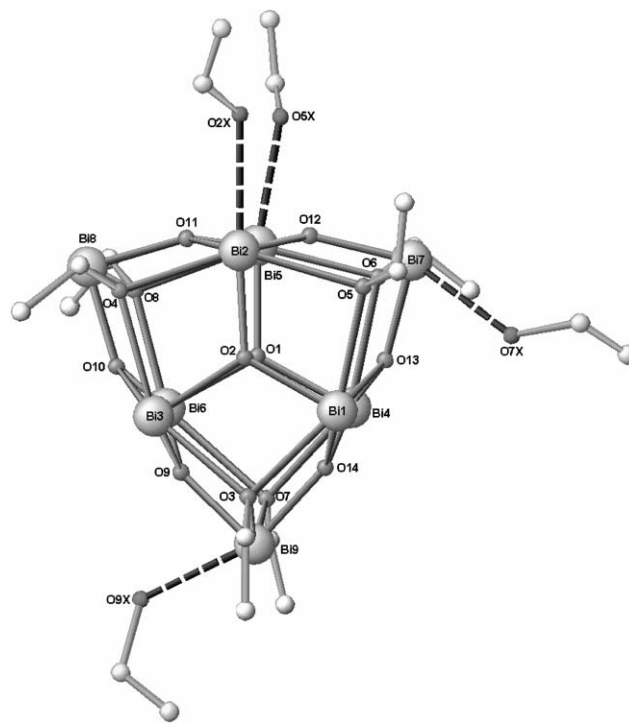
Fig. 3 Ball-and-stick representation of the solid-state structure of **2** viewed along the idealized C_3 axis, with solvent interactions represented by a dashed line.

coordinated to the core (average $d_{O–O} = 2.04(9)$ Å; average O–H–O angle $= 166(9)°$).

In conclusion, Bi_9 polyoxo complexes can be prepared in high yield *via* base hydrolysis under conditions that favor rapid crystallization. While aqueous Bi chemistry is dominated by Bi_6 species, our results illustrate that other cluster motifs are accessible through careful tuning of the reaction conditions. The isolated oxo-hydroxo complex prepared in this fashion is a convenient scaffold for organic modification *via* alcoholysis and exhibits remarkable air stability. Compounds **1** and **2** are attractive reagents for bismuth oxides and organic syntheses.

Notes and references

‡ $Bi_9(\mu_3\text{-}O)_8(\mu_3\text{-}OH)_6(ClO_4)_5$ (**1**): $BiOClO_4$ (0.32 g, 1.0 mmol) and 1,1,1-THME (0.31 g, 3.0 mmol) were combined in deionized water (15 mL). The solution was stirred at 70 °C and the pH adjusted to 6.5 by dropwise addition of 1.0 M aqueous NaOH. The solution was stirred and heated for 5 min. Trace solid was removed by centrifugation. Crystals of **1** deposited within 24 h at 20 °C. Sample purity was determined by comparing powder X-ray diffraction data of the bulk with that predicted from single-crystal diffractometry. Yield 135 mg (45.7% based on Bi). FT-IR (KBr): 3376, 1142, 1108, 1080, 628, 571, 514 cm^{-1}. ^1H NMR (d_6-DMSO, 300 MHz, 25 °C): δ 5.9 (HO). ^{17}O NMR (d_6-DMSO, 54.227 MHz, 25 °C): δ 166.73. Elemental analysis (complexometric titration with xylenol orange[35]): found (calc.): Bi, 71.1 (70.8%).

$Bi_9(\mu_3\text{-}O)_8(\mu_3\text{-}OEt)_6(ClO_4)_5$ (**2**): A suspension of 50 mg (0.02 mmol) **1** in EtOH (3 mL) was stirred and heated to complete dissolution of the solid (*ca.* 30 min) and then cooled to 20 °C. Trapezoidal prisms were obtained by slow diffusion of Et_2O. Yield: 57 mg (91% based on Bi). FT-IR (KBr): 3446, 2965, 2895, 1616, 1397, 1144, 1107, 1080, 941, 868, 668, 627, 556 cm^{-1}. ^1H NMR (d_6-DMSO, 300 MHz, 25 °C): δ 1.04 (t, CH_3, $^3J_{HH}$ = 7.1 Hz), 3.43 (br s, CH_2), 4.32 (s, OH). $^{13}C\{^1H\}$ NMR (d_6-DMSO, 90 MHz, 25 °C): δ 18.78, 56.21. Rapid efflorescence precluded successful elemental analysis.

§ *Structure determinations*: Intensities were measured on a Nonius KappaCCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å). Empirical (multiscan) absorption corrections were applied (μ = 4.4955 cm^{-1}) using Scale Pack in the Denzo package.[36] The structures were solved and refined in monoclinic space groups using direct methods and were refined against F^2 *via* the SHELXTL package.[37] **1**: $Bi_9Cl_5H_{12}O_{37}$, M = 2656.12, colorless block; space group Im (no. 8), Z = 2, a = 9.983(2), b = 16.774(3), c = 10.608(2) Å, β = 92.85(3)°, V = 1774.2(6) Å^3, T = 190 K, reflections collected = 7405, independent reflections = 4119 (R_{int} = 0.0331). Crystals of **1** were found generally to be inherently twinned. Successful deconvolution of the two independent lattices was achieved using the program DIRAX.[38] Attempts to solve the structure in Cm were not successful. Hydrogens were included in calculated positions using default parameters in XP ($d_{O–H}$ = 0.98 Å). All non-hydrogen atoms, with the following exception, were refined anisotropically. One perchlorate, disordered over two sites in the crystal lattice, was modeled with each potential location at partial occupancy. The disordered oxygens were refined isotropically. The two positions refined to occupancies of 44 and 56%. Hydrogens could not be identified for the water in **1** and were not included in final refinement. Final refinement values: $R(I > 2\sigma(I))$, R_1 = 0.0309, wR_2 = 0.0647; R(all data): R_1 = 0.0380, wR_2 = 0.0674, S = 1.071. Residual electron density is between 1.493 – -2.013 e$^-$ Å^{-3}. **2**: $C_{28}H_{78}Bi_9Cl_5O_{42}$, M = 3144.97, colorless trapezoidal prism; space group $P2_1/c$ (no. 14), Z = 4, a = 13.434(3), b = 26.027(5), c = 20.985(4) Å, β = 106.87(3)°, V = 7022(2) Å^3, T = 190 K, reflections collected = 25308, independent reflections = 7352 (R_{int} = 0.0831). Crystals of **2** contain considerable lattice solvent which resulted in rapid efflorescence and crystal decay, even at reduced temperatures. Analysis of the data using the

PLATON software suite indicated the presence of a void space of 81 Å^3, consistent with the loss of approximately 1.5 molecules of ethanol per unit cell. Consequently, only the Bi and O positions were refined anisotropically. Final refinement values: $R(I > 2\sigma(I))$, R_1 = 0.0464, wR_2 = 0.1165; R(all data): R_1 = 0.0701, wR_2 = 0.1373, S = 1.185. Residual electron density 2.054 – -3.014 e$^-$ Å^{-3}. CCDC 268349 and 268350. See http://dx.doi.org/10.1039/b504864h for crystallographic data in CIF or other electronic format.

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