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Synthesis and crystal structure of a novel aluminum–fluorine–potassium compound $[((Me_3Si)_3C)_2Al_2(\mu\text{-}F)F_4K]_x$ with a supramolecular chain

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Abstract

$[((Me_3Si)_3C)_2Al_2(\mu\text{-}F)F_4K]_x$ (**6**) is a new organoaluminum alkali fluoride with an infinite potassium zig-zag chain. The compound is accessible either by reaction of $[(Me_3Si)_3CAlF_2]_3$ with KF or by treating $[(Me_3Si)_3CAlF_2]_3$ with potassium metal. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Aluminum; Fluorine; Alkali ions; Chain; Supramolecular

1. Introduction

There are several known compositions of $[(Me_3Si)_3CAlF_2]_3$ with alkali fluorides [1–5]. The cations are structure directing to yield cubic arrays like $[M(Me_3Si)_3CAlF_3(THF)]_4$ (M = Li (**1**) [1], Na (**2**) [2]) and unusual aggregates $[Ag(toluene)_3]^+[\{((Me_3Si)_3C)_2Al_2(\mu\text{-}F)F_4\}_2Li]^-$ (**3**) [3] (Scheme 1), $[((Me_3Si)_3C)_4Al_4K_2(\mu\text{-}F)_2F_8(THF)_4]$ (**4**) [4], and $[\{Li(Me_3Si)_3CAlF_3(THF)\}_3LiF(THF)]$ (**5**) [5] (Scheme 2). They contain the chelating $[(Me_3Si)_3CAlF_3]^-$ (**1**, **2**, and **5**) or $[(Me_3Si)_3CAlF_2(\mu\text{-}F)F_2AlC(SiMe_3)_3]^-$ (**3** and **4**) anion. It is known that organoaluminum difluorides form various aggregates in the presence of THF due to the Lewis base character of this solvent and the Lewis acidity site of the aluminum. Consequently different structural arrangements were isolated when these systems were treated with THF [6]. Compound **4** for example contains four molecules of coordinated THF. Therefore, we were interested in the THF free analogous compound. The result is a compound of composition $[((Me_3Si)_3C)_2Al_2(\mu\text{-}F)F_4K]_x$ (**6**) containing a potassium zig-zag chain with a complete different coordination sphere at the potassium atom compared to **4**.

2. Results and discussion

Compound **6** was prepared from $[(Me_3Si)_3CAlF_2]_3$ with water free KF in toluene under reflux in moderate yield. At room temperature compound **6** is only slightly soluble in toluene. Suitable crystals for X-ray structural analysis were obtained from hot toluene. An alternative method for the preparation of **6** is the treatment of $[(Me_3Si)_3CAlF_2]_3$ with metallic potassium under reflux in toluene. The by-product of this reaction could not be characterized. The yield of **6** is slightly higher than the latter method (Scheme 3). The structure of **6** consists of an endless potassium zig-zag chain with a K–K distance of 4.7800(7) Å which is slightly longer than that in potassium metal (avg. 4.54 Å) [7] (Fig. 1). The potassium atoms are four-fold coordinated by terminal fluorine atoms of the $[(Me_3Si)_3CAlF_2(\mu\text{-}F)F_2AlC(SiMe_3)_3]^-$ anions (Fig. 2). The K–F bond length ranges from 2.5990(17) to 2.6587(18) Å which is slightly shorter or comparable to that in KF (2.664 Å) [7] or in the range of those in **4** (2.610–2.860 Å). Within the four terminal fluorine atoms of **6** F(4) is weakly coordinating to a second potassium atom with a distance of 3.147(2) Å which is slightly (0.5 Å) longer than the other observed K–F distances in this molecule. The Al–F (terminal) bond length (1.6820(18)–1.6940(19) Å) is slightly longer than those in **3** (1.657–1.688 Å) and in **4** (1.672–1.677 Å), respectively. The Al–F (bridging) bond length (1.8028(17)–1.8144(17) Å) is comparable to that in **3** (1.7881–1.802 Å) and in **4** (1.817–1.823 Å). The F–K–F angles are acute for F(2)#1–K(1)–F(4)#1 (73.30(5)°) and F(3)–K(1)–F(5) (72.57(5)°) and more open for F(3)–K(1)–F(4)#1 (114.14(6)°) and F(2)#1–K(1)–F(5) (109.56(6)°). All potassium atoms in the chain are in plane with a K–K–K angle of 137.74(3)° (Fig. 3). The potassium in **4** is six-fold coordinated by four fluorine and two oxygen of the THF molecules. In contrast,

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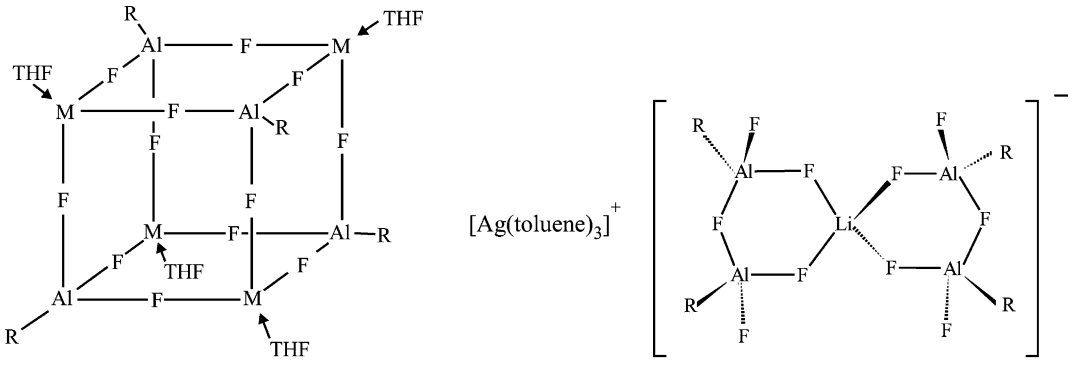
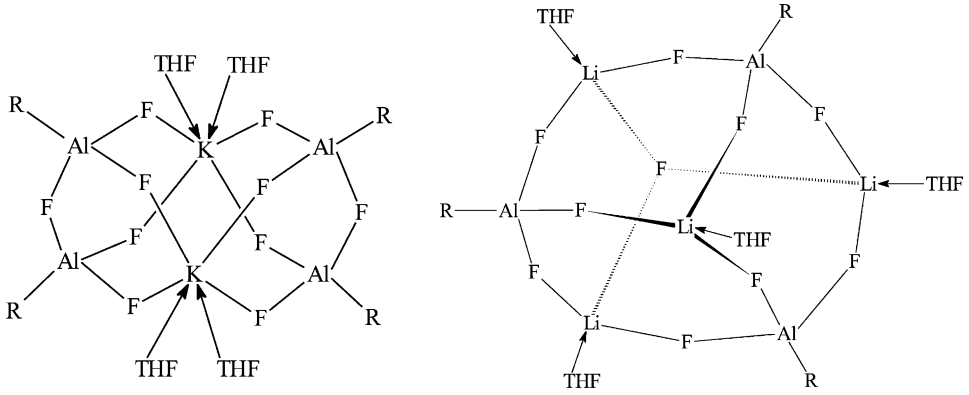


M = Li (**1**), Na (**2**)

R = $C(SiMe_3)_3$

3

Scheme 1.



4

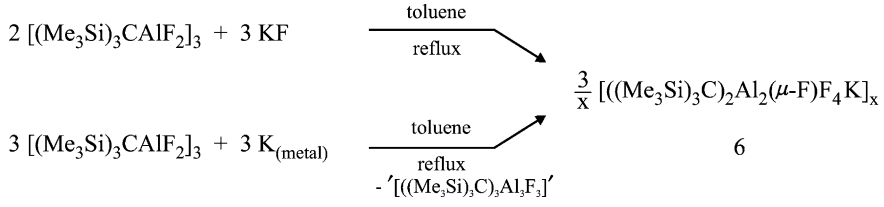
R = $C(SiMe_3)_3$

5

Scheme 2.

the potassium in **6** has the coordination number of four with a fifth fluorine atom in a weak contact (3.147(2) Å).

Compound **6** is slightly soluble in toluene at room temperature. However the solubility increases when heated under reflux. Compound **6** dissolves easily in THF but dissociates in this strong coordinating solvent [8]. The ^{19}F NMR spectrum of **6** shows resonances at δ −152.8 (m, 2F, Al–F–Al), −156.9 (s, 1F), −157.3 (s, 4F, Al–F–K), and −157.5 (s, 4F, Al–F–K). We assume that the multiplet at −152.8 is an unresolved quintet (J = 30 Hz) and the resonances at δ −157.3 and −157.5 are the associated doublets (J = 30 Hz) with the intensity ratio of 1:4 as it is expected for the $[(Me_3Si)_3CAlF_2(\mu\text{-}F)F_2AlC(SiMe_3)_3]^-$ anion in **6**. This coupling is hard to recognize in the ^{19}F NMR spectrum. The resonance at δ −156.9 is unknown. For compound **3** the resonances in the ^{19}F NMR are reported in the same range



Scheme 3.

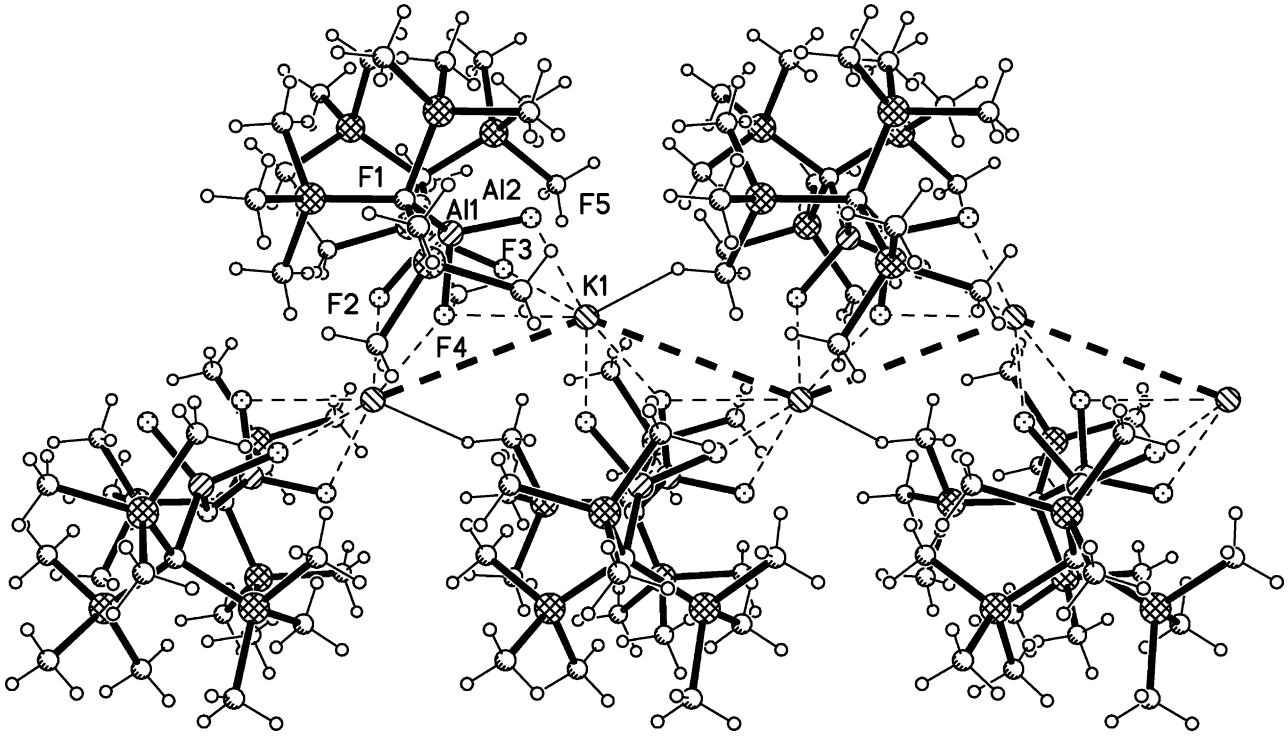


Fig. 1. Arrangement of **6** in the chain. The potassium atoms are in the plane of the paper.

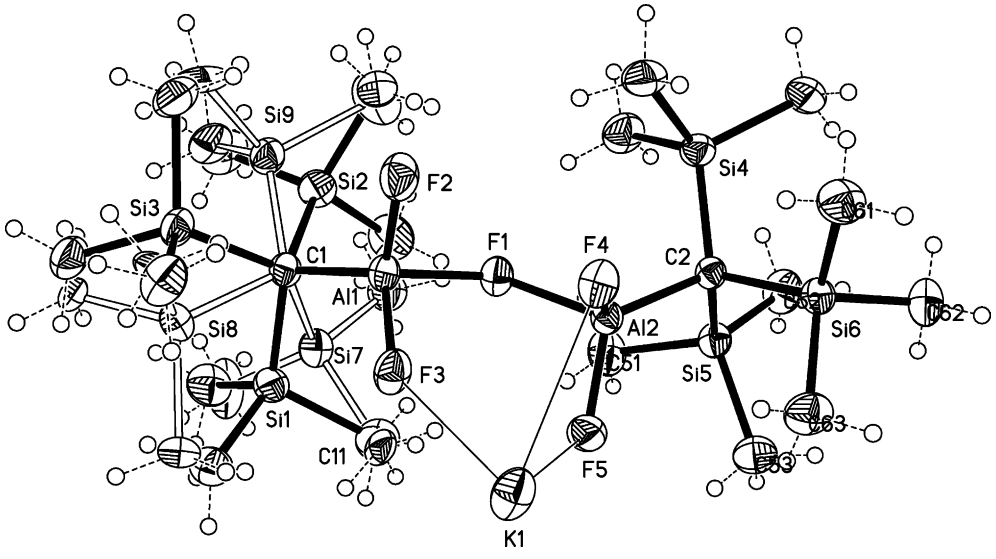


Fig. 2. Ortep plot of **6** showing a single unit of the chain. The disorder at $C(SiMe_3)_3$ is included.

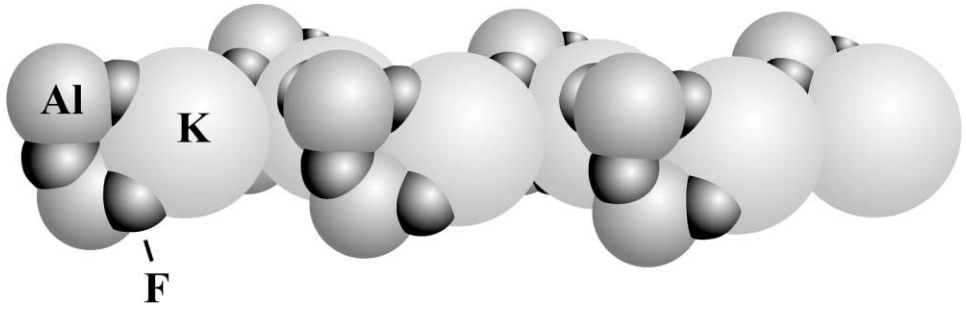


Fig. 3. Van der Waals plot of **6**. The $C(SiMe_3)_3$ ligand is omitted for clarity.

(δ −154.5 (m, 2F), −158.0 (s, 1F), −158.6 (s, 4F), −158.8 (s, 4F)) while the resonance at δ −156.9 is obviously produced by the same impurity.

In summary, in compound **4** we found a strong coordinating ability of THF which displaces in part the fluoride anions at the aluminum center to yield a discrete complex while in the presence of the weakly coordinating toluene a supramolecular chain is formed as it is observed in **6**. The latter is an interesting model for the activation of AlF_3 in the presence of KF. Fluorides of aluminum find use as catalysts for the new chlorofluorocarbon alternatives [9].

3. Experimental

All experiments were performed using standard Schlenk techniques under a dry nitrogen atmosphere due to the sensitive behavior of the reactants and products toward air and moisture. A Braun MB 150-GI Box was used to store the compounds and to prepare the samples for spectroscopic characterization. All solvents were distilled from sodium/benzophenone and degassed prior to use. $[(Me_3Si)_3CAlF_2]_3$ was prepared by a similar method as described in the literature [4] but in quantitative yields and an easier procedure.[1] Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. NMR spectra were recorded on a Bruker AM 250 and were externally referenced to Me_4Si and $CFCl_3$. FT–IR spectra were measured on a Bio-Rad FTS-7 as CsI plates in the range of 4000–220 cm^{-1}. Melting points were measured in sealed glass tubes.

3.1. Synthesis of $[((Me_3Si)_3C)_2Al_2(\mu\text{-}F)F_4K]_x$ (6)

3.1.1. First method

$[(Me_3Si)_3CAlF_2]_3$ (1.04 g, 1.16 mmol) and KF (100 mg, 1.60 mmol) in toluene (20 ml) were heated under reflux for 6 h. All solvents were removed in vacuo. The residue was extracted with hot hexane (20 ml). The solid was again treated with toluene (20 ml) and heated under reflux for 1 h. Crystallization at 20 °C resulted in 180 mg of $[((Me_3Si)_3C)_2Al_2(\mu\text{-}F)F_4K]_x$ (0.28 mmol, 18%) as a colorless crystalline solid with mp >300 °C.

3.2. Second method

$[(Me_3Si)_3CAlF_2]_3$ (892 mg, 1.0 mmol) and K (metal) (39 mg, 1.0 mmol) in toluene (20 ml) were heated under reflux for 6 h. Crystallization at 20 °C resulted in 150 mg of $[((Me_3Si)_3C)_2Al_2(\mu\text{-}F)F_4K]_x$ (0.23 mmol, 23%) as a colorless crystalline solid with mp >300 °C. The colorless crystals were collected by hand.

3.3. Characterization (both synthetic methods gave the same data for (6))

^1H NMR (200 MHz, C_6D_6): 0.42 (s). ^{19}F NMR (188 MHz, C_6D_6): −152.8 (m, 2F, Al–F–Al), −156.9 (s, 1F), −157.3 (s, 4F, Al–F–K), −157.5 (s, 4F, Al–F–K). ^{29}Si (99 MHz, C_6D_6): −3.4. FAB *m/z*: 669 $[M + F]^-$ (10), 315 $(M–(Me_3Si)_3CAlF_2–K)^-$ (100). IR (CsI): 2958(s), 2904(s), 1202(versus), 1100(s), 1022(s), 857(versus), 688(s), 551 (s), 406 (s), 327 (s) cm^{-1}. Elemental analyses for $C_{20}H_{54}Al_2F_5KSi_6$: anal. calcd. for C, 36.89; H, 8.36; found C, 37.1; H, 8.36%.

3.4. Crystallography

A colorless crystal was isolated from the reaction of $[(Me_3Si)_3CAlF_2]_3$ with potassium metal. Crystal structure solution and refinement of **6** is shown in Table 1. Data of compound **6** were collected on a Stoe four circle diffractometer. The structure was solved by direct methods [10] and refined anisotropically with SHELXTL. Hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} of the parent atom. A selection of bond distances and angles are shown in Table 2. In the structure one $C(SiMe_3)_3$ is disordered. It was refined with distance restraints. Due to

Table 1
Data collection and strutural parameters for **6**

Empirical formula	$C_{20}H_{54}Al_2F_5KSi_6$
Formula weight	651.23
Temperature	200(2) K
Wavelength	71.073 pm
Crystal system	Orthorhombic
Space group	*P*2(1)2(1)2(1)
Unit cell dimensions	$a = 8.9174(11)$ Å $\alpha = 90°$. $b = 15.976(2)$ Å $\beta = 90°$. $c = 25.206(3)$ Å $\gamma = 90°$.
Volume	3591.0(8) $Å^3$
Z	4
Density (calculated)	1.205 Mg/m^3
Absorption coefficient	0.433 mm^{-1}
F(000)	1392
Crystal size	0.60 mm × 0.20 mm × 0.20 mm
Theta range for data collection	3.52–25.02°.
Index ranges	$-10 \le h \le 10$, $-19 \le k \le 19$, $-30 \le l \le 30$
Reflections collected	10531
Independent reflections	6330 (R(int) = 0.0361)
Completeness to theta = 25.02°	99.6%
Max. and min. transmission	0.9184 and 0.7811
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6330/571/438
Goodness-of-fit on F^2	1.062
Final R indices ($I > 2\sigma$ (I))	$R_1 = 0.0358$, $wR_2 = 0.0744$
R indices (all data)	$R_1 = 0.0447$, $wR_2 = 0.0796$
Largest diff. peak and hole	0.430 and −0.238 $eÅ^{-3}$

[1] A mixture of $(Me_3Si)_3CAlMe_2 \times THF$ (3.61 g, 10.0 mmol) and Me_3SnF (3.66 g, 20.0 mmol) in THF (30 ml) was stirred for 12 h. After the THF had been pumped off the remaining solid was heated for 4 h at 150 °C in vacuo. Pale yellow $[(Me_3Si)_3CAlF_2]_3$ (2.95 g, 9.95 mmol, 99%) remained.

Table 2
Bond lengths (Å) and angles (°) for **6**

K(1)–F(3)	2.5990(17)	Al(1)–F(3)	1.6820(18)
K(1)–F(2)#1	2.6347(17)	Al(1)–F(2)	1.6940(19)
K(1)–F(4)#1	2.6441(18)	Al(1)–F(1)	1.8144(17)
K(1)–F(5)	2.6587(18)	Al(1)–C(1)	1.953(3)
K(1)–F(4)	3.147(2)	Al(2)–F(5)	1.6865(19)
K(1)–Al(2)	3.5933(11)	Al(2)–F(4)	1.6922(17)
K(1)–Al(1)#1	3.9671(11)	Al(2)–F(1)	1.8028(17)
K(1)–K(1)#2	4.7800(7)	Al(2)–C(2)	1.948(3)
F(3)–K(1)–F(2)#1	132.31(7)	F(4)–Al(2)–F(1)	97.56(8)
F(3)–K(1)–F(4)#1	114.14(6)	Al(2)–F(1)–Al(1)	129.47(9)
F(2)#1–K(1)–F(4)#1	73.30(5)	Al(1)–F(2)–K(1)#2	131.60(10)
F(3)–K(1)–F(5)	72.57(5)	Al(1)–F(3)–K(1)	145.68(9)
F(2)#1–K(1)–F(5)	109.56(6)	Al(2)–F(4)–K(1)#2	143.54(10)
F(4)#1–K(1)–F(5)	168.62(6)	Al(2)–F(4)–K(1)	90.79(8)
F(3)–K(1)–F(4)	65.27(5)	K(1)#2–K(1)–K(1)#1	137.74(3)
F(2)#1–K(1)–F(4)	78.02(5)	K(1)#2–F(4)–K(1)	110.97(5)
F(4)#1–K(1)–F(4)	136.73(5)	Al(2)–F(5)–K(1)	109.54(8)
F(5)–K(1)–F(4)	53.89(5)	F(3)–Al(1)–C(1)	116.87(11)
F(3)–Al(1)–F(2)	106.66(10)	F(2)–Al(1)–C(1)	118.33(11)
F(3)–Al(1)–F(1)	98.73(9)	F(1)–Al(1)–C(1)	114.16(10)
F(2)–Al(1)–F(1)	99.01(9)	F(5)–Al(2)–C(2)	118.42(11)
F(5)–Al(2)–F(4)	104.21(9)	F(4)–Al(2)–C(2)	116.85(10)
F(5)–Al(2)–F(1)	100.46(9)	F(1)–Al(2)–C(2)	116.14(10)

racemic twinning the absolute structure was not determined. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC—162300. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2IEZ, UK.[2]

Acknowledgements

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