

Tuning Metal Stoichiometry in Heterometal Alkoxides: First Structurally Characterised Molecular Precursor to BaZrO₃[☆]

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Manipulable metal ratios are accessible in a series of heterometal Ba-Zr alkoxides by changing the size and the charge of the ligands. The synthesis and characterisation of four mixed-metal Ba-Zr species [BaZr₂(OtBu)₁₀] (**1**), [Ba₂Zr(OtBu)₆(tBuOH)(THF)₂] (**2**), [BaZr(OtBu)₆(THF)₂] (**3**) and [BaZr(OH)(OiPr)₅(iPrOH)₃]₂ (**4**), based on different Ba/Zr stoichiometries, are reported. The molecular structures of **1**, **2**, and **4** have been determined by single-crystal X-ray diffraction studies. **1** exhibits a bow-tie structural motif in which a trigonally distorted six-coordinate barium atom is chelated by two bipyramidal {Zr(OtBu)₅}⁻ units. **2** reveals a triangular "Ba₂Zr(μ₃-OtBu)₂(μ₂-OtBu)₃" core structure formed by the fusion of three octahedra built about two Ba atoms and a Zr atom. The structure is unique in terms of the

distribution of terminal ligands at each of the metal centers. One of the barium atoms possesses one -OtBu and one tBuOH as terminal ligands, while the terminal ligands on the second barium atom are two THF molecules; the zirconium center bears -OtBu groups as the terminal ligands. Hydrolysis of compound **3** with one equivalent of water, followed by alcoholysis (iPrOH) of the resulting product, gave **4**. The structure of **4** shows a planar tetrametallic Ba₂Zr₂ frame capped by two μ₃-hydroxo ligands. The coordination figure of the zirconium atoms resembles a distorted octahedron, whereas the geometry of the barium centers is best described as capped trigonal prisms. Both **3** and **4** are excellent precursors to morphologically pure BaZrO₃ ceramic by the sol-gel process.

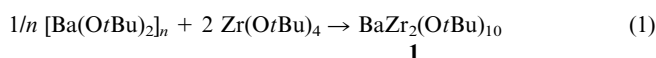
Interest in metal alkoxides is stimulated by their suitability as useful reagents for chemical synthesis of high-purity oxides and metal oxide/metal composites.^{[1][2]} The insoluble and polymeric nature of simple alkoxides of alkaline earth elements [M(OR)₂]^[3] limits their direct application in sol-gel techniques, however, solubilisation can be achieved by the addition of transition metal alkoxides [e.g., Ti(OR)₄, Zr(OR)₄].^[4] Although this strategy of forming soluble heterometallic preceramic aggregates is advantageous, particularly in view of the mixed-metal composition of most of the advanced ceramics [e.g., YBa₂Cu₃O_{7-δ}, MM'O₃ (M^{IV} = Ti, Zr, Sn; M' = Ca, Sr, Ba, Pb)], the nature (with regard to the metal stoichiometry) of product(s) formed in such "heterometal solutions" remains ambiguous or poorly characterised.^[5] Furthermore, the equilibrium among various heterometal species existing in the solution, and the kinetics of their formation, complicate the precursor chemistry. Since various heterometal combinations are possible due to the structure potential (terminal, μ₂ or μ₃) of the alkoxo ligand,^[6] the consequences (e.g., metal segregation, phase inhomogeneity) are encountered during the processing of ceramic material.^[5] Of principal interest in this context are heterometal molecules, tailored to the need of the targeted ceramic which in turn requires (i) the development of synthetic and chemical approaches for a precise control over the metal stoichiometry, and (ii) the unequivocal characterisation of molecular precursors as well as the products ob-

tained from their partial hydrolysis reactions (oxo-alkoxides) as they are the real intermediates of a sol-gel process and can therefore reveal how a molecular compound begins to form extended networks. A recent study on the solubility isotherms of Ba(OR)₂-Zr(OR)₄-ROH (R = Et, iPr) ternary systems reports the formation of various heterobimetallic alkoxides with different Ba/Zr ratios. An oxo-alkoxide of composition BaZrO(OR)₄·n(ROH) is reportedly formed in the equimolar alcoholic solution of barium and zirconium alkoxides.^[2d] To the best of our knowledge, a synthetic approach for a rational control over the Ba/Zr metal stoichiometry has not been described so far.

Results and Discussion

Using [Ba(OtBu)₂]_n and Zr(OtBu)₄ as building "bricks", we have synthesised a series of molecular alkoxides with different (1:2, 2:1, 1:1) Ba/Zr stoichiometries. The manipulation of metal ratios in well-defined molecular derivatives provides optimism when looking towards tailor-made molecules and demonstrates the governing role that ligands [alkoxo (OR), oxo (O²⁻), or neutral (ROH, THF)] can play in anchoring stable mixed-metal clusters. The Ba/Zr derivatives based on 1:1 stoichiometry of the metals have proved to be excellent precursors for clean and selective synthesis (sol-gel) of BaZrO₃ ceramic at much lower sintering temperatures than are usually required for the solid-state synthesis.^[7]

The reaction (1:2 molar ratio) of $[\text{Ba}(\text{OtBu})_2]_n$ with $\text{Zr}(\text{OtBu})_4$ in refluxing toluene (Eq. 1) produces a clear pale yellow solution which on cooling (0°C) offers $\text{BaZr}_2(\text{OtBu})_{10}$ (**1**) as large transparent crystals (72% yield).



The analytical data are compatible with the formulation of **1**, and the molecule is found to be monomeric in benzene (cryoscopy). The NMR data are deceptively simple and only a single set of ligand resonances is observed in the room-temperature ^1H - and ^{13}C -NMR spectra in contrast to the solid-state NMR spectrum (vide infra). The low-temperature NMR studies ($[\text{D}_8]\text{toluene}$) show **1** to be highly fluxional and the intramolecular ligand rearrangements or site exchange processes, causing equivalence (on an NMR time scale) of all 10 *OtBu* groups could not be frozen out, even at -80°C . **1** is stable up to $200^\circ\text{C}/10^{-2}$ Torr; at higher temperatures ($> 230^\circ\text{C}$) partial decomposition was observed with $\text{Zr}(\text{OtBu})_4$ as the only volatile material.

The result of the single crystal X-ray diffraction analysis of $\text{BaZr}_2(\text{OtBu})_{10}$, including the numbering system, is shown in Figure 1a, and the pertinent bond lengths and angles are compiled in Table 1. The central barium atom, encapsulated by six bridging (μ_2)-*OtBu* groups of two tridentate monoanionic $[\text{Zr}(\text{OtBu})_5]^-$ units, is present in a trigonally distorted octahedral geometry. The crystallographically inequivalent Zr centers [Zr(1) and Zr(2)] are present in distorted trigonal bipyramidal environments. With respect to Ba–O distances (Table 1) in the molecule (Figure 1a), the two $[\text{Zr}(\text{OtBu})_5]^-$ units are coordinated to Ba^{2+} in an asymmetric fashion. The Ba–O distances clearly fall in three ranges [Ba–O(1) = 2.651(3), Ba–O(6) = 2.656(3); Ba–O(8) = 2.768(3), Ba–O(3) = 2.806(3); Ba–O(2) = 2.947(3), Ba–O(7) = 2.965(3) Å] and the barium coordination sphere can be precisely defined as “2 + 2 + 2”. The Ba–O(1) and Ba–O(6) distances are significantly shorter than the remaining four Ba–O contacts, and in a “building block” approach, the architecture of **1** can also be described as an interaction of two tetrahedral $\text{Zr}(\text{OtBu})_4$ moieties with a bent O(1)–Ba–O(6) unit. The terminal (av. 1.951 Å) and bridging (av. 2.064 Å) Zr–O distances are comparable with those observed in $[\text{KZr}(\text{OtBu})_5]_2$.^[8] To our knowledge, **1** reveals a structural type unprecedented among metal alkoxides, however, the BaZr_2O_6 core in **1** is comparable with the molecular structures of $[\text{M}(\mu_2\text{-OtBu})_3\text{M}'(\mu_2\text{-OtBu})_3\text{M}]$ ($\text{M} = \text{Ge}^{\text{I}}, \text{Sn}^{\text{II}}, \text{Pb}^{\text{II}}$; $\text{M}' = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ or Pb) alkoxide derivatives.^[9] However, in contrast to the linear array of metallic elements in $\text{M}'\text{M}_2(\text{OtBu})_6$ compounds, the $\text{Zr}\cdots\text{Ba}\cdots\text{Zr}$ arrangement in **1** is bent (149.61°) due to the violation of the three-fold symmetry of $\text{Zr}(\text{OtBu})_5^-$ units and as an effect of the two different orientations of the ZrO_5 bipyramids, with respect to the central BaO_6 unit. An interesting influence of the alkoxide steric profile on the structural type (resulting from same metal stoichiometry) is observed on comparing **1** with the corresponding isopropoxy derivative

$[\text{BaZr}_2(\text{OiPr})_{10}]_2$ ^[4b]; whereas **1** is monomeric and displays a bow-tie structural motif with a slightly bent arrangement of metal atoms, $[\text{BaZr}_2(\text{OiPr})_{10}]_2$ is dimeric and the metallic elements form a closed triangular structure. The relative and total intensities of the signals in the ^{13}C CP-MAS/NMR spectrum of **1** (Figure 1b) corroborates the observed solid-state structure. A line deconvolution experiment corresponds to the presence of 10 *OtBu* groups and the observed spectral pattern arises from the accidental overlapping of some of the *OtBu* groups.

Figure 1a. Ball-and-stick representation of the molecular structure of **1** with selected atom labelling; hydrogen atoms of the *tert*-butyl moieties are omitted for clarity

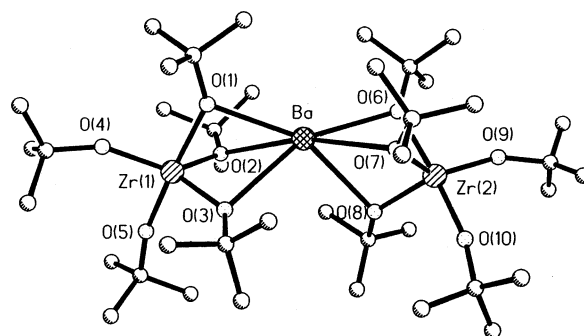


Figure 1b. Solid-state ^{13}C CP-MAS NMR spectrum of **1**

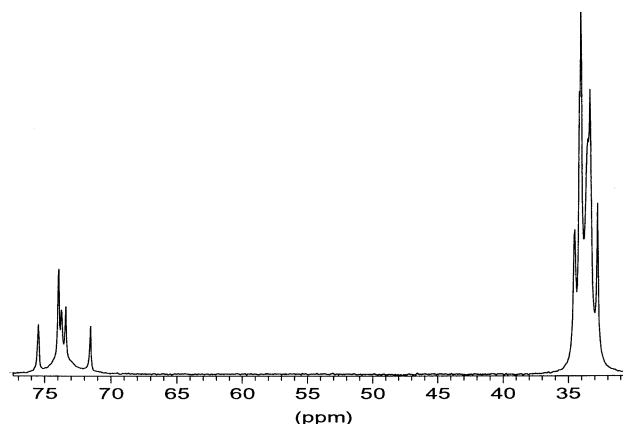
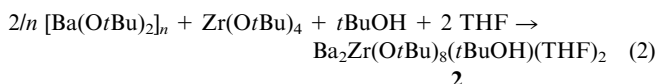


Table 1. Selected bond lengths [Å] and angles [$^\circ$] of compound **1**

Ba–O(1)	2.651(3)	Ba–O(2)	2.947(3)
Ba–O(3)	2.806(3)	Ba–O(6)	2.656(3)
Ba–O(7)	2.965(3)	Ba–O(8)	2.768(3)
Zr–O(4)	1.952(3)	Zr–O(1)	2.149(3)
Zr–O(2)	2.020(3)	Zr–O(3)	2.017(3)
O(1)–Ba–O(6)	144.25(9)	O(8)–Ba–O(3)	95.10(8)
O(1)–Ba–O(3)	60.80(9)	O(1)–Ba–O(2)	57.50(10)
O(3)–Ba–O(2)	63.50(8)	O(4)–Zr(1)–O(2)	133.64(14)
O(4)–Zr(1)–O(3)	126.58(14)	O(3)–Zr(1)–O(2)	97.28(13)
O(1)–Zr(1)–O(5)	175.96(12)	Zr(1)–O(1)–Ba	93.78(10)
Zr(1)–O(2)–Ba	88.21(10)	Zr(1)–O(3)–Ba	92.30(10)

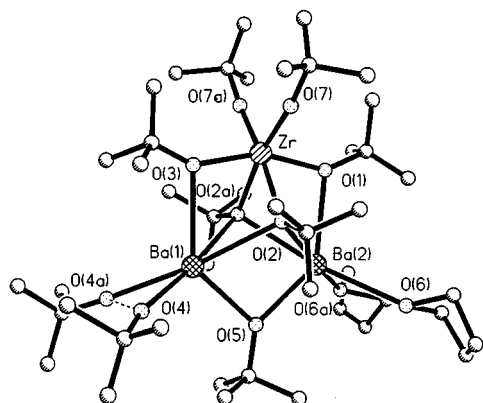
In order to investigate the nature of product formed by reversing the metal ratios in **1**, two equivalents of $[\text{Ba}(\text{OtBu})_2]_n$, dissolved in a THF/*t*BuOH mixture were treated with $\text{Zr}(\text{OtBu})_4$ (1 equiv.) to obtain $\text{Ba}_2\text{Zr}(\text{OtBu})_8(\text{t-}$

BuOH)(THF)₂ (**2**) in a yield of 45% (Eq. 2). Compound **2** is readily soluble in benzene, toluene, and chloroform.



The room-temperature ¹H-NMR spectrum exhibits two resonances for *tert*-butyl protons in a 4:5 integration ratio. The presence of the alcoholic proton is discerned from the NMR signal observed at δ = 4.31 and a broad IR band at 3160 cm⁻¹ (ν OH) indicating an R(M)–O···H–OR bonding.^[10] The THF chemical shifts are observed in the region typical for THF molecules coordinated to metal centers. To probe the persistence of solid-state structure (Figure 2) in solution, low-temperature NMR studies were performed on a [D₈]toluene solution of **2**. The methyl signal intensities decoalesce on lowering the temperature and the best resolved spectrum at –30°C displays four sharp resonances in an intensity ratio of 4:2:1:2. This spectral pattern is characteristically observed for heterometal systems containing the triangulo-MM'₂(OR)₉ unit,^{[4][11]} which in case of **2** can be assigned to the “ZrBa₂(OtBu)₈(*t*BuOH)” substructure, if the *tert*-butyl resonances of the alcohol ligand overlaps with the resonances of three terminal alkoxo ligands present at Ba and Zr centers. These findings are supported by the ¹³C-NMR spectrum (–30°C) which exhibits four resonances each for methyl and tertiary carbon atoms.

Figure 2. Ball-and-stick drawing of the molecular structure of **2**; hydrogen atoms are not drawn for clarity; the dotted line represents the hydrogen bonding between O4 and O4'.



The X-ray study established compound **2** to be Ba₂Zr(OtBu)₈(*t*BuOH)(THF)₂ as depicted in Figure 2. The structure is comprised of a trimetallic framework which, although common among MM'₂(OR)_x alkoxides^[12], is worthy of special note due to the unique ligand (terminal) environments of the metal centers and the inequivalence of the two barium atoms. One of the barium atoms [Ba(1)] achieves an octahedral environment by adding an alcohol (*t*BuOH) ligand, whereas the coordination sphere of Ba(2) is completed by two THF molecules. In contrast to **1**, the zirconium atom in **2** is surrounded by six OtBu groups. The molecule possesses a crystallographic mirror plane passing through the metal atoms and the three doubly bridging oxy-

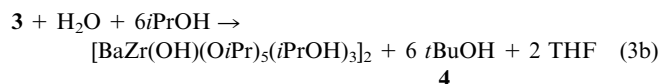
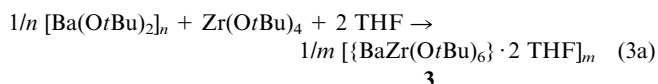
gen atoms [O(1), O(3), and O(5)]. Owing to the much larger size of Ba²⁺ (1.34 Å) compared to Zr^{IV}, the triangular Ba₂Zr core exhibits a long Ba···Ba [3.8617(15) Å] non-bonding contact; the Ba···Zr distances [3.7165(19) Å and 3.7109(18) Å] are almost symmetrical. In view of the published data on other related compounds,^[13] the terminal Ba–O bond lengths clearly allow the distinction of metal–ligand distances; the Ba–O(THF) distances (av. 2.831 Å) being significantly longer than the Ba–O(terminal) bond lengths involving alkoxo or alcohol ligands (av. 2.565 Å). Among the triply bridging (μ₃-)oxygen atoms, O(2) [O(2a)] binds strongly to Ba(2) center [2.687(8) Å] in comparison to Ba(1) [2.740(8) Å]. Although the hydroxylic hydrogen atom could not be located crystallographically, an intramolecular hydrogen bond is evident in the short O(4)···O(4a) (2.471 Å) contact [cf. O(6)···O(6a) = 3.589 Å; O(7)···O(7a) = 2.989 Å]. Furthermore, **2** shows no significant intermolecular contacts of oxygen atoms to other oxygen or metal atoms (> 4 Å) in the crystal as would be the case for intermolecular hydrogen bonding. The Zr–O distances (Table 2) follow the trend: Zr–OR(terminal) (av. = 1.998 Å) < Zr–μ₂–(OR) (av. = 2.105 Å) < Zr–μ₃–(OR) (av. = 2.245 Å). Curiously, the doubly bridging (μ₂-)Ba–O bond lengths (av. = 2.768 Å) are longer than the triply bridging (μ₃-)Ba–O distances (av. = 2.706 Å) which, in analogy to **1**, could lead to the conceptual fragmentation of **2** into neutral building units, Zr(OtBu)₄ and (*t*BuOH)(OtBu)Ba(μ₂-OtBu)₃Ba(THF)₂. Apparently, the coordinating solvents employed in the synthesis of **2** effectively change the degree of aggregation of [Ba(OtBu)₂]_n which seems to alter its Lewis acid-base reaction with Zr(OtBu)₄ to form **2** (Figure 2). Interestingly, the reaction (2:1 molar ratio) of Ba and Zr *tert*-butoxides in the absence of donor solvents produces only BaZr₂(OtBu)₁₀ (**1**) as the soluble species, leaving 1.5 equiv. of Ba alkoxide unreacted, which further supports the preceding argument.

Table 2. Selected interatomic distances [Å] and angles [°] of compound **2**

Ba(1)–O(3)	2.796(14)	Ba(1)–O(2)	2.740(8)
Ba(1)–O(4)	2.565(9)	Ba(1)–O(5)	2.611(15)
Ba(2)–O(1)	2.740(15)	Ba(2)–O(2)	2.673(8)
Ba(2)–O(6)	2.831(11)	Ba(2)–O(5)	2.487(14)
Zr–O(1)	2.123(13)	Zr–O(2)	2.245(8)
Zr–O(3)	2.088(14)	Zr–O(7)	1.998(9)
O(4)···O(4a)	2.471	O(7)···O(7a)	2.989
O(6)···O(6a)	3.589		
O(4)–Ba(1)–O(4a)	57.7(5)	O(6)–Ba(2)–O(6a)	79.0(6)
O(4)–Ba(1)–O(5)	110.9(5)	O(4)–Ba(1)–O(2)	121.7(3)
O(4)–Ba(1)–O(2a)	173.0(4)	O(5)–Ba(1)–O(2a)	76.0(3)
O(2)–Ba(1)–O(2a)	58.0(3)	O(4)–Ba(1)–O(3)	110.9(5)
O(5)–Ba(1)–O(3)	131.9(3)	O(3)–Ba(1)–O(2a)	62.4(3)
O(5)–Ba(2)–O(2)	79.3(3)	O(5)–Ba(2)–O(1)	135.3(5)
O(5)–Ba(2)–O(6)	106.4(4)	O(1)–Ba(2)–O(6)	107.8(4)
O(2)–Ba(2)–O(6a)	167.8(4)	O(2)–Ba(2)–O(1)	62.3(3)
O(7)–Zr–O(7a)	96.6(6)	O(3)–Zr–O(1)	158.3(6)
O(7)–Zr–O(3)	97.8(4)	O(7)–Zr–O(2)	95.4(4)
O(1)–Zr–O(2)	79.8(4)	O(3)–Zr–O(2)	82.7(4)
Ba(1)–O(5)–Ba(2)	98.5(4)	Ba(1)–O(3)–Zr	97.8(5)
Ba(1)–O(2)–Ba(2)	91.0(2)	Ba(1)–O(2)–Zr	95.7(2)

The successful switching of metal ratios from BaZr₂ (**1**) to Ba₂Zr (**2**) prompted us to explore a molecule with a Ba/

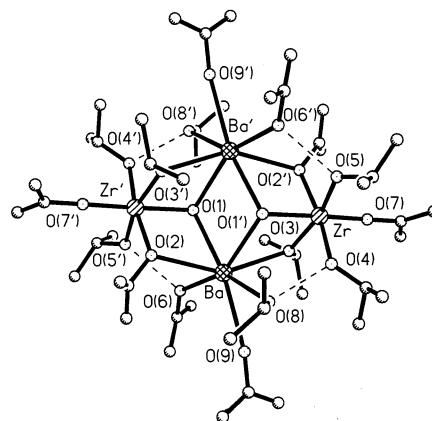
Zr stoichiometry of 1:1 which could act as a model precursor to $\text{MM}'\text{O}_3$ ceramics. A solution of $\text{Ba}(\text{OtBu})_2$ in THF was treated with one equivalent of $\text{Zr}(\text{OtBu})_4$ and the reaction mixture was heated. The clear solution was concentrated in vacuo and cooled (-30°C) to obtain colorless crystals of analytical composition $\text{BaZr}(\text{OtBu})_6(\text{THF})_2$ (**3**) in 65% yield (Eq. 3a). The ^1H -NMR spectrum of **3** displays at room temperature a single resonance for the methyl protons of *OtBu* groups which integrates approximately 6:2 with the resonances corresponding to the two coordinated THF molecules. The ^{13}C -NMR spectrum also shows a single ligand environment. Structurally diagnostic spectra could not be obtained until -73°C . **3** rapidly loses the crystallinity upon removal of the mother liquor, even under a cold stream of nitrogen which precluded a single crystal X-ray diffraction study.



Heterometal aggregates supported by oxo- or hydroxo-assembling ligands are intermediates to oxide ceramics and their characterisation is likely to feature the initial steps of sol-gel chemistry. The hydrolysis of **3** with one equivalent of water followed by alcoholysis with 2-propanol (see Experimental Section) offered $[\text{BaZr}(\text{OH})(\text{OiPr})_5(i\text{PrOH})_3]_2$ (**4**) in a high yield (70%) (Eq. 3b). The room-temperature spectra (^1H and ^{13}C NMR) of **4** are too complex to be diagnostic. The ^1H -NMR spectrum displays several closely associated doublets for the *gem*-dimethyl protons; the methine protons are observed as two multiplets formed by various overlapping septuplets. A similar spectral pattern is observed in the ^{13}C -NMR spectra (solution and solid-state CP MAS). The presence of hydroxylic groups in **4** is established by the intense $\nu(\text{OH})$ band (3340 cm^{-1}) observed in both the solution (CDCl_3) and the solid-state IR spectra and is corroborated by the ^1H -NMR observation ($\delta = 4.65$). The spectral pattern of **4** remains complex even at low temperature (-40°C), however, a downfield migration of $-\text{OH}$ chemical shift is observed on decreasing the temperature. Thus, the fate of compound **4** in solution can not be discerned from the available data.

The solid-state structure of $[\text{BaZr}(\text{OH})(\text{OiPr})_5(i\text{PrOH})_3]_2$ (**4**) reveals a tetranuclear cluster (Figure 3) where the four metal atoms are coplanar due to the requirements of the crystallographic inversion center. The gross structural features of the oxo-metalate framework in **4** are comparable with other compounds adopting an M_4O_{16} edge-shared octahedral arrangement [e.g., $\text{Ti}_4(\text{OEt})_{16}$,^[14] $\text{W}_4(\text{OEt})_{16}$ ^[15]], however, the solvating 2-propanol molecules in **4** provide different coordination numbers to Ba and Zr centers. The Zr atoms are present at the center of slightly distorted octahedra, whereas Ba centers (being seven-coordinate) display a trigonal-prismatic face-capped geometry. The

Figure 3. Ball-and-stick drawing of the molecular structure of **4**; hydrogen atoms are not drawn for clarity



$\text{Ba}_2\text{Zr}_2\text{O}_6$ core is built up from two analogous *seco*-norbucane units fused along one face defined by two barium atoms and two oxygen atoms of the hydroxo groups. A similar face-capping arrangement of hydroxo ligand against a planar tetrametallic (M_4) frame has been observed in $[\text{Eu}_4(\text{OC}_6\text{H}_3i\text{Pr}_2-2,6)_6(\text{OH})_2(\text{NCMe})_6]$ ^[16] and $[\text{Nd}_4(\mu_3-\text{OH})_2(\mu_2, \mu_1\text{-acac})_6(\text{acac})_4]$.^[17] Whereas the doubly bridging oxygen atoms [O(2) and O(3)] are nearly planar (sum of angles = av. 356.61°), the angles around O(1) sum to 316.64° (see Table 3) accounting for a tetrahedral geometry (sp^3 hybridisation) that support the assignment of O(1) [O(1a)] as a μ_3 -hydroxo ligand. The expected dispersion of metal–oxygen bond lengths [$\text{M}-\mu_3\text{-OR} > \text{M}-\mu_2\text{-OR} > \text{M}-\text{O}(\text{terminal})$] is found in ZrO_6 polyhedron with $\text{Zr}-\text{O}$ (terminal) distances (av. 2.048 \AA) being the smallest [cf. $\text{Zr}-\text{O}$ (terminal) in $\text{Zr}_2(\text{OiPr})_8(i\text{PrOH})_2 = 1.984 \text{ \AA}$].^[10b] On the contrary, all the terminal $\text{Ba}-\text{O}$ distances in **4**, are extremely large (av. 2.836 \AA) which can be understood in terms of much reduced donor capacity of the alcohol (ROH) in comparison to the alkoxo (RO^-) ligand. Out of the three terminal alcohol ligands at barium [O(6), O(8), and O(9)], O(6) and O(8) are involved in an intramolecular hydrogen bonding with the terminal alkoxo ligands [O(5) and O(4)] of neighbouring Zr atoms (Figure 3). The short $\text{O}(5)\cdots\text{O}(6')$ (2.664 \AA) and $\text{O}(4)\cdots\text{O}(8)$ (2.614 \AA) separations, together with the bent orientation (away from the $\text{O}\cdots\text{O}$ vector) of $-i\text{Pr}$ fragments, is in accord with the proposed hydrogen bonding.

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Experimental Section

General: All operations were carried out under a dry nitrogen with rigorous exclusion of oxygen and moisture. Tertiary butyl alcohol was dried by distillation from potassium metal and aluminium *tert*-butoxide. All other solvents were distilled from Na/K alloy or LiAlH_4 , prior to use. $\text{Ba}(\text{OtBu})_2$ was prepared by the reac-

Table 3. Selected interatomic distances [Å] and angles [°] of compound **4**

Ba–O(1)	2.718(3)	Ba–O(3)	2.671(3)
Ba–O(8)	2.892(4)	Ba–O(2)	2.679(3)
Ba–O(6)	2.780(3)	Ba–O(9)	2.836(4)
Zr–O(1')	2.172(3)	Zr–O(5)	2.092(3)
Zr–O(4)	2.103(3)	Zr–O(7)	1.951(3)
Zr–O(3)	2.107(3)	Zr–O(2')	2.107(3)
O(1)–Ba–O(1')	74.13(9)	O(2)–Ba–O(1)	63.59(8)
O(1')–Ba–O(3)	61.43(9)	O(1)–Ba–O(9)	160.78(12)
O(9)–Ba–O(6)	89.57(15)	O(9)–Ba–O(8)	57.81(16)
O(3)–Ba–O(2)	149.26(9)	O(3)–Ba–O(1)	87.65(9)
O(3)–Ba–O(6)	105.07(10)	O(2)–Ba–O(6)	77.06(10)
O(1')–Ba–O(6)	143.38(9)	O(1)–Ba–O(6)	71.31(9)
O(3)–Ba–O(9)	95.72(14)	O(2)–Ba–O(9)	115.02(13)
O(1')–Ba–O(9)	123.97(14)	O(3)–Ba–O(8)	87.93(12)
O(2)–Ba–O(8)	107.37(11)	O(1)–Ba–O(8)	141.37(10)
O(6)–Ba–O(8)	146.28(11)	O(1')–Zr–O(7)	176.60(12)
O(7)–Zr–O(4)	94.07(14)	O(7)–Zr–O(5)	98.27(13)
O(7)–Zr–O(3)	97.15(13)	O(5)–Zr–O(4)	90.79(12)
O(5)–Zr–O(3)	164.43(12)	O(4)–Zr–O(3)	90.25(12)
Zr–O(3)–Ba	108.68(12)	Zr'–O(1)–Ba'	106.03(10)
Ba–O(1)–Ba'	105.87(8)	Zr'–O(1)–Ba	104.74(10)
O(4)–Zr–Ba	77.02(9)	O(6)–Ba–Zr'	69.26(8)
O(8)–Ba–Zr	70.15(9)	O(5)–Zr–Ba'	81.71(8)

tion of barium metal and alcohol in the presence of dry ammonia following a published procedure^[18] ($\text{C}_8\text{H}_{18}\text{BaO}_2$: calcd. C 33.88, H 6.39, Ba 48.42; found C 33.01, H 6.43, Ba 48.52). $\text{Zr}(\text{OtBu})_4$ was obtained by the alcoholysis of $\text{Zr}(\text{NEt}_2)_4$ which was synthesised following the literature method.^[19] – ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR: Bruker AC-200 spectrometer and chemical shifts referenced to residual solvent peaks. – ^{13}C CP-MAS NMR: Bruker MSL 200S spectrometer. – IR: Bio-Rad FTS-165 spectrometer. – Elemental analyses: LECO CHN 900 elemental analyser. Established analytical procedures were used to determine the metal contents in the new derivatives.

Synthesis of $[\text{BaZr}_2(\text{OtBu})_{10}]$ (1): $\text{Zr}(\text{OtBu})_4$ (4.45 g; 11.59 mmol) in toluene (15 ml) was added to a slurry of $\text{Ba}(\text{OtBu})_2$ (1.64 g; 5.78 mmol) in toluene. The clear solution obtained after the dis-

solution of $\text{Ba}(\text{OtBu})_2$ was refluxed (16 h) and cooled at 0°C for 24 h, whereupon colourless crystals of **1** were formed (4.36 g; 72%). – ^1H NMR (C_7D_8 , 20°C): δ = 1.51 (CH_3). – ^{13}C NMR (C_7D_8 , 20°C): δ = 32.88 (CH_3); 73.12 (CMe_3). – ^{13}C CP-MAS NMR: δ = 32.74, 33.32, 33.50, 34.02, 34.14, 34.49 (CH_3); 71.51, 73.37, 73.72, 73.89, 75.47 (CMe_3). – MW: calcd. 1069; found 1051. – $\text{C}_{40}\text{H}_{90}\text{BaO}_{10}\text{Zr}_2$: calcd. C 45.71, H 8.29, Ba 13.06, Zr 17.36; found C 45.37, H 8.29, Ba 12.95, Zr 17.05.

Synthesis of $[\text{Ba}_2\text{Zr}(\text{OtBu})_8(\text{tBuOH})(\text{THF})_2]$ (2): To $\text{Ba}(\text{OtBu})_2$ (1.08 g; 3.80 mmol), dissolved in a mixture of *tert*-butyl alcohol (5 ml) and THF (30 ml), was added $\text{Zr}(\text{OtBu})_4$ (0.74 g; 1.93 mmol) in 30 ml of hexane. The reaction mixture was stirred overnight at 50°C. The clear pale yellow solution obtained was reduced to one fourth and left at ambient temperature. Colourless cubes of $\text{Ba}_2\text{Zr}(\text{OtBu})_8(\text{tBuOH})(\text{THF})_2$ (**2**) grew over a period of two weeks. Yield: 0.98 g [45% based on $\text{Zr}(\text{OtBu})_4$]. – ^1H NMR (C_7D_8 , 20°C): δ = 1.35 [$\text{HOC}(\text{CH}_3)_3 + \text{CH}_3$]; 1.56, 1.84 (CH_3); 1.47 (OCH_2CH_2); 3.57 (OCH_2CH_2); 3.35 (OH). – ^1H NMR (C_7D_8 , –30°C): δ = 1.40, 1.66, 1.73, 1.75 (CH_3); 1.42 (OCH_2CH_2); 3.52 (OCH_2CH_2). – ^{13}C NMR (C_7D_8 , –30°C): δ = 25.74 (OCH_2CH_2); 33.20, 34.72, 35.01, 35.57 (CH_3); 67.94 (OCH_2CH_2); 69.19, 70.76, 71.89, 75.18 (CMe_3). – $\text{C}_{44}\text{H}_{128}\text{Ba}_2\text{O}_{11}\text{Zr}$: calcd. C 45.39, H 11.07, Ba 23.59, Zr 7.83; found C 45.08, H 10.85, Ba 23.18, Zr 7.70.

Synthesis of $[\text{BaZr}(\text{OtBu})_6(\text{THF})_2]$ (3): To $\text{Ba}(\text{OtBu})_2$ (1.78 g; 6.27 mmol) in THF (40 ml) was added $\text{Zr}(\text{OtBu})_4$ (2.42 g; 6.30 mmol) and the resulting mixture was stirred at 50°C for 16 h. The sticky solid obtained after the removal of volatiles in vacuo was dissolved in a minimum amount of THF and cooled (–30°C) to yield $\text{BaZr}(\text{OtBu})_6(\text{THF})_2$ (**3**) as a crystalline material which turned into a waxy solid, on removing the mother liquor. Yield: 3.22 g [63% based on $\text{Zr}(\text{OtBu})_4$]. – ^1H NMR (C_7D_8 , 20°C): δ = 1.48 (CH_3), 1.44 (OCH_2CH_2), 3.60 (OCH_2CH_2). – ^{13}C NMR (C_7D_8 , 20°C): δ = 25.19 (OCH_2CH_2), 32.95 (CH_3), 67.61 (OCH_2CH_2), 73.08 (CMe_3). – $\text{C}_{32}\text{H}_{70}\text{BaO}_8\text{Zr}$: calcd. Ba 16.92, Zr 11.24; found Ba 16.47, Zr 11.30.

$[\text{BaZr}(\text{OtBu})_6]_n$: Obtained by prolonged pumping of **3** in vacuo at 50°C. – ^1H NMR (C_6D_6 , 20°C): δ = 1.50 (CH_3). – ^{13}C NMR (C_6D_6 , 20°C): δ = 32.95 (CH_3), 73.08 (CMe_3).

Table 4. Crystal data and data collection parameters for the derivatives **1**, **2**, and **4**

	1	2	4
Empirical formula	$\text{C}_{40}\text{H}_{90}\text{BaO}_{10}\text{Zr}_2$	$\text{C}_{44}\text{H}_{128}\text{Ba}_2\text{O}_{11}\text{Zr}$	$\text{C}_{24}\text{H}_{60}\text{BaO}_9\text{Zr}$
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	$\text{Cmc}2(1)$	$P2(1)/n$
a [Å]	10.508(2)	17.159(3)	11.060(2)
b [Å]	10.631(2)	20.749(4)	15.625(3)
c [Å]	28.500(6)	17.934(4)	21.648(4)
α [°]	81.70(3)	90	90
β [°]	89.59(3)	90	98.76(3)
γ [°]	61.84(3)	90	90
V [Å ³]	2770.7(9)	6385(2)	3697.4(12)
Z	2	4	4
Crystal size [mm]	$0.45 \times 0.30 \times 0.26$	$0.30 \times 0.25 \times 0.10$	$0.40 \times 0.30 \times 0.25$
D_c [Mg m ^{–3}]	1.260	1.216	1.296
μ [mm ^{–1}]	1.114	1.422	1.377
T [K]	293(2)	293(2)	293(2)
Independent reflections	7261	3018	5629
Observed reflections [with $I > 2\sigma(I)$]	6785	2661	4360
GOF on F^2	1.140	1.119	1.012
R	0.0349	0.0538	0.0336
R_w	0.0377	0.0640	0.0473
Max. residual [e Å ^{–3}]	0.797	0.794	0.582
Min. residual [e Å ^{–3}]	–0.817	–0.730	–0.342

Synthesis of $[\text{BaZr}(\text{OH})(\text{OiPr})_5(\text{iPrOH})_3]_2$ (4): To a THF (50 ml) solution of 1.67 g (2.50 mmol) of $[\text{BaZr}(\text{OtBu})_6]_n$, 2.5 mmol solution of water in THF (20 ml) was added dropwise. The workup of the reaction mixture gave a pasty mass poorly soluble in non-polar solvents even on heating and in the presence of *t*BuOH, however, it readily dissolved in hot 2-propanol to give a clear solution. 2-Propanol was pumped off and the resulting solid was redissolved in a minimum amount of *i*PrOH. Large colourless cubes of $[\text{BaZr}(\text{OH})(\text{OiPr})_5(\text{iPrOH})_3]_2$ (4) were formed after 2 d. Yield: 1.26 g {70%, based on the initial amount of $[\text{BaZr}(\text{OtBu})_6]_n$ }. — ^1H NMR (CDCl_3 , 20°C): δ = 1.16, 1.17, 1.24, 1.27, 1.29, 1.43, 1.50 (CH_3); 4.43, 4.74 (CH); 4.65 (OH). — ^{13}C NMR (CDCl_3 , 20°C): δ = 26.12, 27.10, 27.37, 27.49, 27.60, 27.75, 28.27, 28.38, 28.52 (CH_3); 66.66, 68.28, 68.78, 69.45, 70.03, 71.17, 71.33, 71.52, 71.76, 71.97 (CH). — ^{13}C CP-MAS NMR: δ = 27.22, 27.68, 28.15 (CH_3); 63.37, 63.60, 67.44, 68.43, 69.19, 69.60, 70.00, 70.82 (CH). — $\text{C}_{24}\text{H}_{60}\text{BaO}_9\text{Zr}$: calcd. C 39.96, H 8.37, Ba 19.04, Zr 12.64; found C 39.22, H 8.13, Ba 18.79, Zr 12.40.

Crystallography: Monocrystalline specimens were selected from the bulk samples of compounds **1**, **2**, and **4** and sealed in Lindemann capillaries of appropriate dimensions, under inert gas. Crystal data and structure refinement parameters are given in Table 4. Diffraction data were collected with Stoe AED 2 (**1** and **2**) and Stoe IPDS (**4**) diffractometers. The intensities were corrected for Lorentz and polarisation factors, and a semi-empirical absorption correction (ψ scans) was applied for **1** and **2**. The structures were solved by direct methods (SHELXS-86)^[20a] and refined by full-matrix least-squares procedures on all F^2 values (SHELXS-97).^[20b] All non-hydrogen atoms were refined anisotropically. The two hydroxylic protons in **4** were located by difference Fourier techniques and were refined together with the geometrically fixed hydrogen atoms. Crystallographic data for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-101435. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

☆ Dedicated to Professor Heinrich Nöth on his 70th birthday.

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