The Synthesis, Crystal and Molecular Structures of Bimetallic Ethoxides of Barium and Titanium, and Calcium and Titanium: $[M\{Ti_2(\mu_3\text{-}OEt)_2(\mu\text{-}OEt)_3(OEt)_4\}_2]$ (M = Ca, Ba)

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The X-ray single-crystal studies of $[M\{Ti_2(OR)_9\}_2]$ (M = Ca, Ba; R = Et) obtained from EtOH solutions in 1 : 4 metal–titanium ratios show that these complexes, both in the solid state and in solution, are composed of symmetric molecules, in which the central eight-coordinated metal atom is bound to two face-sharing bioctahedral $[Ti_2(OR)_9]$ groups.

The investigation of bimetallic alkoxides of titanium has recently received additional impetus due to their possible application in the synthesis of perovskite oxide phases such as $BaTiO_3$.[1] Information of the composition, structure and properties of these compounds is of particular importance for the elucidation of the mechanism of the so-called alkoxide route to oxide materials.

On the basis of the data obtained on $Ca(OR)_2$–$Ti(OR)_4$–L (L = ROH, C_6H_6, R = Et) systems formation of only $[Ca\{Ti_2(OR)_9\}_2]$ **1**,[2] was observed, whereas in the analogous Ba system three complexes were obtained *viz.* $[Ba\{Ti_2(OR)_9\}_2]$ **2**, $[Ba\{Ti_2(OR)_{10}\}]\cdot 5ROH$ **3** and $[Ba_4\{Ti_2O(OR)_{14}\}]\cdot 8ROH$ **4**. Compounds **2** and **3** precipitate from solutions containing barium and titanium alkoxides in ratios corresponding to the compositions of the complexes. By contrast, crystallization of **4** occurs as soon as the Ba : Ti ratio exceeds 1 : 1 (the mixture of the two complexes, **3** and **4**, was erroneously previously considered[3] to be a single complex $[Ba\{Ti(OR)_6\}]$. Oxidation of 'basic' solutions (*i.e.* containing an excess of $Ba(OR)_2$ relative to the composition of **2**) by traces of oxygen[4] represents a route to the formation of oxocomplexes. For the solutions of barium and titanium isopropoxides which exhibit stronger tendency to oxidation only precipitation of the oxocomplex $[Ba\{TiO(OPr^i)_4\}]\cdot 7/8Pr^iOH$ was observed.[5]

Compounds **1** and **2** crystallize as needles upon cooling at ambient temperature of their ethanol solutions (15–20%, M : Ti = 1 : 3–4). Compound **3** was isolated as prismatic crystals from solutions containing 8% of $Ba(OR)_2$ and 16% of $Ti(OR)_4$ (Ba : Ti ≈ 1 : 2).

X-Ray single-crystal investigation of **1** and **2**† confirmed unambiguously that the central atom (M = Ba or Ca) in the molecules is coordinated by two face-sharing bioctahedral $[Ti_2(OR)_9]$ groups *via* two μ_3- and two μ-OR groups (Fig. 1).

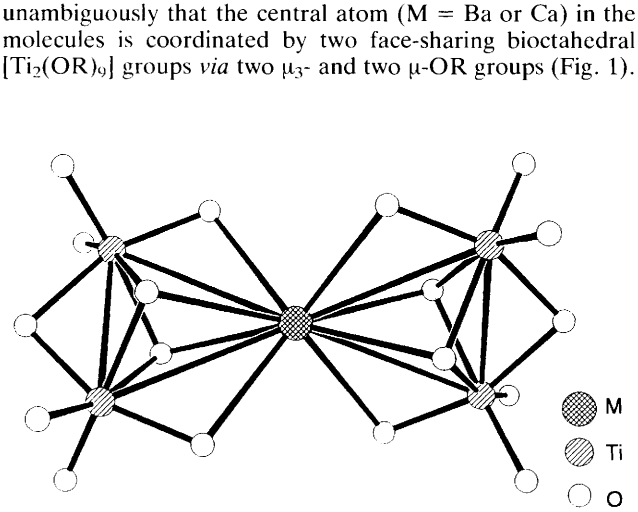

Fig. 1 The structures of $[M\{Ti_2(OR)_9\}_2]$ (M = Ca **1** and Ba **2**) Et-groups are omitted for clarity. Selected interatomic distances: Ca–O 2.458(8)–2.518(9), Ba–O 2.74(2)–2.84(2), Ti–O (terminal) 1.770(11)–1.803(12) **1**; 1.70(3)–1.90(3) **2**, Ti–μ–O(Ca) 1.902(8)–1.935(8) **1**, Ti–μ–O(Ba) 1.86(2)–1.94(2) **2**, Ti–μ–O(Ti 2.023(9)–2.060(13) **1**, 2.03(2)–2.10(3) **2**, Ti–μ_3–O(Ti) 2.079(8)–2.148(10) **1**, 2.07(2)–2.16(2) **2**.

Thus the Ba and, quite unexpectedly Ca are eight-coordinate showing strongly distorted tetragonal antiprismatic geometry. Some difference between the mutual orientation of the $[MTi_2]$ triangles is observed: in the Ba derivative the angle between the normals to the corresponding planes was smaller than in the Ca compound (the average values for two independent molecules in the structures were 65.7° for **1** and 58.5° for **2**). This difference is most probably associated with the shorter M–OR distances in **1**, which also probably leads to some 'flattening' of the Ti_2O_9 units in the Ti···Ti direction in **2** relative to **1** (M–(μ-O)–Ti 97–98° in **1** and 99–102° in **2**).

Comparison of M^{II}–OR bond lengths in **1** and **2** shows that they are similar to those in the corresponding metal oxides $M^{II}O$ and are essentially independent of the nature of the bonding mode of the OR-group. At the same time, the Ti–O bond lengths exhibit a clear-cut correlation with the bonding mode of the OR groups [Ti–O (terminal) < Ti–(μ-OBa) < Ti–μ-OTi < Ti=μ_3-OTi], which provides evidence of high stability of the $[Ti_2(OR)_9]$ groups.

Whereas the Ti–O and M–O bond distances in **1** and **2** are accurate, some of the O–C and C–C distances are unreliable (some values are *ca.* 1.0 Å). Such apparent shortening is probably a consequence of intense thermal motion of the hydrocarbon groups typical for very loosely packed alkoxide crystals [some comments on this may be found in ref 1(*a*)].

It is noteworthy that **1** and **2** (as well as $[Ba\{Zr_2(OPr^i)_9\}_2]$ and $[Ba\{Zr_4(OH)(OPr^i)_{17}\}]$[6] are stable, and such or related species probably exist in solutions of all barium alkoxotitanates (R = Et, Bu^n, Pr^i).

The bonding mode of the Ti_2X_9 group to M is also observed in $[Mg_2(\mu\text{-}Cl)_2\{Ti_2(OPr^i)_8Cl\}_2]$[7] in which Mg is six-coordinate.

The data obtained allow us to propose a new point of view on different steps of $BaTiO_3$ formation from metal alkoxide solutions. Previously $BaTi(OR)_6$ was thought to exist in solutions of Ba and Ti alkoxides[8a–c]. As has been stated in ref. 3 in solutions of ratio Ba : Ti = 1 : 1 complex **2** undergoes decomposition with formation of oxocomplexes with 1 : 1, stoichiometry which enables formation of pure samples of $BaTiO_3$ after prolonged refluxing.

The transformations discussed above are possible owing to a lack of stability of monomeric octahedral species $[Ti(OR)_6]$, which have not been observed in the solid state.[1] For complexes **1** and **2** (the only crystalline alkoxotitanates observed not containing oxo-ligands), stabilization of $[Ti(OR)_6]$ units is achieved, by dimerisation[9] with a rather short Ti···Ti distance (*av.* 3.033 Å in **1**, 3.015 Å in **2**), which exceeds the value observed in metallic titanium by only 0.1 Å. For all other structurally characterised titanium heterometallic alkoxides, *e.g.* $[Sm_4\{TiO(OPr^i)_{14}\}]$ or $[NaPb_2\{Ti_2O(OPr^i)_{10}\}Cl]$,[10] one of the positions in the coordination octahedron of Ti is occupied by an oxo group which is less sterically demanding compared with alkoxides. However, the titanium atom has a coordination number 5[1] in the structures of $MTi(OR)_5$ (M = Li, Na).

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Footnotes

† *Crystal data* for **1**: $C_{36}H_{90}CaO_{18}Ti_4$, M = 1042.8, triclinic, space group $P\bar{1}$, a = 15.168(8), b = 19.184(9); c = 21.736(10) Å, α = 67.55(3), β = 70.36(4), γ = 80.25(4)°, V = 5499(5) Å^3, Z = 4, D_c = 1.260 g cm^{-3}.

Crystal data for **2**: $C_{36}H_{90}BaO_{18}Ti_4$, M = 1129.7 monoclinic, space group $P2_1/c$, a = 29.952(10), b = 20.117(9), c = 20.748(8) Å, β = 108.29(3)°, V = 11870.0(15.9) Å^3, Z = 8, D_c = 1.276 g cm^{-3}. The X-ray diffraction experiments were carried out with a Siemens P3/PC diffractometer [T = 188 K **1**, 298 K **2**, graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, θ–2θ-scan technique, $2\theta < 50°$]. The structures were solved by direct methods using SHELXTL PLUS (PC version) programs. Anisotropic least-squares refinement of nonhydrogen atoms (no attempts to locate or refine H atoms were undertaken) converged at R = 0.073, R_w = 0.083 for 6097 independent reflections with $I > 3\sigma(I)$ for **1** and R = 0.092, R_w = 0.089 for 4507 independent reflections with $I > 3\sigma(I)$ for **2**. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issues No. 1.

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