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Aluminum Alkoxide Fluorides Involved in the Sol–Gel Synthesis of Nanoscopic AlF_3

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In the search for intermediates during the sol–gel synthesis of nanoscopic AlF_3, the fluorolysis of aluminum isopropoxide by HF in pyridine has been investigated. By varying the Al to HF ratio from 0.5 to 2, three aluminum alkoxide fluorides, $Al_3F(Py)(O\textit{i}Pr)_8$, $Al_7F_{10}(\mu_4\text{-}O)(O\textit{i}Pr)_9(Py)_3\cdot 1.34Py$, and $Al_{10}F_{16}(\mu_4\text{-}O)_2(O\textit{i}Pr)_{10}(Py)_4\cdot 4.17Py$, were isolated and structurally characterized. The structures of these compounds are discussed as possible snapshots in the consecutive *fluorolytic* sol–gel formation of nanoscopic AlF_3 and give deeper insight into the probable reaction pathway.

Introduction

The reaction of $Al(O\textit{i}Pr)_3$ with anhydrous hydrogen fluoride (aHF) in the presence of a suitable organic solvent proceeds by a sol–gel-route and yields, after solvent removal, nanoscopic, X-ray amorphous AlF_3 with a high surface (*HS*) area.[1] Due to its high degree of distortion as a result of the sol–gel-stage, this *HS*-AlF_3 represents one of the strongest Lewis acids known and is comparable to SbF_5.[2] Less is known so far about the mechanism of this *fluorolytic* sol–gel route, but the sol formation step seems to be crucial for the properties of the nanoscopic metal fluorides finally obtained.[3] However, neither the structures of the gels nor the decisive reactions causing their formation are known in detail.

MAS NMR spectroscopy is a valuable tool to gain deeper insight into the fine structures of the gels;[4] however, the synthesis and isolation of defined crystalline intermediates from different stages of the progressive fluorination process would provide more detailed information. Therefore, we have focused our activities on the isolation and the determination of the structure of the crystalline intermediates of the *fluorolytic* sol–gel synthesis of nanoscopic *HS*-AlF_3. In 2004, we presented the first example of an isolated mixed aluminum alkoxide fluoride, $Al_3F(O\textit{i}Pr)_8\cdot dmso$,[5] and since then, only one more example was published: $\{(F)Al[OC(CF_3)_3]_2\ (thf)\}_2$ with the four-membered-ring unit $[(\sigma^5Al)_2(\mu F)_2]$.[6] Both structures are stabilized by donor molecules (dmso or thf). However, in performing the $Al(O\textit{i}Pr)_3$/aHF reactions in these solvents no further crystalline compounds could be synthesized by varying the stoichiometric ratios of Al/F. On the other hand, $Al(O\textit{i}Pr)_3$ dissolved in pyridine neither undergoes reactions nor structural changes caused by the solvent; however, it crystallizes as a packing of well-known tetrameric $Al[(\mu\text{-}O\textit{i}Pr)_2Al(O\textit{i}Pr)_2]_3$ "Mitsubishi" molecules.[7] Thus, pyridine was found to be a very suitable donor solvent for studying the sol formation step, since nanoscopic *HS*-AlF_3 can finally be obtained even from this solvent. Herein we report the results of the preparation and crystal structure determinations of differently fluorinated polynuclear $Al(O\textit{i}Pr)_{3-x}F_x$ compounds, which allow a defined insight in the stepwise O*i*Pr-against-F exchange along this synthesis path.

Results

The reaction of aluminum isopropoxide with 0.5 to 1.0 equivalents of aHF in pyridine affords the new compound $Al_3F(O\textit{i}Pr)_8(Py)$ (**1**) in approximately 50% yield.[8] Compound **1** crystallizes in three different crystalline modifications,[9] which, however, contain the same molecule (Figure 1). It represents a trinuclear Al unit consisting of the central σ^6-Al atom (Al1), which is coordinated by the terminal F1 atom and the donor molecule and is in addition connected by two pairs of bridging O*i*Pr groups with two σ^4-Al centers (Al2 and Al3). The latter are further coordinated by two terminal O*i*Pr groups each (Figure 1). The molecular structures of **1** and $Al_3F(O\textit{i}Pr)_8(dmso)$[5] revealed nearly equal Al–O and Al–F distances even though the Al–N(Py) donor bond [2.098(2) Å] in structure **1** is longer than the corresponding Al–O(dmso) bond [1.915(2) Å].

By raising the aHF/$Al(O\textit{i}Pr)_3$ ratio to larger than 2, highly fluorinated but X-ray amorphous solids were isolated from the reaction mixtures. At an aHF/$Al(O\textit{i}Pr)_3$ ratio of 3, the compositions of the obtained solids were almost identical with those obtained from the "classical" alcoholic (*i*PrOH) system as described elsewhere.[1] However, at aHF/$Al(O\textit{i}Pr)_3$ ratios between 1.5 and 2.0, small amounts of

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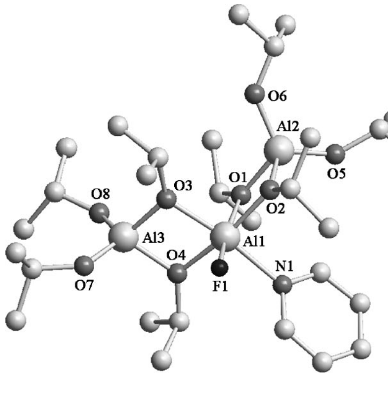

Figure 1. Molecular structure of $\mathrm{Al_3F(O\mathit{i}Pr)_8(Py)}$ (**1**). Hydrogen atoms are not shown for clarity. Selected bond lengths (in Å; eds values are 0.001–0.002 Å): Al1–O1 1.950, Al1–O2 1.902, Al1–O3 1.926, Al1–O4 1.913, Al1–F1 1.723, Al1–N1 2.098, Al2–O1 1.790, Al2–O2 1.800, Al2–O5 1.695, Al2–O6 1.705, Al3–O3 1.786, Al3–O4 1.809, Al3–O7 1.704, Al3–O8 1.704.

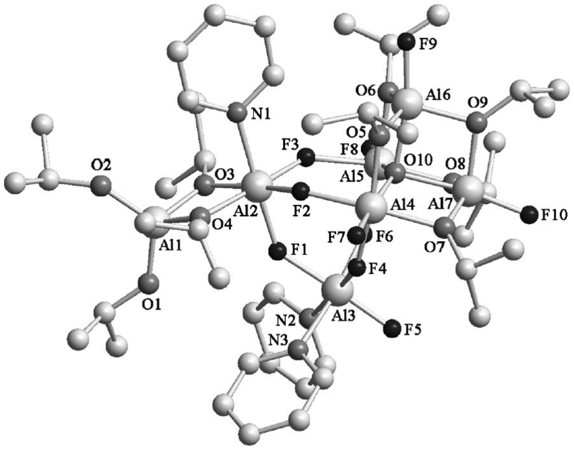

Figure 2. Molecular structure of $\mathrm{Al_7F_{10}(\mu_4\text{-}O)(O\mathit{i}Pr)_9(Py)_3{\cdot}1.34Py}$ (**2**). Hydrogen atoms and Py solvate molecules are not shown for clarity. Selected bond lengths (in Å; eds values are 0.002–0.003 Å): Al1–O1 1.694, Al1–O2 1.697, Al1–O3 1.802, Al1–O4 1.797, Al2–O3 1.884, Al2–O4 1.895, Al2–F1 1.843, Al2–F2 1.776, Al2–F3 1.787, Al2–N1 2.073, Al3–F1 1.845, Al3–F4 1.794, Al3–F5 1.722, Al3–F6 1.798, Al3–N2 2.047, Al3–N3 2.050, Al4–O5 1.939, Al4–O7 1.942, Al4–O10 1.842, Al4–F2 1.909, Al4–F4 1.856, Al4–F7 1.692, Al5–O6 1.941, Al5–O8 1.939, Al5–O10 1.824, Al5–F3 1.945, Al5–F6 1.863, Al5–F8 1.689, Al6–O5 1.835, Al6–O6 1.846, Al6–O9 1.833, Al6–O10 1.892, Al6–F9 1.692, Al7–O7 1.828, Al7–O8 1.835, Al7–O9 1.850, Al7–O10 1.919, Al7–F10 1.695.

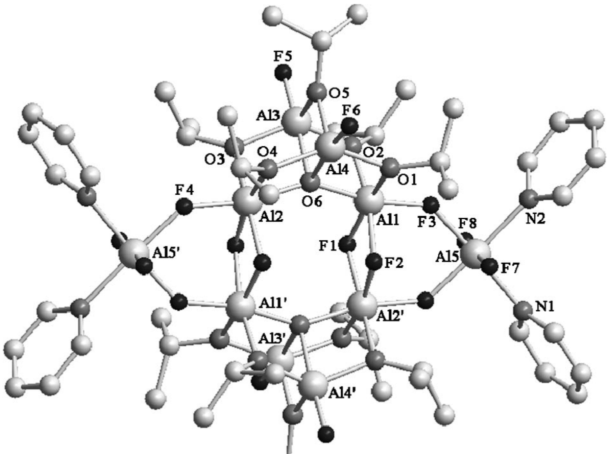

Figure 3. Centrosymmetric molecular structure of $\mathrm{Al_{10}F_{16}(\mu_4\text{-}O)_2(O\mathit{i}Pr)_{10}(Py)_4{\cdot}4.17Py}$ (**3**). Hydrogen atoms and Py solvate molecules are not shown for clarity. Selected bond lengths (in Å; eds values are 0.003–0.004 Å): Al1–O1 1.910, Al1–O2 1.902, Al1–O6 1.829, Al1–F1 1.845, Al1–F2 1.850, Al1–F3 1.797, Al2–O3 1.904, Al2–O4 1.902, Al–O6 1.830, Al2–F1 1.847, Al2–F2 1.847, Al2–F4 1.793, Al3–O1 1.845, Al3–O3 1.838, Al3–O5 1.826, Al3–O6 1.953, Al3–F5 1.682, Al4–O2 1.861, Al4–O4 1.851, Al4–O5 1.817, Al4–O6 1.898, Al4–F6 1.681, Al5–F3 1.856, Al5–F4 1.852, Al5–F7 1.722, Al5–F8 1.723, Al5–N1 2.073, Al5–N2 2.080.

crystals were obtained,[8] which have been identified by single-crystal X-ray diffraction analysis as the new polynuclear compounds $\mathrm{Al_7F_{10}(\mu_4\text{-}O)(O\mathit{i}Pr)_9(Py)_3{\cdot}1.34Py}$ (**2**) and $\mathrm{Al_{10}F_{16}(\mu_4\text{-}O)_2(O\mathit{i}Pr)_{10}(Py)_4{\cdot}4.17Py}$ (**3**).[9]

The molecular structure of **2** features tetra-, penta-, and hexacoordinate aluminum atoms (Figure 2), whereas the centrosymmetric structure of **3** contains only penta- and hexacoordinate Al atoms (Figure 3). The common feature of the two structures is that they contain tetracoordinate oxygen atoms (μ_4-O) as well as two types of fluorine atoms, bridging (F_b) and terminal (F_t). Terminal isopropoxide groups (O_t) were observed only at σ^4Al atoms (e.g. Al1 with O1 and O2 in structure **2**), whereas the corresponding bridging isopropoxide groups (O_b) are connected to σ^5- and σ^6-Al atoms as found in both compounds, **2** and **3**. Hence, in structure **3** all O*i*Pr groups (O1–O5) are bridging.

In all three structures **1**–**3**, Al–F and Al–O bond lengths depend on the coordination number of Al atom as well as on functions of F or O atoms (terminal or bridging). The shortest Al–F and Al–O bonds (1.68–1.70 Å) are those connecting σ^4- and σ^5-Al atoms with terminal F_t or O_t atoms, whereas σ^6Al–F_t bonds are little bit longer (1.69–1.72 Å). As expected, larger differences were found for Al–O_b distances, σ^4Al–O_b (1.79–1.81 Å) being less elongated than corresponding σ^5Al–O_b (1.83–1.86 Å) and σ^6Al–O_b (1.88–1.94 Å) bonds.

μ_4-O atoms in structure **2** (O10) and **3** (O6) have strongly distorted tetrahedral environments formed by two σ^5- and two σ^6-Al atoms, the Al–(μ_4-O) distances being in a comparatively wide range of 1.82–1.95 Å. In contrast, σ^6Al–N(Py) bond lengths lie in a narrow range of 2.05–2.10 Å.

The source of μ_4-O atoms in **2** and **3** cannot be determined with certainty at present. A hydrolysis route as an initial step for μ_4-O formation is unlikely, as we worked under strictly anaerobic conditions. More probably, ether elimination due to interaction between two bridging OR groups results in the formation of μ_4-O. This might be assisted by raising the Lewis acidity of Al sites by increasing the degree of fluorination. The formation of μ_4-O atoms have been reported for a considerable number of aluminum oxoalkoxides,[11] and once formed, they should be very resistant against further fluorination. Thus, we can not rule out that such μ_4-O atoms may survive the mild post-fluorination step and might be present to a small extent even in the final *HS*-AlF_3 materials. Thus, they could be either a stabilizing factor of the highly distorted, highly *Lewis* acidic *HS*-AlF_3 or just be tolerated by this phase without having any impact on it. The crystallization of only small amounts of **2** and **3** can be explained by the dynamic behavior of the differently oligomerized and fluorinated species in solution.

Applying a formal approach, compound **2** can be thought to be formed by bridging the monofluorinated species $[Al_3(O\mathit{i}Pr)_8F]$ with a hypothetical tetrameric unit "$Al_4(O)(O\mathit{i}Pr)F_9$" thus forming $Al_7(O)(O\mathit{i}Pr)_9F_{10}$. However, compound **3**, $Al_{10}F_{16}O_2(O\mathit{i}Pr)_{10}$, is rather formed from two tetranuclear $Al_4(\mu_4\text{-}O)$ units bridged by two fluorinated monomers.

New compounds **1**–**3** with their very different degrees of oligomerization and fluorination clearly show that in the course of the fluorolytic sol–gel synthesis various fluorinated oligomers exist, resulting finally, under stoichiometric conditions, in the formation of a very open gel framework. It seems that μ_4-O-containing fluorinated oligomers provide good starting conditions for the crystallization, although they probably do not represent the major species in this reaction system.

Conclusion

By performing the reaction of $Al(O\mathit{i}Pr)_3$ with aHF in pyridine as solvent, we were able to work out the synthesis of three discrete mixed polynuclear aluminum alkoxide fluoride compounds, which were structurally characterized. These three compounds might be considered as snapshots in the consecutive *fluorolytic* sol–gel formation, giving deeper insight into the probable reaction pathway.

Acknowledgments

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[8] All experiments were performed by using Schlenk line (argon) and glove box techniques. Pyridine was purified according to standard procedures, $Al(O\mathit{i}Pr)_3$ was recrystallized from pyridine, and fluorine/aluminum ratios were adjusted by pyridine solutions (≤ 1 M) of $Al(O\mathit{i}Pr)_3$ and aHF. A typical experimental procedure for the synthesis of **1**: $Al(O\mathit{i}Pr)_3$ (5.1 g, 27 mmol) was dissolved in pyridine (40 mL) in a 150 mL Schlenk flask, and a pyridine solution of aHF (19 mmol, 26.7 mL, 0.71 M) was added; the reaction mixture was stirred at 50 °C for 24 h, concentrated thereafter to about half of the starting volume by removal of volatiles and stored at –35 °C. The precipitated crystals were filtered, washed with cold pyridine, and dried on the vacuum line for 1 h to afford pure compound **1** (2.65 g, 4.1 mmol; 45% yield). In case of compounds **2** and **3** the procedures were similar but average F/Al ratios were between 1.5 and 2.0. Crystals were obtained either directly by concentrating the reaction mother liquids or by recrystallization of the solid products after removal of all volatiles.

[9] Crystal data: The data for **1**–**3** were collected with an IPDS diffractometer (Stoe) at 100 K (graphite monochromated Mo$K\alpha$-radiation, $\lambda = 0.71073$ Å). Absorption corrections were not applied. $Al_3F(O\mathit{i}Pr)_8(Py)$ (**1**): $M = 651.73$, orthorhombic (**1a**), monoclinic (**1b**) and triclinic (**1c**) modifications. Only the data for **1a** are given below, those for **1b** and **1c** are available from the CCDC: $Pbca$, $a = 9.563(1)$ Å, $b = 25.044(2)$ Å, $c = 31.910(3)$ Å, $V = 7642(1)$ Å^3, $Z = 8$; reflections collected: 52243, independent reflections: 9827. The structure was solved with SHELXS-97.[10] The final anisotropic LS refinement (SHELXL-97[10]) with 407 parameters converged to $wR_2 = 0.141$ and $R_1 = 0.059$. $Al_7F_{10}(\mu_4\text{-}O)(O\text{-}\mathit{i}Pr)_9(Py)_3\cdot 1.34Py$ (**2**): $M = 1270.00$, monoclinic, $P2_1/n$, $a = 17.973(3)$ Å, $b = 19.033(2)$ Å, $c = 19.700(3)$ Å, $\beta = 99.74(2)°$, $V = 6642(2)$ Å^3, $Z = 4$, $wR_2 = 0.098$ (for 14630 reflections and 749 parameters), $R_1 = 0.058$ [for 5276 reflections with $I > 2\sigma(I)$]. One of the two pyridine solvate molecules is disordered and was refined with partial occupancy. $Al_{10}F_{16}(\mu_4\text{-}O)_2(O\text{-}\mathit{i}Pr)_{10}(Py)_4\cdot 4.17Py$ (**3**): $M = 1842.63$, triclinic, $P\bar{1}$, $a = 13.585(1)$ Å, $b = 13.715(1)$ Å, $c = 14.047(1)$ Å, $\alpha = 63.201(6)$, $\beta = 81.407(7)$, $\gamma = 84.117(6)°$, $V = 2308.1(3)$ Å^3, $Z = 4$, $wR_2 = 0.212$ (for 10563 reflections and 604 parameters), $R_1 = 0.098$ [for 6840 reflections with $I > 2\sigma(I)$]. In this case, most pyridine solvate molecules have incomplete occupancies and are strongly disordered. Although the crystals for X-ray analysis were prepared in a cold stream of nitrogen, they always showed solvent loss and disorder. CCDC-734179(**1a**), -734180(**1b**), -734181(**1c**), -734182(**2**), and -734183(**3**) 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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