Magnesium Alkoxide Fluoride

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$Mg_6F_2(OMe)_{10}(MeOH)_{14}$—An Alkoxide Fluoride of an Alkaline Earth Metal[**]

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Sol–gel synthesis, which was developed for metal oxides, can also be applied to the synthesis of nanoscopic metal fluorides. By using anhydrous hydrogen fluoride (aHF) in a suitable organic solvent, the metal–alkoxide bond undergoes fluorolysis instead of hydrolysis.[1,2] Metal fluorides with remarkably high surface areas (hs-MF_x) are thereby formed. Unlike those obtained by conventional methods, nanoscopic metal fluorides are extremely strong Lewis acids and are of interest for heterogeneous catalysis. Furthermore, the ease of preparation of stable metal fluoride colloidal solutions (sols) opens the way to new applications, such as optical or protective corrosion-resistant coatings. Owing to the highly distorted structures of the nanoscopic phases formed, insight into the mechanism of the process was only available by theoretical calculations and MAS-NMR investigations.[3] We have isolated a monofluorinated intermediate from the aHF-Al-$(OiPr)_3$-system,[4] which thus confirmed the theoretical predictions.[3] During our investigations into the synthesis of hs-MgF_2[5] from the reaction of $Mg(OCH_3)_2$ with alcoholic aHF solution, it was possible to obtain an intermediate which was identified as a magnesium alkoxide fluoride. Herein we report the selective synthesis of the first alkoxide fluoride of an alkaline earth metal and its double-cubane structure with unusual bridging fluoride ligands.

$[Mg_6(\mu_4\text{-}F)_2(\mu_3\text{-}OMe)_4(OMe)_4(MeOH)_{12}][H(MeO)_2]_2$ (**1**) is the first example of a magnesium alcoholate fluoride.[6] The asymmetric unit of the structure contains a cation, $[Mg_3F(\mu_3\text{-}OMe)_2(OMe)_2(MeOH)_6]^+$, and a solvated methoxide ion, which can be considered as $(MeOH\cdots OMe)^-$. The whole hexanuclear dicationic complex, $[Mg_6(\mu_4\text{-}F)_2(\mu_3\text{-}O)_4(OMe)_4(MeOH)_{12}]^{2+}$, is centrosymmetric, and it is connected to both $[H(MeO)_2]^-$ anions by pairs of hydrogen bonds (Figure 1). The cationic complex contains two equivalent trinuclear fragments which are fused together by a dimetalladifluoro four-membered ring $(Mg1F)_2$. The Mg–F bonds are 213.8(1) pm long, and the atom Mg1 achieves σ^6 coordination through two terminal (Mg1–O 202.0–202.3(1) pm) and two μ_3 methoxide groups (Mg1–O 206.9–207.5(1) pm). The other two magnesium atoms, Mg2 and Mg3, are coordinated by one μ_4 fluorine atom (Mg–F 217.6–218.6(1) pm), two μ_3-OMe groups (Mg–O 206.9–207.5(1) pm), and three MeOH molecules (Mg–O 202.7–207.8(1) pm). In the dicubane structure of **1**, two of the central polyhedron vertices are occupied by an $\sigma^4\mu_4$ fluorine atom which forms the origin of four covalent Mg–F bonds (Mg–F 214–219 pm). To our knowledge, such a "swing" arrangement of μ_4-fluorine atoms has not been reported in the coordination chemistry of organofluoro metal derivatives. Only one example with $\sigma^4\mu_4$-coordination of the fluorine atoms, but with square-pyramidal geometry, could be found in the inorganic fluorooxopolymolybdate $[Mo_4O_{12}F_3]^{3-}$.[7] The bridging arrangement of the metal atoms in **1** has been found in the structure of the calcium ethoxide $[Ca_6O_2(OEt)_8]\cdot 14\,EtOH$, but in that case, the bridging is with μ_4 oxygen atoms instead of fluorine atoms.[8] It is worth noting that both the Mg2 and Mg3 cubane fragments in the hexanuclear magnesium cage of compound **1** stem from the cubane structure of the reactant. Indeed, if no HF is

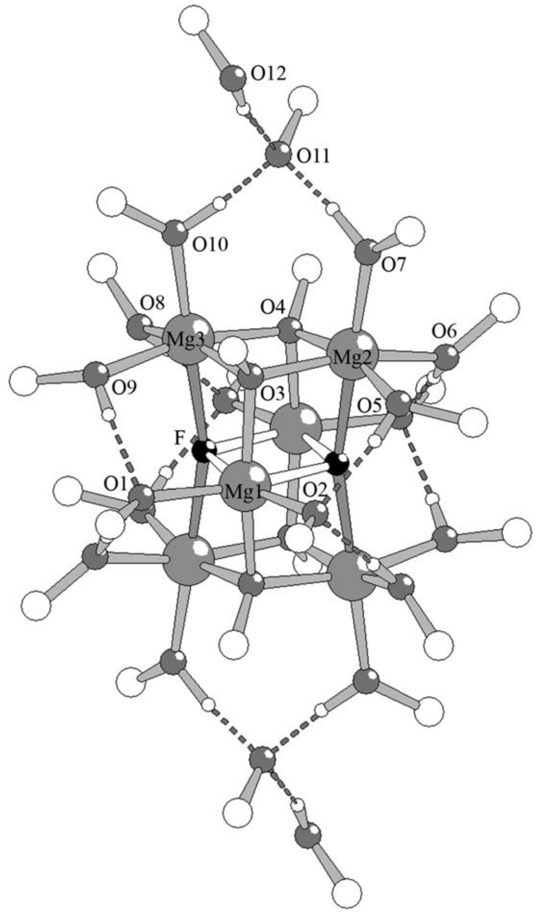

Figure 1. The structure of **1** with a hexanuclear dication and two anionic MeO···HOMe units connected to the cation by a total of four hydrogen bonds. The methyl hydrogen atoms are omitted for clarity.

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added, the tetranuclear magnesium methoxide complex $[\mathrm{Mg(OMe)_2{\cdot}}y\mathrm{MeOH}]_4$ precipitates. The molecule structure of that molecule, $[\mathrm{Mg_4(\mu_3\text{-}OMe)_4(OMe)_{4\text{-}x}(MeOH)_{8+x}}]^{x+}$, consists of neutral cubane units ($x = 0$ with $y = 2$)[9] or of neutral ($x = 0$) and cationic ($x = 4$) cubane units with $y = 3.5$.[10] In contrast to the structures of the alkaline earth metal alkoxides, for which the hydrogen atoms could not be localized,[8–10] in the structure of **1**, all hydrogen atoms could be localized and refined. The MeO groups could clearly be differentiated from the coordinated MeOH, and this fact allowed the contribution of hydrogen bonding to the stabilization of the structure to be made clear. There are eight intramolecular hydrogen bonds ($d_{\mathrm{O\cdots O}}$ 255.5–257.4(2) pm): four between the MeOH molecules acting as hydrogen donors (O5, O6, O8, and O9) coordinated to Mg2 and Mg3, and both terminal OMe groups (O1 and O2) at Mg1 each bond to two hydrogen atoms (Figure 1). Atom O11 of the methoxide ion acts as a triple hydrogen-bond acceptor, forming two strong hydrogen bonds involving atoms O7 and O10 of the apical methanol molecules ($d_{\mathrm{O\cdots O}}$ 247.9 and 248.7(2) pm) and one weaker bond involving atom O12 of the external methanol molecule ($d_{\mathrm{O\cdots O}}$ 269.9(2) pm). The hexanuclear cation and the $(\mathrm{MeOH{\cdots}OMe})^-$ ions thus form the stable triple-ion structure of **1** through hydrogen bonding. In the crystal structure, no bonding interactions are observed between the discrete cation–anion units. These units form layers parallel to the *bc* plane (Figure 2), and the layers are stacked along [100].

When the temperature was increased above 100 K during the X-ray structure determination, the single crystal underwent a reversible phase transition at 240(±5) K.[6] The space group changed from $P2_1/c$ (**1**) to $C2/m$ (**1a**) as a consequence of the higher symmetry of the structure, and this change is accompanied by the increase of the molecular point symmetry from C_i to C_{2h}. Upon warming the crystal further to 310 K, a new unit cell was found with a volume that was 12% smaller.[6] This change in volume is in accord with the loss of four molecules of methanol from **1a**.

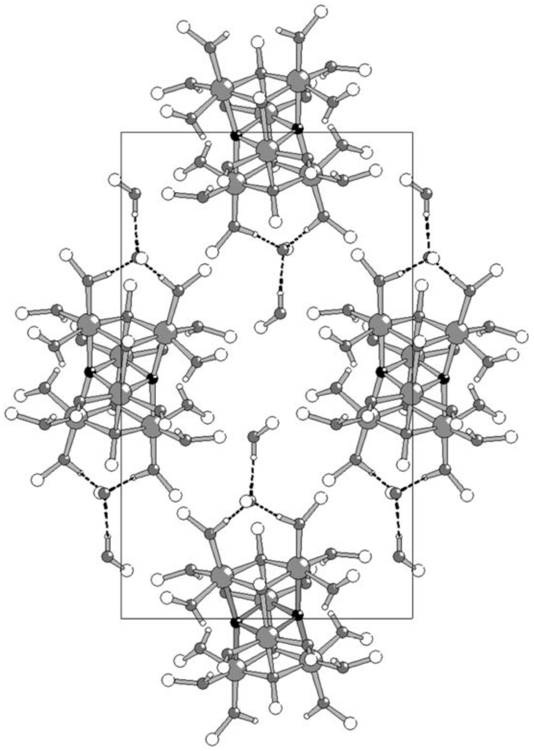

Figure 2. The stacking in the crystal structure of **1** parallel to the *bc* plane.

Knowing the product constitution from the X-ray structural analysis, we were able to develop a simple and reproducible synthesis for the compound **1**. If three equivalents of $\mathrm{Mg(OMe)_2}$ are allowed to react with one equivalent of HF dissolved in MeOH at 0 °C, the ^{19}F NMR spectrum obtained from the resulting solution has a signal at approximately $\delta = -180$ ppm. A similar ^{19}F NMR signal position (at $\delta = -182$ ppm) was found in the structural characterization of the only other organofluoro alkaline earth metal compound with a dimetalladifluoro four-membered ring (a β-diketiminato magnesium fluoride) which was assigned to the μ_2-F atoms.[11] After the methanol was distilled off at 10 °C in vacuum, no HF was found in the distillate, which indicates complete HF consumption. The product formed after recrystallization from methanol had the formula of **1** (determined by elemental analysis of C, H, and F, see Experimental Section). The temperature-dependent behavior observed for the single crystal was also found for the powder X-ray analysis of the bulk product obtained from the synthesis. In the powder diffraction pattern, only reflections that corresponded to reflections from the single crystal analysis of **1a** were initially observed. With time, and under a flow of inert gas at room temperature, the changes to the cell parameters that were described above were confirmed. Thermal analysis (TG/DTG) supported a two-step decomposition process for **1a**: when compound **1a** is heated under a stream of dry inert gas, starting at room temperature and increasing up to about 100 °C, four molecules of MeOH are initially released from the hexanuclear triple-ion structure, giving a compound that starts to decompose at above 250 °C. The initial methanol loss is clearly initiated by the removal of the external methanol solvate. Through the loss of four molecules of methanol, **1a** is then most likely converted into the neutral complex **2**, $[\mathrm{Mg_6(\mu_4\text{-}F)_2(\mu_3\text{-}OMe)_4(OMe)_6(MeOH)_{12}}]$ in the second step. This structural change, brought about by partial loss of methanol, also explains the observed decrease of the unit-cell volume.

In summary, as a result of the fluorolysis of magnesium alkoxide, not only nanoscopic sols are formed, but also stable crystalline intermediates having a dicubane structure with unusual fluorine linkages can be obtained. Thus, once structural information for aluminum alkoxide fluoride is included,[4] it will help to gain insights into the mechanism of anhydrous sol–gel synthesis of metal fluorides.

Experimental Section

All experiments were conducted under an inert atmosphere (argon, 99.998%) in a glove box and/or in a glass high-vacuum apparatus. Methanol was dried over magnesium turnings (Aldrich, 99.98%) by heating to reflux, and was freshly distilled before use. High-resolution

^{19}F NMR spectra were obtained with a Bruker AV 400 spectrometer (282.2 MHz) and referenced to CCl_3F (0 ppm). X-ray diffraction (XRD) patterns were recorded with a XRD-7 Seiffert FPM diffractometer using $Cu_{K\alpha}$ radiation. The samples were prepared in a dry box and covered with polystyrene film to exclude air during acquisition. Thermal analysis (TG/TDG) experiments were performed on a Netzsch STA 409 C instrument equipped with a quadrupole mass spectrometer (Balzers QMG 422). Measurements were performed in a N_2 atmosphere. The release of methanol was detected by mass spectrometry over a temperature range of 30 to 500 °C.

1: Magnesium methoxide (1 g, 11.6 mmol) was dissolved in dry MeOH (30 mL), and HF dissolved in MeOH (11.7 M, 0.37 mL, 3,84 mmol) was added at 0 °C. After storage at −20 °C for two weeks, colorless, column-shaped crystals were obtained which were identified by X-ray single crystal analysis to be compound **1**. The powder samples, obtained from the reaction at about 10 °C and by immediate distilling off the solvent, were analyzed by XRD, TG/DTG, and elemental analysis. Both analytical and structural results for the powder samples are compatible with the data for isolated single crystals **1** and **1a**.

Elemental analysis (%) calcd for **1**: C 30.58, H 9.13, F 4.03; found: C 28.6, H 8.4, F 4.5. The lower C and H values and the higher value for F result from the loss of methanol during sample preparation.

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[6] Crystal data for $C_{24}H_{86}F_2Mg_6O_{24}$ (942.79 g mol^{-1}): Data were collected for **1** (170 K) and **1a** (250 K) using an IPDS diffractometer (STOE) with $Mo_{K\alpha}$ radiation (71.073 pm). Structures were solved and refined with SHELX97 (anisotropic for all non-hydrogen atoms, isotropic for acidic hydrogen atoms; the coordinates of hydrogen atoms of the methyl groups were calculated). **1**: monoclinic, $P2_1/c$ (No.14), crystal dimensions $0.5\times0.5\times0.25$ mm^3, $a=1073.5(2)$, $b=1199.7(2)$, $c=2022.3(4)$ pm, $\beta=97.44\ (2)°$, $V=2582.5(8)\times10^6$ pm^3, $Z=2$, $wR_2=0.106$ for all 5658 reflections and 293 parameters, $R_1=0.039$ for 4157 reflections with $I>2\sigma(I)$. **1a**: monoclinic, $C2/m$ (No.12), crystal dimensions $0.4\times0.3\times0.3$ mm^3, $a=2044.63(9)$, $b=1210.89(7)$, $c=1074.71(5)$ pm, $\beta=101.027(4)°$, $V=2611.7(2)\times10^6$ pm^3, $Z=2$, $wR_2=0.153$ for all 3162 reflections and 163 parameters, $R_1=0.053$ for 2398 reflections with $I>2\sigma(I)$. Unit-cell parameters for **2**: orthorhombic I, $a=11.82(1)$, $b=11.98(1)$, $c=16.29(2)$ pm, $V=2307(4)\times10^6$ pm^3. CCDC-656257 (**1**) and CCDC-656258 (**1a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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