Synthesis, Crystal and Molecular Structure of Calcium Oxo Ethoxide, $[Ca_6(\mu_4\text{-}O)_2(\mu_3\text{-}OEt)_4(OEt)_4]\cdot 14EtOH$

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The hexanuclear complex of calcium oxo ethoxide ethanol solvate, $[Ca_6O_2(OEt)_8]\cdot 14EtOH$ **1** has been isolated after the prolonged refluxing of an ethanol solution of calcium ethoxide in the presence of the oxygen in air and studied by X-ray diffraction; the metal–oxygen framework is built of two $[Ca_4O_4]$ cubes sharing a common $[Ca_2O_2]$ face, which involves both oxo groups.

The ever increasing interest of the chemical community in the alkaline earth alkoxides is mostly due to the prospects of their use as precursors of metal oxide materials. Therefore, reliable information on the structure of compounds formed in alkoxide solutions under conditions similar to those existing at the early stages of hydrolysis may be extremely important for the elucidation of mechanisms of formation of complex oxide phases, such as $BaTiO_3$, other perovskite-type oxides and superconductors (Bi-containing complexes). The theoretical interest in alkaline earth alkoxide derivatives is associated with their structural ambivalence manifested in their ability to form both ionic and molecular crystals.

Thus, the calcium, strontium and barium methoxides and ethoxides obtained by desolvation of $M(OR)_2\cdot 4ROH$ appear to be non-volatile, insoluble in non-polar organic solvents, fine crystalline powders with a three-dimensional polymeric structure of the CdI_2 type.[1,2] Recently, a number of Ca and Ba alkoxides $M(OR)_2$, mostly the derivatives of bulky, branched

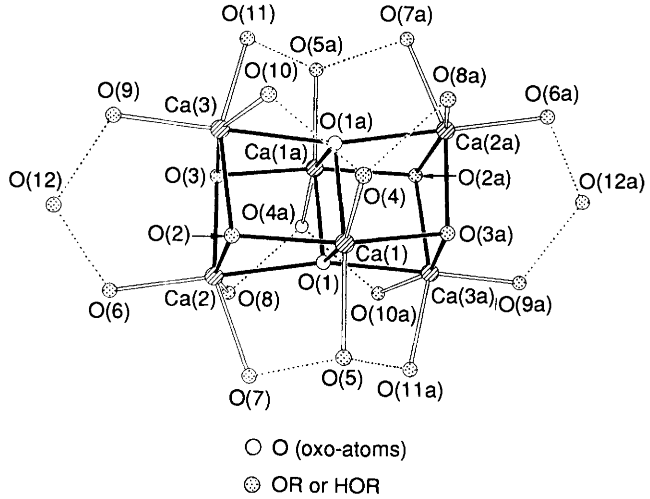

Fig. 1 Molecular structure of $Ca_6(\mu_4\text{-}O)_2(\mu_3\text{-}OEt)_4(OEt)_4\cdot 14EtOH$ **1**. Selected bond distances (Å): Ca(1)–O(1) 2.406(6), Ca(1)–O(2) 2.359(6), Ca(1)–O(4) 2.349(7), Ca(1)–O(5) 2.358(5), Ca(1)–O(1a) 2.402(4), Ca(1)–O(3a) 2.363(5), Ca(2)–O(1) 2.476(5), Ca(2)–O(2), 2.322(6), Ca(2)–O(3) 2.329(5), Ca(2)–O(6) 2.300(7), Ca(2)–O(7) 2.370(5), Ca(2)–O(8) 2.367(7), Ca(3)–O(2) 2.332(5), Ca(3)–O(3) 2.312(6), Ca(3)–O(9) 2.251(6), Ca(3)–O(10) 2.352(8), Ca(3)–O(11) 2.373(6), Ca(3)–O(1a) 2.529(5).

or polydentate radicals such as Ar, CR_3, $CHMe_2$, SiR_3 and C_2H_4OMe[3,4] have been structurally characterized.

The present paper reports the synthesis and structure of one more representative of this molecular alkoxide series with a rather compact alkyl group, *viz*. calcium oxo ethoxide. Crystallization from freshly prepared samples obtained by dissolution of calcium metal in absolute ethanol (<0.05% H_2O) yields the needle-shaped $Ca(OEt)_2\cdot 4EtOH$ crystals. Their partial desolvation with the formation of $Ca(OEt)_2\cdot 2EtOH$ powder occurs on heating to 60 °C even under a layer of mother liquor.[1]

The hexagonal plates crystallize quantitatively from 2–3% ethanol solutions of $Ca(OEt)_2$ after refluxing for 8–10 h under the conditions of complete isolation from atmospheric moisture. The X-ray diffraction study has shown that these plates are in fact the crystals of a hexanuclear oxo ethoxide, $[Ca_6(\mu_4\text{-}O)_2(\mu_3\text{-}OEt)_4(OEt)_4]\cdot 14EtOH$ **1**.† Crystallization of **1** does not occur in complete isolation from oxygen (deaerated alcohol in He atmosphere). Therefore, it may be assumed that the oxo groups in molecule **1** originate from the oxidation of $Ca(OEt)_2$ with the formation of peroxide compounds and their subsequent decomposition.[5]

Hexanuclear molecules of **1** (Fig. 1) occupy a special position in the crystallographic inversion centre, the metal–oxygen framework represents two $[Ca_4O_4]$ cubes sharing a common $[Ca_2O_2]$ face, which involves both μ_4-oxo-groups O(1) and O(1a). All other oxygen vertices of the cubes O(2), O(3), O(2a) and O(3a) are occupied by the O atoms of the μ_3-OEt groups. All Ca atoms have a distorted octahedral coordination, the central Ca(1) and Ca(1a) atoms bearing two, and the peripheral Ca(2), Ca(3), Ca(2a) and Ca(3a) bearing three terminal groups. Along with the 20 metal-bonded ligands complex **1** has two more groups [involving the O(12) and O(12a) atoms], which do not form direct bonds with the Ca atoms and are kept within the aggregate apparently by means of H-bonds. Although it was impossible to locate the H atoms objectively in the present X-ray study, it seems logical to assume that four terminal OEt groups correspond to the O(4), O(5), O(4a) and O(5a) atoms bonded to the Ca(1) and Ca(1a) metal centres. This assumption is in good agreement with the possible system of H-bonds, which can be proposed on the basis of the O···O short contacts, shown in Fig. 1 as dotted lines. Only twelve such contacts have been found in the molecule, which means that two 'active' H atoms do not participate in hydrogen bonding. Most of the O···O distances fall within the range of 2.521–2.565 Å; only those involving the noncoordinated O(12) and O(12a) atoms are significantly shorter: O(6)···O(12) 2.464(9), O(9)···O(12) 2.395(9) Å. It seems quite probable that the narrow band at 3683 cm^{-1} characteristic of the free alcohol OH-group[6] in the IR spectrum of **1** corresponds to the O(12)H hydroxy group. Additional stabilization of this O–H bond manifested in its high vibration frequency may be due to the significant electrostatic contribution brought about by the double acceptor role played by the O(12) atom in the two strong H-bonds corresponding to the above-mentioned short O···O contacts. The broad band at 3340 cm^{-1} corresponds to all other metal-coordinated ethanol molecules involved in the hydrogen bonding [the IR-spectrum of **1** in the range of 3000–400 cm^{-1}‡ is identical to that of $Ca(OEt)_2$[7]].

The Ca–O bond lengths with the μ_4-oxo groups O(1) and O(1a) within the common $[Ca_2O_2]$ face, Ca(1)–O(1) 2.406(6) and Ca(1)–O(1a) 2.402(4) Å, are very similar to those found in the ionic CaO structure[8] and somewhat shorter than their analogues involving the Ca(2) and Ca(3) atoms, Ca(2)–O(1) 2.476(5) and Ca(3)–O(1a) 2.529(5) Å. It is noteworthy that the Ca–μ_3-OEt bonds parallel to the plane of the common face of the bis-cubane (2.312–2.332 Å) are also somewhat shorter than those oriented in the perpendicular direction, *i.e.* along the long axis of bis-cubane moiety [Ca(1)–O(2) 2.359(6) and Ca(1a)–O(3) 2.363(5) Å]. At the same time the terminal Ca–OR bonds as a rule do not show significant differences as compared to the bridging Ca–OR bonds [the only exceptions are somewhat shorter Ca(3)–O(9) 2.251(6) and Ca(2)–O(6) 2.300(7) Å bonds]. This is a feature characteristic of bimetallic alkoxides {*e.g.* $[NaWO(OEt)_5]$,[9] $[BaTiO(OPr^i)_4]_4$[10]}, whose 'molecules' are indeed formed of ion-pairs. In the case of **1** the oxo groups may be treated as its anionic part, and the rest of the hexanuclear molecule $[Ca_6(OEt)_8(EtOH)_{14}]^{4+}$ as a cation. The Ca–OEt distances as a whole are close to those found in other $Ca(OR)_2$ alkoxides[1–3] as well as $Ca(Hal)_2\cdot n ROH$[11] complexes.

The CaOC bond angles at the μ_3-OEt oxygens are naturally smaller than those at the terminal OEt groups [the average values are 119.2 at O(2) and O(3), and 127.5° at O(4) and O(5)]. The largest bond angles (av. 133.7°) are observed at the O(6)–O(11) atoms which according to our assumption (*vide supra*) belong to the solvating ethanol molecules and probably form more covalent Ca–O bonds than alkoxy groups.

A similar metal–oxygen bis-cubane framework has been recently reported in the structure of bimetallic alkoxide $Li_5Sm(OBu^t)_8$ with the common $[LiSmO_2]$ face.[12] In contrast to **1** the latter has only two terminal OR-groups bonded to the Sm atom and exhibits considerable difference between the Sm–O bonds involving terminal and μ_3-OR groups. This observation seems natural taking into account an undoubtedly much more significant covalent contribution in the Sm–O bonding than in Ca–O bonds. The distorted bis-cubane

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† *Crystal data* for **1**: $C_{44}H_{124}Ca_6O_{24}$, M = 1276.5, monoclinic, space group $P2_1/c$, a = 12.697(3), b = 22.501(4), c = 13.835(3) Å, β = 112.88(2)°, V = 3642(1) Å^3, Z = 2, D_c = 1.165 g cm^{-3}. The X-ray diffraction experiment was carried out with a Siemens P3/PC diffractometer (T = 193 K, graphite-monochromated Mo-Kα radiation, λ = 0.71069 Å, θ–2θ scan technique, $2\theta < 50°$). The structure was solved by the direct methods using SHELXTL PLUS programs (PC Version). Anisotropic least-squares refinement [H atoms bonded to carbons included in calculated positions with the common refined U_{iso} = 0.022(1) Å^2] converged at R = 0.063, R_w = 0.080 for 2767 observed independent reflections with $I > 3\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

‡ IR spectrum of **1**, ν/cm^{-1}: 3683, 3340, 2957, 2925, 2856, 2847, 2813, 2716, 2608, 1434, 1382, 1319, 1108, 1058, 882, 801, 505, 465 and 317.

moiety, similar to that of **1**, was also found in several lithium amide complexes, *e.g.* in a crystal of tetrahydrofuran (thf) solvate of isopropylbenzamidelithium complex.[13]

Crystals of **1** easily lose solvating EtOH molecules, although they are less hygroscopic than $Ca(OEt)_2 \cdot n EtOH$. They are non-volatile according to the mass-spectroscopic data and almost completely insoluble in ethanol. However, after mechanical grinding or prolonged refluxing under ethanol the decomposition of **1** with the formation of $Ca(OEt)_2 \cdot 2EtOH$ powder accompanied by some increase of solubility in EtOH occurs. In this respect **1** behaves quite similarly to other oligomeric oxo alkoxides: $[Ti_7O_4(OEt)_{20}]$, $[Al_{10}O_4(OEt)_{22}]$, $[Nb_8O_{10}(OEt)_{20}$.[14] Destruction of the oligomer and formation of the smaller species occurs immediately upon dissolution of crystals of these complexes and therefore the equilibrium between crystalline and liquid phases can never be attained.

Complex **1** is soluble in non-polar organic solvents: its solubility at 20 °C is *ca.* 20% in toluene and about 10% in hexane and thf [as calculated to $Ca(OEt)_2$], which is twice as much as for $Ca(OEt)_2 \cdot 4EtOH$ and many times as much as for $Ca(OEt)_2 \cdot 2EtOH$.

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