## Cluster Compounds

## From a Bismuth Oxido Diketonate to a Giant Bismuth **Oxido Cluster\*\***

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(1)

hfac

Homo- and heterometallic oxido alkoxides, diketonates, and carboxylates have attracted considerable attention as precursors for oxide-based materials.<sup>[1]</sup> Structurally well defined and properly functionalized metal oxido clusters are also used as nanoscale building blocks in the assembly of organic-inorganic hybrid networks.<sup>[2]</sup> A number of oxidobridged units obtained from the hydrolysis of medicinally important bismuth compounds (nitrate, salicylate, citrate)<sup>[3]</sup> indicate that polyoxidobismuth species play an important role in pharmaceuticals as well. Major pathways for introduction of the oxido groups during cluster formation include microhydrolysis, ether elimination, and oxidation.<sup>[1c,4]</sup> Several bismuth oxido clusters  $[Bi_m O_n]^{(3m-2n)+}$  with surface capping ligands such as hydroxide,<sup>[5]</sup> alkoxides,<sup>[6]</sup> aryl oxides,<sup>[7]</sup> siloxides,<sup>[8]</sup> carboxylates,<sup>[9]</sup> and phosphonates<sup>[10]</sup> were isolated recently by using solvolytic methods. In addition, a few heterometallic bismuth compounds in which metal atoms are connected through oxido bridges<sup>[8b,11]</sup> have also been synthesized by similar approaches.

The common problem associated with hydrolytic pathways is the inherent difficulty of composition control,<sup>[4,12]</sup> which often results in the formation of mixtures of different species. Herein we report on a new synthetic approach to overcome this problem. We attempted to obtain bismuth oxido clusters using diketonate co-ligands that are known to serve as modifiers to prevent hydrolysis of oxido species<sup>[13]</sup> and as surface capping groups to stabilize nanoscale building blocks.<sup>[14]</sup> For this purpose we proposed controlled introduction of oxido centers by using a "non-innocent" fluorinated tetraol, a deprotonated form of which has been hypothesized<sup>[15]</sup> to generate both oxido and diketonate ( $\beta$ -dik) ligands on decomposition. Thus, the first bismuth oxido diketonate complex  $[Bi_9O_7(\beta-dik)_{13}]$  (1) was isolated and fully characterized. Moreover, its subsequent aggregation in solution led to a remarkable nanosized molecule,  $[Bi_{38}O_{45}(\beta-dik)_{24}]$  (2), which contains the largest homometallic bismuth oxido cluster reported to date.

The fluorinated bis(gem-diol) 1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraol (H<sub>4</sub>hfpt) can be instantly obtained<sup>[15]</sup> by hydration of hexafluoroacetylacetone (Hhfac). We have shown that in the presence of a proton acceptor H<sub>4</sub>hfpt acts as a controlled source of both diketonate and oxido groups by undergoing facile cleavage of two C–O bonds (Scheme 1). The first bismuth oxido diketonate was obtained in quantitative yield by reaction of triphenylbismuth with H<sub>4</sub>hfpt and Hhfac [Eq. (1)].

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Hhfac

Scheme 1.

+2H<sub>2</sub>C

 $18 \left[ \text{Bi}(\text{C}_6\text{H}_5)_3 \right] + 7 \text{H}_4\text{hfpt} + 19 \text{Hhfac} \rightarrow$ 

 $2 \left[ Bi_9 O_7 (hfac)_{13} \right] (1) + 54 C_6 H_6$ 

HO

CF

H₄hfpt

The crystal structure of 1<sup>[16]</sup> features bismuth atoms in two distinctly different chemical and coordination environments (Figure 1). Six bismuth atoms form a slightly distorted octahedron, seven faces of which are centered by oxido groups. The eighth face is unsymmetrically capped with an oxygen atom from one of the diketonate ligands. Three of the

The composition of 1 was established by elemental

analysis and single-crystal X-ray structure determination. X-

ray powder diffraction analysis confirmed the purity of the



Figure 1. Molecular structure of [Bi<sub>9</sub>O<sub>7</sub>(hfac)<sub>13</sub>] (1). Only the core bismuth (orange) and oxygen atoms (red) are shown as balls. Fluorine and hydrogen atoms of the  $\beta$ -diketonate ligands are omitted for clarity. Bond lengths [Å]: Bi-O(oxido) 2.091(4)-2.485(4), Bi-O(hfac) 2.193(4)-2.831(5) (see Supporting Information for further details).

seven oxido groups centering the octahedron act as  $\mu_4$ -bridges to which  $Bi(hfac)_x$  (x = 3 or 4) arms are attached. This structure directly resembles the oxido alkoxide and oxido silanolate clusters  $[Bi_6(\mu_3-O)_4\{\mu_3-OBi(OR)_4\}_3(\mu_3-OR)]$  (R =  $C_6F_5$ ,<sup>[6]</sup> SiMe<sub>3</sub>,<sup>[8b]</sup>) described recently. However, the latter are slightly different in that the eighth face of the Bi<sub>6</sub> core is centered by a  $\mu_3$ -OR group, and all three arms have four OR ligands coordinated to the bismuth atom.

The structure of 1 helps to explain the behavior of this nonanuclear compound in solution. The molecule remains

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intact in noncoordinating solvents such as dichloromethane (low solubility) according to NMR spectroscopy (Figure 2 a,b) and mass spectrometry. Single peaks observed for both <sup>1</sup>H and <sup>19</sup>F in the NMR spectra of **1** indicate that the



Figure 2. <sup>1</sup>H and <sup>19</sup>F NMR spectra of 1 in  $CD_2Cl_2$  (a, b), 1 in  $(CD_3)_2CO$  (c, d; peaks marked with an asterisk correspond to  $[Bi(hfac)_3]$ , and 2 in  $(CD_3)_2CO$  (e, f) at room temperature.

diketonate ligands exhibit fluxional behavior in solution at room temperature. The solubility of 1 in CH<sub>2</sub>Cl<sub>2</sub> is essentially increased by addition of a small amount of Hhfac to the solution, and single crystals of 1 can be grown therefrom by lavering with hexanes. On the other hand, in coordinating solvents (acetone, THF, acetonitrile) dissociation of the nonanuclear core molecule occurs, as evidenced by the appearance of two peaks in both <sup>1</sup>H and <sup>19</sup>F NMR spectra (Figure 2 c,d). One peak in each spectrum was identified as corresponding to the solvated form of [Bi(hfac)<sub>3</sub>]. Mass spectrometric investigation of the acetone solution containing 1 revealed a series of new peaks centered around 5030, 5467, 5903, 6374, 6749, 7250, 7658, and 8062 Da (Figure 3a). These peaks indicate aggregation processes of the Bi-oxido core in acetone, since the molecular mass of the initial  $[Bi_9O_7(hfac)_{13}]$ cluster is 4684. After one week, the single group of peaks observed around 12230 Da in the mass spectrum of the above



*Figure 3.* Negative-ion MALDI-TOF mass spectra of **1** in acetone a) immediately on dissolution and b) after one week.

solution (Figure 3b) confirmed that a high-nuclearity species was formed.

The crystal structure of the new oxido diketonate product  $2^{[16]}$  obtained from solution revealed a giant  $[Bi_{38}O_{45}]^{24+}$  core cluster with 24 diketonate groups located on its surface (Figure 4a). The nearly spherical molecule of **2** has a size of



**Figure 4.** a) Molecular structure of  $[Bi_{38}O_{45}(hfac)_{24}]$  (2). Only the core bismuth (orange) and oxygen atoms (red) are shown as balls. b)  $Bi_6O_9$  core unit. Bond lengths [Å]:  $Bi-O(\mu_6)$  2.52–2.62,  $Bi-O(\mu_4)$  2.27–2.47 (see Supporting Information for further details).

about 21 Å and contains the largest known homometallic bismuth oxido cluster. A unit with more bismuth atoms was found<sup>[8b]</sup> in the recently heterometallic cluster  $[Bi_{50}Na_2O_{64}(OH)_2]^{22+}$ . Within the bismuth oxido core a central Bi<sub>6</sub> unit can be identified whose metal atoms are connected only to oxido centers. All other 32 bismuth atoms are coordinated to both oxido and diketonate ligands, though eight of those that are directly attached to the  $\mu_4$ -O atoms of the central core make relatively long (2.69-3.08 Å) contacts with capping groups. The central unit consists of an octahedron of bismuth atoms, each face of which is centered by an oxido ligand (Figure 4b). In addition, a  $\mu_6$ -O atom, which is unique for homometallic bismuth oxido clusters, resides at the center of the octahedron, on an inversion center. The molecule of 2 has no other symmetry elements. The surface diketonate ligands exhibit some degree of disorder; nevertheless, they could be successfully refined, and the whole structure is thus well ordered.

Alternatively, the structure of the bismuth oxido cluster in **2** can be described as assembled from 13 octahedral edgesharing  $Bi_6$  units. The arrangement of bismuth atoms is close to an fcc structure in which all of the tetrahedral and some of the octahedral voids are occupied by oxygen atoms. While the basic structural motif in **2** resembles that in  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>, the



individual Bi–O bond lengths and Bi-O-Bi bond angles show some significant deviations.

Aggregation of the bismuth oxido cluster occurs on dissociation of  $[Bi(hfac)_3]$  from **1** according to Equation (2).

$$45 \left[ \text{Bi}_9 \text{O}_7(\text{hfac})_{13} \right] \to 7 \left[ \text{Bi}_{38} \text{O}_{45}(\text{hfac})_{24} \right] (2) + 139 \left[ \text{Bi}(\text{hfac})_3 \right]$$
(2)

Integration of the NMR spectrum in THF gave a proton ratio for **2**:[Bi(hfac)<sub>3</sub>] of 29.8:70.2 (the theoretical value is 28.7:71.3). Such ligand redistribution in polar solvents is a well-known phenomenon<sup>[17]</sup> for heteroleptic metal  $\beta$ -diketonates. While **2** is insoluble in noncoordinating and aromatic solvents, the striking feature of this giant molecule is its solubility without decomposition in coordinating solvents such as acetone, THF, acetonitrile, DMSO, alcohols, and diethyl ether. Oxido diketonate **2** can be recrystallized from these solutions, for which both <sup>1</sup>H and <sup>19</sup>F NMR spectra show single peaks (Figure 2e,f), and the mass spectrum is similar to that shown in Figure 3b.

In conclusion, we have demonstrated that a fluorinated tetraol indeed functions as a source of both diketonate and oxido groups in the presence of a base acting as an irreversible proton sink. This synthetic pathway has been confirmed by the isolation of the first bismuth oxido diketonate [Bi<sub>9</sub>O<sub>7</sub>-(hfac)<sub>13</sub> in quantitative yield. Our preliminary results indicate that oxido diketonates of other metals can be obtained by this approach. Importantly, the technique can also be applied to the synthesis of heterometallic oxido diketonates that are immediate precursors for functional oxide materials. We found that in coordinating solvents the nonanuclear oxido diketonate undergoes dissociation of [Bi(hfac)<sub>3</sub>] followed by aggregation into the giant oxido cluster  $[Bi_{38}O_{45}(hfac)_{24}]$ . The latter could serve as a model for studying the chemistry of bismuth oxide nanoparticles. Moreover, the assembly of this molecule shows the way for construction of other nanosized oxido clusters of metals that exhibit a similar coordination environment in their oxido compounds, such as lead and the lanthanides.

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