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Synthesis and molecular structure of $Bi_4Ba_4(\mu_4\text{-}O)_2(\mu_3\text{-}OEt)_8$-$(\mu\text{-}OEt)_4(\eta^2\text{-}thd)_4$ (Hthd = 2,2,6,6-tetramethylheptane-3,5-dione). An example of the formulation of a mixed-metal alkoxide assisted by dioxygen

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The reaction between bismuth ethoxide and $[Ba(thd)_2]_4$ (Hthd = 2,2,6,6-tetramethylheptane-3,5-dione) afforded the octanuclear $Bi_4Ba_4(\mu_4\text{-}O)_2(\mu_3\text{-}OEt)_8(\mu\text{-}OEt)_4(\eta^2\text{-}thd)_4$ species in high yield, the structure being determined by single-crystal X-ray diffraction; the formation of this species was precluded in anaerobic media.

Numerous advanced oxide materials based on bismuth display attractive properties for applications in microelectronics or optoelectronics for instance.[1a] In recent years [1b] novel materials with interesting ferroelectric properties have appeared in the literature, $Bi_4Ti_3O_{12}$ and $MBi_2Ta_2O_9$ (M = Sr or Ba) are representative examples. The compound $SrBi_2Ta_2O_9$ possesses a high relative permittivity and shows almost no fatigue up to 10^{12} cycles,[2] it is thus a very good candidate for non-volatile memories and dynamic random access memories instead of $PbTi_{1-x}Zr_xO_3$ (PZT).

Chemical routes to such materials remain scarce. We have previously reported investigations on the bismuth–titanium system.[3,4] We wish to report now the results obtained on the Bi–Ba system. Mixed-metal alkoxides based on bismuth are, to the best of our knowledge, limited to the alkali-metal species $Na_4Bi_2O(OBu^t)_8$, $KBi(OBu^t)_4$,[5] several Na–Bi aryloxides such as $Na_2Bi_4O_2(OC_6F_5)_{10}$, $[NaBi(OC_6F_5)_4(thf)]_\infty$ or $Na_4Bi_2(\mu_6\text{-}O)(OC_6F_5)_8(thf)_4$,[6–8] and a few transition-metal species namely $[BiCl_3OV(OC_2H_4OMe)_3]_2$[9] $Bi_4Ti_3O_4(OEt)_{16}$ and $BiTi_2O(OPr^i)_9$.[4] As can be noticed, formulations containing elements related to materials are scarce. This is probably due to the limited reactivity of bismuth alkoxides toward other metal alkoxides. Reactions between bismuth alkoxides $Bi(OR)_3$ (R = Et or Pr^i) and other oxide precursors, namely β-diketonates $[M(thd)_2]_m$ (M = Ba, Sr or Ca; Hthd = 2,2,6,6-tetramethylheptane-3,5-dione) were thus investigated.

The reaction between freshly prepared $Bi(OEt)_3$ and $[Ba(thd)_2]_4$ in toluene (Bi : Ba stoichiometry 1 : 1) proceeded by rapid dissolution of the bismuth species at room temperature.† A crystalline compound whose analytical data account for a Bi : Ba stoichiometry of 1 : 1 was isolated in high yield. Its IR spectrum shows four absorption bands in the ν(C=O) vibration region at 1587, 1575, 1533 and 1500 cm^{-1} respectively. These observations, especially the absence of an absorption band at 1550 cm^{-1}, are in favour of a η^2 co-ordination mode for the β-diketonate ligands.[12] This was confirmed by the molecular structure established by single-crystal X-ray diffraction of this crystalline compound, namely $Bi_4Ba_4(\mu_4\text{-}O)_2(\mu_3\text{-}OEt)_8(\mu\text{-}OEt)_4$-$(\eta^2\text{-}thd)_4$ **1**.‡ The structure (Fig. 1) is based on a central $[Ba_4O_2(thd)_4]$ unit connected to four $Bi(OEt)_3$ moieties and displays a C_2 axis. The two μ_4-oxo ligands O(1) and O(2) act as assembling ligands between two Bi and two Ba atoms. Triply bridging ethoxide ligands are additional assembling ligands between barium and bismuth atoms. The barium atoms are eight-co-ordinate, each atom being connected to one oxo ligand, one μ-OEt and the chelating tetramethylheptanedionate. The bismuth atoms are four-co-ordinate with a distorted pyramidal environment and a stereochemically active lone pair. The barium–oxygen distances spread over the range 2.59(3) to 3.00(3) Å following the order Ba–O (thd) < Ba–μ_4-O ≈ Ba–μ-OR < Ba–μ_3-OR. The Bi–O distances range from 2.09(2) Å for the oxo ligand to 2.46(2) Å for the doubly bridging OEt ones. The latter values are quite similar to the data observed for $BiTi_2(\mu_3\text{-}O)(\mu\text{-}OPr^i)_4(OPr^i)_5$.[4] The bite angles of the β-diketonato ligands have usual values [average 67.1(10)°]. The μ_4-oxo ligands have a severely distorted tetrahedral surrounding [Ba–O–M, M = Bi or Ba, varying from 98.8(3)° to 150.0(16)°].

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† All reactions were conducted under nitrogen using Schlenk tubes and vacuum-line techniques. Compounds $Bi(OBu^t)_3$[10] and $[Ba(thd)_2]_4$[11] were prepared according to the literature and purified by sublimation under vacuum. The compound $Bi(OEt)_3$ was freshly prepared by alcoholysis (2 ml ethanol) of $Bi(OBu^t)_3$ (0.89 g, 2.09 mmol) in toluene (8 ml). The reaction medium was stirred for 30 min and evaporated to dryness. A solution of $Ba(thd)_2$ (1.02 g, 2.02 mmol) in toluene (20 ml) was then added to a suspension of $Bi(OEt)_3$ in toluene. Solubilisation occurred instantaneously. After stirring for 5 h at room temperature, the filtrate was concentrated to ≈7 ml. Small colourless prisms of **1** were obtained at −20 °C (0.98 g, 70%). Compound **1** was soluble in common organic solvents but poorly soluble in ethanol; **1** decomposed at 170 °C/2 × 10^{-4} Torr (1 Torr = 133.322 Pa) into metallic bismuth. FTIR (cm^{-1}): 1587, 1575, 1533, 1500 ν(C=O); 1413, 1270, 1242, 1223, 1185, 1150, 1129, 1091, 1040, 954, 933, 886, 874, 820, 789, 752, 728, 592, 538, 514, 469 ν(M–O); ^1H NMR ($CDCl_3$) δ 5.48, 5.47 (s, CH, 4 H), 4.75, 4.72, 4.53, 4.51, 4.18 (q, CH_2, 24 H, 4 : 4 : 4 : 4 : 8, *J* = 7 Hz), 1.31, 1.1 (t, CH_3, 36 H, 27 : 9, *J* = 7 Hz), 1.06, 1.04 (s, CH_3 72 H) (Found: C, 30.77; H, 5.27; Ba, 20.65; Bi, 31.53. Calc. for $C_{34}H_{68}Ba_2Bi_2O_{11}$: C, 30.35; H, 5.09; Ba, 20.41; Bi, 31.06%).

‡ Crystal data for **1**: $C_{68}H_{136}Ba_4Bi_4O_{22}$, *M* = 2691.10, orthorhombic, space group *Pbcn*, *a* = 15.799(4), *b* = 22.635(9), *c* = 25.456(7) Å, *U* = 9103(8) Å^3, D_c = 1.96 g cm^{-3}, *Z* = 4, μ(Mo-Kα) = 94.4 cm^{-1}. Crystals suitable for X-ray analysis were obtained directly from the reaction medium. 4822 Data, of which 4238 were unique, were collected at low temperature (−100 °C) on an Enraf-Nonius CAD-4 diffractometer with 2–20°. The structure was solved by direct methods (SHELXS 86)[13] and successive Fourier maps. Computations were performed by using the PC version of CRYSTALS.[14a] Only barium and bismuth atoms were anisotropically refined because of the low number of reflections. The structure was refined by least-squares techniques with approximation in three blocks to the normal matrix. 1623 Reflections with $I > 3\sigma(I)$ were used to solve and refine the structure: *R* = 0.057, *Rw* = 0.064 (217 variables). Empirical absorption correction using DIFABS[14b] was applied. CCDC reference number 186/860.

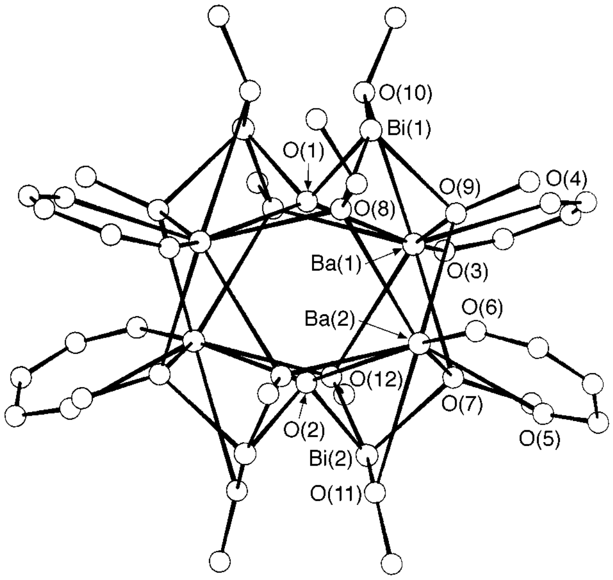

Fig. 1 Molecular structure of $Bi_4Ba_4(\mu_4\text{-}O)_2(\mu_3\text{-}OEt)_8(\mu\text{-}OEt)_4(\eta^2\text{-thd})_4$ showing the atom numbering scheme. Pertinent bond lengths (Å) and angles (°): Bi(2)···Bi(2) 3.288(4), Ba(1)···Bi(1) 3.832, Ba(1)···Ba(2) 4.282, Ba(2)···Bi(2) 3.842, Ba(1)–O(1) 2.87(1), Ba(1)–O(3) 2.59(3), Ba(1)–O(4) 2.64(3), Ba(1)–O(7) 2.77(3), Ba(1)–O(9) 2.82(3), Ba(1)–O(10) 3.00(3), Ba(2)–O(8) 2.90(3), Bi(1)–O(1) 2.09(2), Bi(1)–O(8) 2.17(3), Bi(1)–O(9) 2.20(3), Bi(1)–O(10) 2.39(3); O(3)–Ba(1)–O(4) 67.6(9), O(1)–Bi(1)–O(8) 80.8(10), O(1)–Bi(1)–O(9) 81.1(9), O(1)–Bi(1)–O(10) 67.6(9), O(8)–Bi(1)–O(9) 83.2(11), O(9)–Bi(1)–O(10) 91.0(10), Ba(1)–O(1)–Ba(1) 150.0(16), Ba(1)–O(1)–Bi(1) 99.7(3), Ba(1)–O(10)–Bi(1) 90.9(8)

The Ba_4 cycle is *gauche* with Ba···Ba distance of 4.28 Å, and Ba(1)–Ba(2)–Ba(1′)–Ba(2′) and Ba(2)–Ba(1′)–Ba(2′)–Ba(1) torsion angles of 45.38° and −44.22° respectively. The Bi(1)–Bi(1′) and Bi(2)–Bi(2′) directions [Bi···Bi distances of 3.288(4) Å] are nearly perpendicular to the C_2 axis of the molecule thus leading to a distorted Bi_4Ba_4 dodecahedron.

The proton NMR spectra for $Bi_4Ba_4O_2(OEt)_{12}(thd)_4$ in $CDCl_3$ or C_7D_8 are a function of the concentration thus suggesting the presence of different molecular species. No peaks corresponding to bismuth ethoxide were observed, thus excluding dissociation. The major species (≈90% in concentrated $CDCl_3$ solutions) shows a singlet at δ 5.47 for the methine groups of the β-diketonate ligands and three types of CH_2 groups resonating as quadruplets at δ 4.75, 4.53 and 4.18 (integration ratio 4:4:4). These data are consistent with the solid-state structure. The minor species displays signals corresponding to OEt as well as thd ligands. The most likely hypothesis is the presence of isomers of **1**. They can derive from a change in the co-ordination modes of the thd ligands acting as bridging–chelating ligands while alkoxide ligands of type μ_3 become μ. This hypothesis is supported by the FTIR spectra of **1** in toluene, which show the appearance of ν(CO) stretching absorption bands at 1550 cm^{-1} characteristic of bridging β-diketonates,[12] as well as in the ^1H NMR by the increase of the intensity of the peak at high field attributed to the μ-OEt ligands.

Compound **1** can be considered as resulting from the association between $Bi(OEt)_3$ and $Ba_4O_2(thd)_4$. The building up of mixed-metal alkoxides *via* assembling oxo ligands is a common feature especially if large oxophilic metals are involved. The oxo ligand is generally considered to be derived from the formation of a dialkyl ether and appears as a means of achieving high co-ordination numbers for the metal.[15] Compound **1** is obtained reproducibly in high yield (70%) and the initial bismuth ethoxide moieties are retained in the molecular structure of **1**. The formulation of **1** as an oxo species is thus puzzling. Molecular oxygen is actually the source of the oxo ligand. Indeed, no reaction is observed if bismuth ethoxide and barium 2,2,6,6-tetramethylheptane-3,5-dionate are mixed in toluene or hexane under vacuum and thus in totally anaerobic conditions. Addition of dioxygen induces a reaction and thus the rapid dissolution of bismuth ethoxide. No reaction was observed with other potential O-donors such as carbon dioxide, another possible impurity of the solvent, or nitrous oxide. The ability of the very oxophilic barium center to react with dioxygen has been demonstrated and hexanuclear barium–thd–peroxide species have been isolated although the factors favoring their formation are not widely known.[16] On the other hand, bismuth(III) species are known to be oxidation catalysts.[17] The reaction and/or uptake of dioxygen is extremely rapid and no intermediate species could be evidenced. The formation of tetranuclear barium oxo clusters Ba_4O_4 *in situ* was reported either by addition of dioxygen or by ‘aging’; they were shown to act as a polydentate ligand toward niobium pentaethoxide[18] or titanium isopropoxide[19] *via* their peripheral oxo ligands. However, for those systems, oxo ligands were not necessary to ensure the build up of the mixed-metal species, their effect was only a modification of the stoichiometry between the metals and of the structure. Our observations are in direct contrast since no reaction was observed in the absence of dioxygen. The assembling $Ba_4O_2(thd)_4$ tetradentate ligand can be formally considered as being derived from the initial tetranuclear barium tetramethylheptanedionate by substitution of the four bridging β-diketonate ligands by two oxo ligands. Triply bridging ethoxide ligands of the bismuth alkoxide moieties ensure further connection between the barium atoms. No reaction was detected between $[Ba(thd)_2]_4$ and dioxygen in toluene over at least 2 weeks. This observation suggests assistance of the bismuth species for the activation of dioxygen and formation of the barium oxo species.

In conclusion, we had previously reported that controlled hydrolysis reactions could promote the formation of heterometallic alkoxides for inert systems by generating the necessary oxo ligand.[3,4] The study of the Bi–Ba system shows dioxygen to be another reactant able to promote homogeneity at a molecular level.

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