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The structure of the LiOMe·2MeOH crystal solvate. A new structural type for tetrameric alkoxides

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The solvate LiOMe·2MeOH (1) was isolated from a solution of LiOMe in MeOH, its tetrameric unit $[Li_4(\mu\text{-}OR)_4(\mu\text{-}ROH)_2(ROH)_4]\cdot 2ROH$ may be described as two distorted squares $[Li_2(\mu\text{-}OR)(\mu\text{-}ROH)]$, linked by bridging alkoxy groups and two hydrogen bonds; 1 easily loses the solvate alcohol yielding polymeric LiOMe.

Lithium alkoxides along with the alkoxides of other alkaline metals are widely used as reagents and catalysts in organic synthesis, in particular in exchange reactions with MX_n (X = halogen), one of the most important synthetic routes to the alkoxides of polyvalent metals.[1,2] The alkoxides of alkaline metals have received additional attention lately in the ever expanding studies driven by the search for volatile and soluble precursors of mixed oxide materials. In spite of the fast growth in the number of structural studies of akaline and alkaline-earth metal alkoxides with branched alkyl groups, as well as of their adducts with THF, Py, *etc.*, only a few structures of alcohol solvates were reported; such solvates are formed exclusively by the first members of the homologous series, and full X-ray crystal structures were published for just four of them, namely $KOBu^t\cdot Bu^tOH$,[3] $Mg(OMe)_2\cdot 3.5MeOH$,[4] $Ca_6O_2(OEt)_8\cdot 14ROH$[5] and $[Ba(OBu^t)_2(Bu^tOH)_2]_4$.[6] The potassium complex features infinite linear chains made up of $[K_2(\mu\text{-}OR)_2(\mu\text{-}ROH)_2]_\infty$ tetrahedra, three other structures are built of cubane-shaped molecules with intra- (or, in the case of Mg, inter-) molecular hydrogen bonds. Molecules with analogous structural motifs were found earlier in the structures of a number of adducts with non-alcohol solvents, *e.g.* $[LiOR(THF)]_4$, R = c-C_5H_7, $C(=CH_2)Bu^t$, $\overline{C=CH(CH_2)_3}$.[7,8]

The LiOR·2ROH solvates are known only for methoxy and ethoxy derivatives; their composition was determined on the basis of tensiometric measurements. In the present paper we report the crystal structure of LiOMe·2MeOH (**1**). Plate-shaped crystals of **1**† of approximately 0.4 mm size suitable for the X-ray diffraction experiment‡ were grown over the course of two weeks from a solution of LiOMe in MeOH by slow cooling to 0 °C. The LiOMe solution concentration was approximately 13% by weight and was prepared by dissolution of the metal (having a metallic lustre) in an excess of absolute alcohol under a dry argon atmosphere. The reaction mixture was cooled to ambient temperature in order to prevent boiling which leads to turbulence and subsequent precipitation of solvate free LiOMe.[9]

The molecular structure of **1** (Fig. 1) is based on a tetrameric cubane-shaped lithium–oxygen framework. However, although cubane cages in general are encountered most frequently in the alkoxide structures, the cubane-shaped aggregate found in molecule **1** has no documented analogues in the structural chemistry of alkoxides. Indeed, in contrast to most alkoxide structures with the cubane structural motif, the "top" and "bottom" M_2O_2 faces of the cube in **1** are superimposed metal-over-metal, oxygen-over-oxygen rather than the conventional metal-over-oxygen way. As a result, the distorted square Li_2O_2 faces in **1** (they are in fact non-planar, the folding angle along the O(1)···O(2) line being equal to 24.4°) are kept together in the cube by the bridging Li–O–Li and H-bonding O–H···O interactions rather than the M–O bonds as in other alkoxide cubane systems. The cubane has therefore two bridging methoxide groups in the Li_2O_2 faces as well as two methoxides bridging the Li···Li edges of the cube. There are also two methanol molecules in the Li_2O_2 faces and four terminal MeOH molecules in each tetramer. Two additional methanol molecules per cubane aggregate (their oxygen atoms are labelled O(6)) are not bonded to the metal framework, and are linked to the aggregates *via* three H-bonds. Although all these bonds should be regarded as intermolecular they are distinctly different, the O(6)–H···O(4′)(x, $-y$, $0.5 - z$) bond (with the O(6)H-group serving as H-donor) being substantially shorter (O(6)···O(4′) 2.429 Å) than the O(6)···H–O(3) (O(6)···O(3) 2.627 Å) and O(6)···H–O(5) (O(6)···O(5) 2.610 Å) bonds with the O(6) atom acting as the acceptor. The $H_3C(6)O(6)H$ methanol molecule plays the role of H-bond centre linking the tetrameric aggregates in the crystal. However in contrast to the $Mg(OMe)_2\cdot 3.5MeOH$ complex with a H-bonded three-dimensional structure, the tetramers in **1** are linked into two-dimensional layers normal to the *a* crystallographic axis.

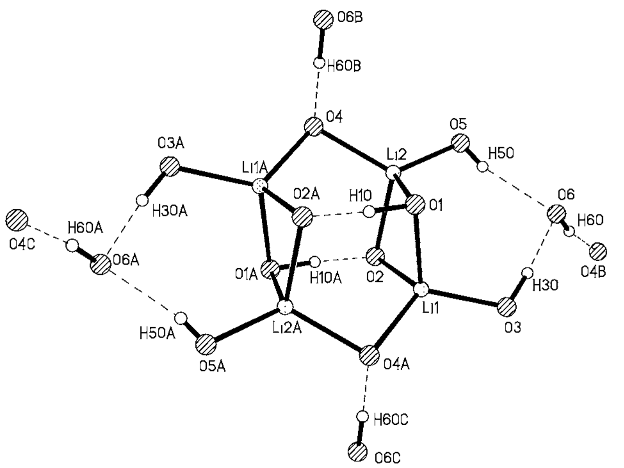

Fig. 1 ORTEP[12] diagram of LiOMe·2MeOH (Me groups in methoxide ligands and in methanol molecules are omitted). Selected geometric parameters: Li(1)–O(1) 1.975(4), Li(1)–O(2) 1.941(4), Li(1)–O(3) 1.900(4), Li(1)–O(4A) 1.973(4), Li(2)–O(1) 1.942(4), Li(2)–O(2) 1.968(3), Li(2)–O(5) 1.906(4), O(1)–H(1O) 1.13(4), H(1O)···O(2A) 1.30(4), O(1)···O(2A) 2.427(3) Å; O(1)–H(1O)···O(2A) 172°.

Four Li atoms in each tetramer form a rectangular array with distinctly different edges: the shorter one (Li(1)···Li(2)

2.655(5) Å) spanned by two (O(1) and O(2)) and the longer one (Li(1) ··· Li(2A) 2.999(5) Å) only by one (O(4)) bridging oxygen. It is noteworthy that there is actually no regular difference between the bridging Li–O(alkoxy) (Li(1)–O(2) 1.941(4), Li(1)–O(4A) 1.973(4), Li(2)–O(4) 1.964(3), Li(2)–O(2) 1.968(3) Å) and Li–O(alcohol) (Li(1)–O(1) 1.975(4), Li(2)–O(1) 1.942(4) Å) bonds. The terminal Li–O(alcohol) distances, though, are indeed noticeably shorter (Li(1)–O(3) 1.900(4) and Li(2)–O(5) 1.906(4) Å).

The aggregates observed in the structure of **1** are obviously not very stable. It is easily desolvated: at 25 °C the vapour pressure is as high as 50 mmHg and even in methanol solution it loses solvating alcohol at 28 °C.[9] Condensation of the LiO_4 tetrahedra leads to the formation of a polymeric LiOMe structure (belonging to the *anti*-PbO type[10,11]) with tetradentate (rather than bidentate as in **1**) oxygen atoms; this transition from **1** to LiOMe is accompanied by an increase in the density from 1.053 to 1.300 g cm^{-3}.

Notes and references

† Elemental analysis for **1**: found: C, 35.82; H, 11.35; Li, 6.62. Calc. for $C_3H_{11}LiO_3$: C, 35.29; H, 10.78; Li, 6.86%.

‡ Crystal data for **1**: $C_{12}H_{44}Li_4O_{12}$, $M = 408.23$, monoclinic, $a = 14.981(8)$, $b = 13.289(7)$, $c = 12.952(5)$ Å, $\beta = 92.86(4)°$, $U = 2575(2)$ Å^3, $T = 200(2)$ K, space group $C2/c$ (no. 15), $Z = 4$, μ(Mo-Kα) = 0.088 mm^{-1}, 5812 reflections measured, 2779 unique ($R_{int} = 0.115$) were used in all calculations. The crystals are very unstable and there was a 15% reduction in the diffraction intensity even in the course of the low-temperature experiment; the appropriate crystal decay correction was applied. The final $wR(F^2)$ was 0.1804 for all data, $R(F)$ was 0.0586 for 1505 observed data with $I > 2\sigma(I)$. CCDC reference number 186/2148. See http://www.rsc.org/suppdata/dt/b0/b005782g/ for crystallographic files in .cif format.

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