Synthesis and Crystal Structure of the Double Barium–Titanium Isopropoxide $[Ba_4Ti_4(\mu_4\text{-}O)_4(\mu_3\text{-}OR)_2(\mu\text{-}OR)_8(OR)_6(ROH)_4][Ba_4Ti_4(\mu_4\text{-}O)_4(\mu_3\text{-}OR)_2(\mu\text{-}OR)_9(OR)_5(ROH)_3]$

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An X-ray structural study of the crystals isolated from the solutions obtained by the reaction of Ba metal with $Ti(OPr^i)_4$ in isopropyl alcohol has been carried out; the crystals of the compound, which is a precursor for the synthesis of $BaTiO_3$, contain molecules of two different kinds $[Ba_4Ti_4O_4(OR)_{16}(ROH)_4]$ and $[Ba_4Ti_4O_4(OR)_{16}(ROH)_3]$, where R = Pr^i.

Chemical reactions which occur in solutions of metal alkoxides are of importance for synthesis of complex oxides by the sol–gel method. $BaTiO_3$ was among the first complex oxides to be synthesized from alkoxides, but the mechanism of its formation is not yet clear.[1–3] The existence of the two crystalline Ba–Ti ethoxides, *viz.* $BaTi(OEt)_6$ and $BaTi_4(OEt)_{18}$ was shown during solubility studies on the systems $Ba(OEt)_2$–$Ti(OEt)_4$–L (where L = EtOH or C_6H_6) at 20 °C.[4] Kirby[5] reported slow crystallization of the bimetallic complex from the isopropoxide solution (crystallization is considerably speeded up by seeding). He suggested the composition $BaTi(OPr^i)_6$ for these crystals and emphasized the necessity for an X-ray structural study for unambiguous determination of the composition of the complex.

In the present study we have somewhat changed the technique for preparation of the crystals in comparison with that in ref. 5, and now report our results. Ba metal (5.0 g, 36.5 mmol) was dissolved in a refluxing solution of $Ti(OPr^i)_4$ (10.4 g, 3.66 mmol) in Pr^iOH (140 ml) [$Ti(OPr^i)_4$ was prepared by the direct anodic oxidation of Ti in absolute Pr^iOH[6]]. The Pr^iOH used was rigorously dried before use (water content *ca.* 0.01%). Initially, the dissolution of Ba with evolution of hydrogen was accompanied by accumulation of a precipitate of $Ba(OPr^i)_2$; further refluxing and dissolution of Ba led to gradual dissolution of the precipitate. By the end of the metal dissolution (after 2–3 hours), a transparent dark yellow solution was obtained. Colourless prismatic crystals of $BaTiO(OPr^i)_4\cdot7/8Pr^iOH$ precipitated on cooling to room temperature.

An X-ray structural study of the complex† shows that it is a bimetallic oxoalkoxide; its structure can be represented as $[Ba_4Ti_4O_4(OR)_{16}(ROH)_4][Ba_4Ti_4O_4(OR)_{16}(ROH)_3]$ **1**, where R = Pr^i. The two crystallographically independent complexes (*A* and *B* in Fig. 1) differ mainly in the number of solvating alcohol molecules in the crystal: 4 and 3 for complexes *A* and *B* respectively. Both complexes have the same metal–oxygen core: a distorted cube with alternating Ba and O (oxo groups) atoms in its vertices. Each oxo atom is bonded to one of the Ti atoms which are also linked to the Ba_4O_4 core by the bridging alkoxide groups: Ti–OR–Ba. Two different types of Ba, Ti and oxo-O atoms should be distinguished; in Fig. 1 they are designated as Ba, Ti, O (1, 2) and Ba, Ti, O (3, 4).

The fragments including the Ti(1) and Ti(2) atoms in molecule *A* are attached to the two Ba atoms (belonging to one face of the Ba_4O_4 cube) with one μ_2- and one μ_3-OR groups. Both these Ti atoms have two terminal OR groups, and the fifth position in their coordination sphere is occupied by an oxo group which belongs to the same face of the cube as the Ba atoms. As a whole the coordination polyhedra of Ti(1) and Ti(2) may be described as distorted tetrahedral pyramids with the apical positions occupied by oxo atoms and the bases formed by O-alkoxide ligands. Ti(3) and Ti(4) atoms are each attached to the three Ba atoms by three μ-bridging OR alkoxide groups. Each of these Ti atoms has one terminal OR group, and the fifth positions in their coordination spheres are occupied by the oxo-atoms linked to the same three Ba atoms. The coordination polyhedra of Ti(3) and Ti(4) atoms may be considered as trigonal bipyramids (the sum of the angles in the equatorial plane is 360°) with oxo groups and terminal alkoxide groups in the axial positions. The coordination polyhedra of the Ti(1) and Ti(2) atoms may also be described as distorted trigonal bipyramids; in molecules *A* and *B* the angles between the axial ligands are respectively O(5)Ti(1)O(8) 162.2(4) and 159.1(4)°; and O(9)Ti(2)O(12) 162.1(5) and 161.1(4)°, wherein, in contrast to the coordination polyhedra of Ti(3) and Ti(4) oxo atoms occupy equatorial rather than axial positions.

μ_4-Oxo atoms differ in the degree of distortion of the coordination polyhedra; whereas the bond angles at O(1a) and O(2a) vary in the range 88.6–150.4° (the corresponding angles in complex *B* are 90.8–153.0°), the O(3) and O(4) atoms are characterized by almost regular tetrahedral coordination (bond angles of 100.4–113.4 and 101.6–115.0° for molecules *A* and *B* respectively).

Each Ba atom has a coordination number of 7, the two kinds of Ba atoms having a different disposition of the ligands in the coordination polyhedra. In the case of Ba(1) and Ba(2) the μ_3-OR groups are located in *trans* positions relative to the solvating alcohol molecules, whereas for the Ba(3) and Ba(4) atoms the *trans* positions relative to solvating molecules are occupied by the oxo atoms. In molecule *A* each of the four Ba atoms is coordinated by the oxygen of the solvating Pr^iOH molecule; the hydroxy H atoms participate in hydrogen bonds with the four terminal OR groups of the Ti(1) and Ti(2) atoms [O(7a) · · · O(23a) 2.74(2), O(8a) · · · O(22a) 2.82(2), O(11a) · · · O(24a) 2.71(2), O(12a) · · · O(21a) 2.81(2) Å].

In molecule *B* the seventh place in the coordination sphere of Ba(4b) is occupied by the alkoxide O(11b) atom which in this case becomes μ_2-bridging. Thus, there are only three hydrogen bonds in molecule *B* [O(7b) · · · O(23b) 2.75(2), O(8b) · · · O(22b) 2.86(2), O(12b) · · · O(21b) 2.88(2) Å].

Bond lengths Ba–O (2.566–3.051 Å) with the oxygen atoms of different kinds in structure **1** do not differ from the analogous values in the structures of BaO, $Ba(OH)_2\cdot nH_2O$ and barium inorganic salts.

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† *Crystal data* for $C_{117}H_{280}Ba_8O_{47}Ti_8$: M = 3917.6, triclinic, space group $P\bar{1}$, a = 13.947(4), b = 14.742(4), c = 50.035(10) Å, α = 82.81(2), β = 84.59(2), γ = 62.09(2)°, V = 9012(4) Å^3, D_c = 1.341 g cm^{-3}, for Z = 2, μ(Mo-Kα) = 21.04 cm^{-1}; 17 367 data were collected at 296 K on a Siemens P3/PC diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). The structure was solved by direct methods. Ba and Ti atoms were located in the *E*-map; all remaining non-hydrogen atoms were found in the subsequent difference Fourier maps. The structure was refined by least-squares with anisotropic thermal parameters. No attempts to locate or refine H atoms were undertaken. The refinement of 1621 variables for 13 153 reflections with $F^2 > 3\sigma(F)$ converged at R = 0.0607, R_W = 0.0720. The structure solution was carried out by the SHELXTL PC program package using an IBM PC AT computer and the refinement was performed by a modified SHELX-76 program. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

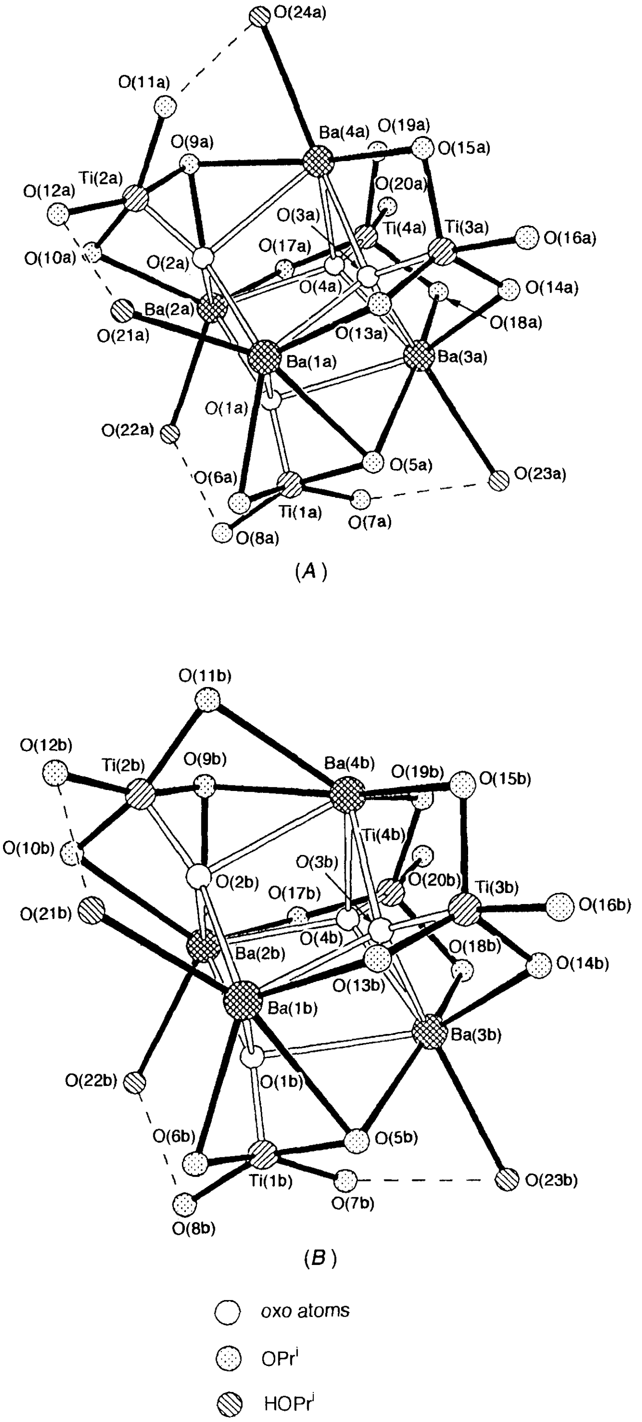

Fig. 1 The structure of molecules $[Ba_4Ti_4(\mu_4\text{-}O)_4(\mu_3\text{-}OR)_2(\mu\text{-}OR)_8(OR)_6(ROH)_4]$ (*A*) and $[Ba_4Ti_4(\mu_4\text{-}O)_4(\mu_3\text{-}OR)_2(\mu\text{-}OR)_9(OR)_5(ROH)_3]$ (*B*). Main mean bond lengths (Å): Ti(1,2)–O(oxo) 1.713, Ti(3,4)–O(oxo) 1.798, Ti–OR(terminal) 1.917, Ti–OR(bridging) 1.946, Ba–O(oxo) 2.712, Ba–O(H)R 2.893, Ba–OR 2.797.

The Ti–O (oxo) distances involving the Ti(1) and Ti(2) atoms [Ti(1a)–O(1a) 1.699(8), Ti(2a)–O(2a) 1.73(1), Ti(1b)–O(1b) 1.708(9) Ti(2b)–O(2b) 1.715(8) Å] are much shorter than those involving the Ti(3) and Ti(4) atoms [Ti(3a)–O(3a) 1.80(1), Ti(4a)–O(4a) 1.780(8), Ti(3b)–O(3b) 1.80(1), Ti(4b)–O(4b) 1.810(7) Å], which is in good agreement with the different positions which the oxo atoms occupy in the two different kinds of Ti atom trigonal bipyramids.

The Ti–OR distances (1.881–1.999 Å) are much longer than the Ti–O (oxo) values (*vide supra*).‡ It is noteworthy that the Ti–OR values in the structure **1** do not in fact depend on the function (bridging or terminal) of the alkoxide groups, in contrast to the structures of $Ti_4(OMe)_{16}$[8] and $Ti_2Cl_2(OPh)_4$[9] with octahedral and the trigonal bipyramidal coordinated Ti atoms respectively, where the terminal Ti–OR bonds are considerably shorter (1.74 Å) than those involving bridging OR groups (1.91–2.12 Å). It is also noteworthy that the coordination of the Ti(2a) and Ti(2b) atoms remains independent on the character of the O(11)R group [terminal or bridging corresponding to the presence or absence of the solvating Pr^{i}OH molecule at the Ba(4a) or Ba(4b) atoms respectively].

The data discussed above allow us to regard the structure **1** as ionic, consisting of the four pairs of cations Ba^{2+} {or $[Ba(ROH)]^{2+}$} and anions $[TiO(OR)_4]^{2-}$ analogous to the structure which has been reported by us for the bimetallic Na–W complex $[Na(ROH)_2]_2^+[WO(OEt)_5]_2^-$.[10]

The presence of the Ba–O–Ti bridges in the complex studied may presumably be explained by the decomposition of the double metal alkoxide formed as a result of the interaction between $Ba(OR)_2$ and $Ti(OR)_4$ [reaction (1)],

$$Ba(OR)_2 + Ti(OR)_4 \rightarrow BaTiO(OR)_4 + R_2O \qquad (1)$$

which is accompanied by elimination of ether, which was detected by GLC. Presumably, in contrast to the earlier assumptions,[11,12] it is oxo- rather than alkoxo-titanate which acts as a precursor for the preparation of $BaTiO_3$.

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‡ The interatomic Ti–O (oxo) distances are very short in comparison with those in other known titanium alkoxides. For instance, in $[Ti_6O_4(OPr^i)_{12}(OAc)_4]$ values are about 2.02 and 1.80 Å for tri- and bi-dentate oxo atoms respectively.[7]