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$Al_5Br_7 \cdot 5THF$—The First Saltlike Aluminum Subhalide

Christoph Klemp, Gregor Stößer, Ingo Krossing, and Hansgeorg Schnöckel*

In memory of Josef Goubeau

Al^{III} halides have been studied intensively in the solid state, in solution, and in the gas phase,[1, 2] whereas for aluminum subhalides for a long time only the monomeric AlX high-temperature molecules had been characterized by gas-phase IR spectroscopy.[3, 4] With the development of matrix isolation spectroscopy, subsequently dimeric Al_2X_2 species were also investigated.[4, 5] A further development of this technique for preparative applications was presented by the cocondensation technique, which provided access to a donor-stabilized metastable AlX solution.[5] From these solutions, Al^{II} and Al^{I} halides, in the form of $Al_2Br_4 \cdot 2$anisole and $Al_4Br_4 \cdot 4NEt_3$, respectively, were structurally characterized for the first time in 1994,[6] and additional isomers of the type $Al_2X_4 \cdot 2D$ and $E_4X_4 \cdot 4D$ (D = Donor) have since been found.[7] The first polyhedral subhalide $Al_{22}X_{20} \cdot 12D$, which we reported on recently in this journal,[8] represented a new compound type. Herein we report on the first example for the mixed-valent compound type $Al_5X_7 \cdot 5D$.

Cocondensation of the high-temperature molecule AlX (X = Cl, Br, I) with a toluene/THF mixture according to the method described in reference [5] gave dark red-brown, metastable AlX · THF/touene solutions. The AlI solution decolorized at room temperature, without the deposition of aluminum, and colorless crystals of $Al_2I_4 \cdot 2THF$ (**1**) were isolated after cooling of the concentrated solution.[9] Compound **1** displays the typical $D \cdot X_2Al{-}AlX_2 \cdot D$ structure.[10] In contrast, in addition to aluminum, among others, the well-known $AlCl_3 \cdot THF$[2b] precipitated from the the AlCl solution at room temperature.

Besides aluminum and $Al_{22}Br_{20} \cdot 12THF$[8] the AlBr · THF/toluene solution afforded a colorless, brittle compound (**2**) of the composition "$Al_5Br_7 \cdot 5THF$", which crystallizes in the triclinic crystal system. An X-ray crystal structure analysis revealed that **2** is a salt comprising $[Al_5Br_8 \cdot 4THF]^-$ ions and $[Al_5Br_6 \cdot 6THF]^+$ ions (**2a** and **2b**, respectively; Figure 1).[9] The Al_5 framework of both ions consists of a central Al atom, which is tetrahedrally surrounded by four Al atoms. In the case of the (approximately S_4-symmetric) anion, these four Al atoms each bear two Br atoms and a coordinated THF molecule. In constrast, in the (approximately C_2-symmetric) cation only two $AlBr_2 \cdot THF$ groups as well as two $AlBr \cdot 2THF$ groups are arranged about the central Al atom. Thus the formula $[Al(AlBr \cdot 2THF)_2(AlBr_2 \cdot THF)_2]^+[Al(AlBr_2 \cdot THF)_4]^-$ provides a better description of the bonding situation. This ion pair possesses two Al atoms with the formal

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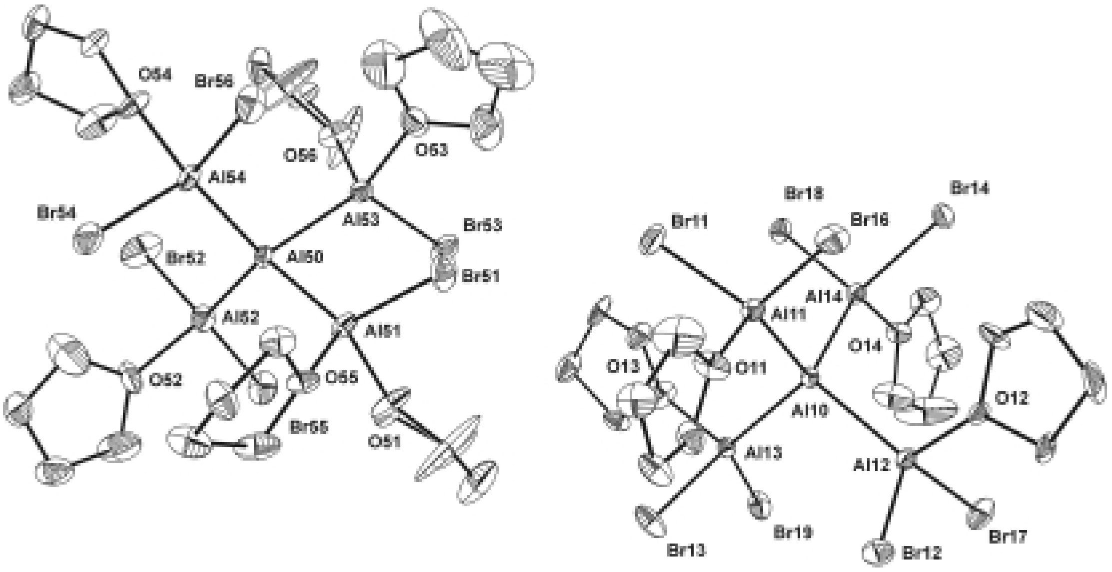


Figure 1. Molecular structure (without H atoms) of $[Al_5Br_6\cdot 6THF]^+$ **2b** (left) and $[Al_5Br_8\cdot 4THF]^-$ **2a** (right) in the solid state (triclinic distorted CsCl structure). Distances are given in Table 1. Anion and cation have very similar molecular structures, since **2b** can be converted into **2a** by substitution of the O55 and O56 atoms (THF) for Br atoms. In the crystal all Br atoms with the exception of Br55 and Br56 lie in layers, which are arranged tilted to the molecular layers.

oxidation state 0, two with +1, and six with +2; thus, the average oxidation state is +1.4.

The measured distances and those calculated by density functional theory (DFT) methods[11] in **2a** and **2b** are given in Table 1 together with those of comparable compounds. As expected the average measured bond lengths in the anion are slightly longer than those in the cation, and the calculated distances prove to be slightly longer owing to the consideration of the compounds in the gas phase. In the $AlBr_2$ groups of the cation one of the two Al^{II}–Br distances is lengthened (Br52 and Br54 in Figure 1), whereas the other resembles Al^{I}–Br distances. Accordingly, the small differences in the lengths of the bonds to the Al atom (e.g. Al–Br) are not so dependent on the oxidation state but rather on the Coulombic repulsion and steric effects within each of the molecules, since these relationships are also confirmed by ab initio calculations of the molecules in the gas phase.[12]

Table 1. Average measured and (in parentheses) calculated[11] bond lengths [pm] of **2b**, **2a**, and two related compounds.

	2b	**2a**	$Al_2Br_4\cdot 2$anisole	$Al_{22}Br_{20}\cdot 12THF$[a]
Al–Al	253.2 (255.3)	254.3 (258.3)	252.7 (254.7)	252.6 (254.1)
Al–Br	234.6/238.0 (236.4/239.3)	236.8 (236.7)	230.6 (233.8)	229.9 (–)
Al–O	188.4 (197.1)	190.5 (197.8)	193.0 (202.6)	189.2 (193.7)

[a] (Al-$AlX_2\cdot$D group), calcd: X = Cl, D = H_2O.

Compound **2** decomposes on warming above 100°C, leading to the deposition of small amounts of aluminum. The mass spectrum of **2** does not show a peak for the molecular ion. Instead a peak is detected for $[AlBr_3\cdot THF]^+$ (m/z 238.9) (direct ionization at 90°C); however, dominant fragments are $[AlBr_2\cdot THF]^+$ (m/z 258.9) and $[AlBr_2\cdot THF]^+ - C_3H_7$ (m/z 215.8).

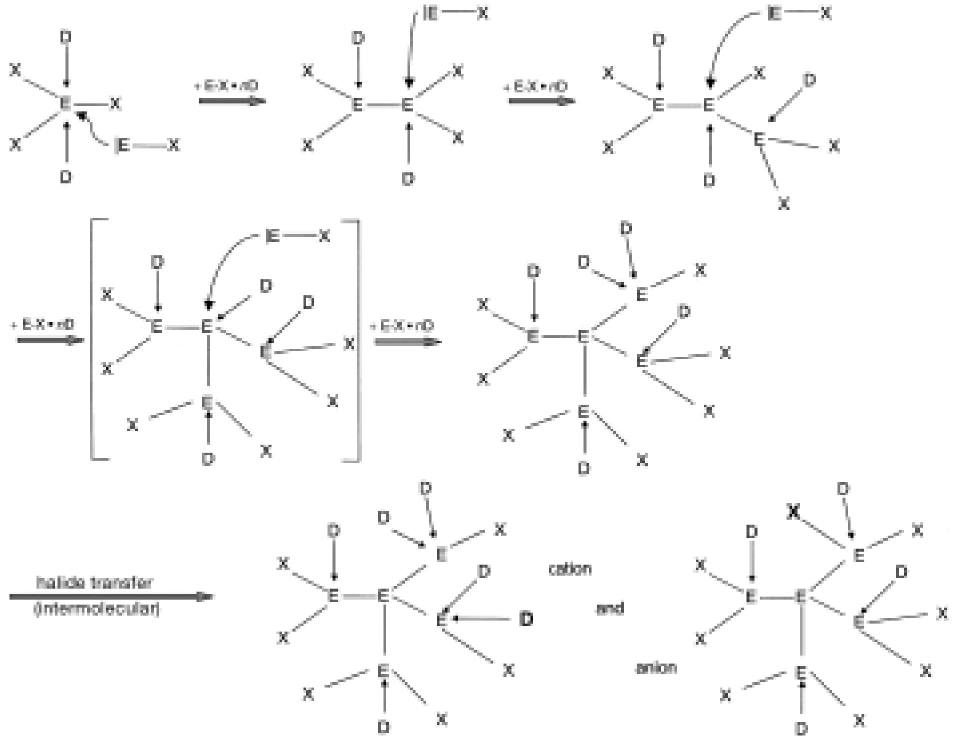
Whereas a chloro compound analogous to **2** has not been obtained to date under similar experimental conditions, the reaction of a $AlCl\cdot OEt_2$/toluene solution with $SiCl_4$ or $GeCl_4$ led to the compounds $Si(AlCl_2\cdot OEt_2)_4$ and $Ge(AlCl_2\cdot OEt_2)_4$, respectively, which are isoelectronic to the anion **2a**.[13] The cocondensation of GaCl with toluene/OEt_2 gave the neutral compound $Ga_5Cl_7\cdot 5OEt_2$ (**3**), which is analogous to **2**, with only one $Ga^{I}Cl\cdot 2OEt_2$ group.[14, 15] With **1** and these compounds a mechanism for the formation of **2** can be deduced, which is presented in Scheme 1.

Starting from $E^{III}X_3\cdot D$ (E = Al, Ga; X = Cl, Br, I), the (comproportionation) products $E_2X_4\cdot 2D$, $E_3X_5\cdot 3D$, ($E_4X_6\cdot 4D$), and $E_5X_7\cdot 5D$ can be formed by successive addition (insertion) of $E^{I}X\cdot D$. For the first product of the (oxidative) insertion of $E^{I}X\cdot D$ in a E^{III}–X bond there are numerous examples in the chemistry of aluminum and gallium[16, 17] besides the $Al_2I_4\cdot 2THF$ compound presented here. The intermediate of a second insertion has been structurally characterized in the form of $Ga_3I_5\cdot 3PEt_3$.[17] The third intermediate, $E_4X_6\cdot 4D$ or better $E(EX_2\cdot D)_3\cdot D$, has so far not been trapped, since evidently an additional E(I)X·D molecule coordinates readily so that $E_5X_7\cdot 5D$ (cf. **3**) forms directly.[18]

Two of these $E_5X_7\cdot 5D$ molecules can be converted into the ionic compound $[E_5X_6\cdot 6D]^+[E_5X_8\cdot 4D]^-$, thus **2b**·**2a**, by mutual exchange of a halide ion for a donor. The experimental findings that in the case of gallium the neutral compound $Ga_5Cl_7\cdot 5OEt_2$ forms, however, in the case of aluminum, the ionic compound $[Al_5Br_6\cdot 6THF]^+[Al_5Br_8\cdot 4THF]^-$ is obtained[19] can be supported by quantum-chemical calculations: According to DFT calculations the energies ΔE_R necessary for the halide transfer in the gas phase are +170 kJ mol^{-1} for reaction (1) and +190 kJ mol^{-1} for reaction (2).

$$2\,Al_5Br_7\cdot 5THF \rightarrow [Al_5Br_6\cdot 6THF]^+ + [Al_5Br_8\cdot 4THF]^- \qquad (1)$$

$$2\,Ga_5Cl_7\cdot 5THF \rightarrow [Ga_5Cl_6\cdot 6THF]^+ + [Ga_5Cl_8\cdot 4THF]^- \qquad (2)$$



Scheme 1. Potential mechanism for the formation of **2-cha;-/cha;, postulated on the basis of the characterization of trapped analogous intermediates.**

The solvation enthalpies, which need to be considered in solution particularly for the ionic products, are almost identical for the Al and Ga compound and can hardly reach the order of magnitude of ΔE_R.[20] Therefore the significant difference in energies for the above-mentioned reactions is attributed to the different (gas-phase) reaction energies ΔE_R, whereby ΔE_R is larger for the gallium compound on the basis of the stronger M−X bond. Thus the formation of **2a** and **2b** should be favored over that of the hypothetical ionic Ga compound, which is confirmed by the crystal structures of **2a**, **2b**, and **3**.

Compound **2** is the first compound that contains binary aluminum subhalide ions with Al−Al bonds,[21] and through its Al^0 central atom (calculated partial charge ca. -0.8) **2** represents the smallest Al-centered cluster; it could possibly play a key role in metal formation. In the chemical deposition of Al by disproportionation of Al^I compounds the intermediary character of Al subhalides is confirmed by the formation of numerous trapping products: The metalloid clusters $Al_7R_6^-$, $Al_{12}R_8^-$, $Al_{14}R_6I_6^{2-}$, and $Al_{77}R_{20}^{2-}$ ($R = N[SiMe_3]_2$)[22–24] are already indicative of sections from the α-Al lattice. In contrast, for the electrolytic deposition of Al the question still remains, whether—and if yes, at what stage—subhalides formed such as Al_2X_4, Al_3X_5, Al_5X_7, or even larger subhalides (or their ionic form) can be considered as intermediates that contribute to the metal deposition by disproportionation.[25]

Experimental Section

1: AlI (40 mmol) was cocondensed with toluene (85 mL) and THF (15 mL), and 10 mL of the resulting 0.4 M AlI solution was concentrated to a quarter of the volume at room temperature; the solution slowly decolorized but without deposition of aluminum. Compound **1** crystallized overnight at $-30\,^\circ C$ in the form of large colorless needles (m.p. $\approx 0\,^\circ C$). Yield: 380 mg (12 %).

2: In analogy to the preparation of **1**, AlBr (40 mmol) was cocondensed with toluene (85 mL) and THF (15 mL), and 10 mL of the resulting 0.4 M AlBr solution (4 mmol AlBr) was concentrated to half the volume at room temperature. After one day amorphous aluminum deposited. After two further days colorless, brittle platelets of **2** (in addition to yellow $Al_{22}Br_{20}$ crystals) crystallized from the concentrated filtrate, which could be recrystallized from THF. Yield: 78.1 mg (0.037 mmol, 9.25 %).

Mass spectrometry: Varian-MAT-711 and Finnigan-MAT-MS8223 spectrometers; EI: 70 eV; DI at 50–150 °C. Measured and calculated masses as well as isotope patterns are in agreement.

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[9] X-ray structure analyses of **1** and **2**: The data were collected on a STOE-IPDS diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$) and graphite monochromator. The structures were solved by direct methods and refined anisotropically against F^2 for all observed reflections. Hydrogen atoms were refined in calculated positions according to a riding model. Programs used: SHELXS and SHELX(T)L (G. M. Sheldrick, Universität Göttingen), Resview, Diamond. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-143867 (**1**) and CCDC-143868 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). **1**: Colorless needle, $0.3 \times 0.1 \times 0.1$ mm³, measurement temperature 180 K, orthorhombic, space group $Pca2_1$

(no. 29), $a = 30.060(3)$, $b = 9.0121(6)$, $c = 16.0246(11)$ Å, $V = 4341.1(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.644$ Mg m^{-3}, $\mu_{Mo} = 2.938$ mm^{-1}, $\theta_{min} = 2.26°$, $\theta_{max} = 20.81°$, reflections: 16026 measured, 4302 independent, 3400 observed, 350 parameters, numerical absorption correction, $R_{int} = 0.0544$, $R_1 = 0.0428$, $wR_2 = 0.1089$, GOF = 1.046, 1 restraint, max./min. residual electron density 0.501/ – 0.462 e Å^{-3}. The THF molecules in **1** are slightly disordered. This disorder was incorporated in the stucture refeinement by increased anisotropic temperature factors and H atoms (at calculated positions). Four toluene molecules (likewise disordered) per Al_2I_4 unit are housed in the crystal, which evidently contribute to the low melting point (ca. 0 °C). **2**: Colorless platelets, $0.3 \times 0.2 \times 0.05$ mm^3, measurement temperature 200 K, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.980(4)$, $b = 19.075(5)$, $c = 21.080(7)$ Å, $\alpha = 109.88(4)$, $\beta = 102.07(4)$, $\gamma = 103.97(2)°$, $V = 3818(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.835$ Mg m^{-3}, $\mu_{Mo} = 7.496$ mm^{-1}, $\theta_{min} = 1.93°$, $\theta_{max} = 24.01°$, reflections: 23476 measured, 11262 independent, 6457 observed, 964 parameters, numerical absorption correction, $R_{int} = 0.0947$, $R_1 = 0.0546$, $wR_2 = 0.1366$, GOF = 0.879, 100 restraints (for THF in the disordered portion), max./min. residual electron density 0.884/ – 1.049 e Å^{-3} (localized around Br atoms). Several crystals of **2** from different solutions were investigated by X-ray crystallography. The structure refinement repeatedly revealed a disorder, in particular, of the ligand-bearing Al atoms, in the molecules **2a** and **2b**, which was described by two completely isomeric molecules for **2a** and for **2b**, whereby the one isomer (83 %) can be converted into in the other isomer (17 %) by reflection at the respective central atom (two local inversion centers at Al10 and Al50 in Figure 1). The four ligand-bearing Al atoms of the S_4-symmetric Al frameworks are thus the only atoms that are not inversion-symmetric, in contrast to the ligand shell (bromide and THF), which, however, determines the packing in the crystal. For a 1:1 disorder and only one type of molecule (thus only one inversion center), this problem could have been solved through the choice of an appropriate space group, as an analogous problem has shown.[8] Here the detailed description using two complete molecules (with $R_1 = 0.0546$ for a reflection/parameter ratio of 6.7) was favored over a description using only disordered Al atoms (with $R_1 \approx 0.09$ for a reflection/parameter ratio of 10). The superposition of these disorders can falsify bond lengths; thus, especially the distances to the central Al atoms (in particular in **2b**) should not be considered and quoted for an exact discussion.

[10] The bond lengths in **1** lie in the expected range and are similar to those of $Al_2I_4 \cdot 2\,OEt_2$, which were compared with calculated distances in ref. [7a].

[11] All quantum-chemical calculations were carried out with the RIDFT module (B-P86/SVP functional) of the TURBOMOLE program[26] with SV(P) basis set on the following systems: $[Al_5Br_6 \cdot 6\,THF]^+$ in C_1, $[Al_5Br_8 \cdot 4\,THF]^-$ in S_4, $Al_5Br_7 \cdot 5\,THF$ in C_1 (and analogously for Ga), $Al_2Br_4 \cdot 2\,H_2O$ in C_{2h}, $Al_{22}Cl_{20} \cdot 12\,H_2O$ in C_i.

[12] The population analysis[27] of **2a** shows a partial charge of – 0.76 for the central Al^0 atom and +0.12 for the surrounding Al^{II} atoms. In **2b** these values are – 0.81 for Al^0, +0.07 for Al^{II}, and +0.19 for Al^I atoms. The partial charge of the Br atom bound to Al^I (– 0.17) is less negative than those for the Br atoms bound to Al^{II}. For these the value is – 0.20 and for Br52 as well as Br54 (longer Al–Br bond) – 0.24.

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[18] An overview of other follow-up products of such insertion reactions with subsequent AlX_3 cleavage revealed compound $Si(AlCl_2 \cdot OEt_2)_4$ which is isoelectronic to **2a**. In the presence of AlCl and AlR this finally leads to a remarkable $SiAl_{14}R_6$ cluster.[28]

[19] An analogous case in the third and fourth periods of Group 15 is PCl_5, which exists in the ionic components PCl_4^+ and PCl_6^-, whereas $AsCl_5$ is unstable in the ionic form.

[20] Calculated reaction energies and free reaction enthalpies do not differ in this reaction, because no entropy is produced. The solvation enthalpy liberated in the reaction in solution is almost identical for the ionic Al and Ga compounds and can here amount to maximal 185 kJ mol^{-1} (dielectric constant $\varepsilon_r \rightarrow \infty$) according to the Born equation.[29] For decreasing polarity it sinks for a THF solution ($\varepsilon_r = 7.52$) to 160 kJ mol^{-1}, for diethyl ether ($\varepsilon_r = 4.27$) to 142 kJ mol^{-1}, and for toluene ($\varepsilon_r = 2.2$) to 101 kJ mol^{-1}. The solvation enthalpy of the uncharged starting materials is neglected in this approximation. Whether the halide transfer favored for **2** already occurs in solution or first in connection with the crystallization, has yet to be verified.

[21] The organometallic contact ion pair $Cp^*_3Al_5I_6$ is to date the only example for Al–Al bonds in a cationic component ($Cp^*_2Al_3I_2^+$).[30]

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[25] As a low-valent halide, **2** provides a potential reaction channel in the electrolytic deposition of Al, by which initially formed AlX species can immediately react further with AlX_3 present in excess to give Al_2X_4. Further follow-up reactions such as our observed formation of **2**, however, presumably proceed only for large local AlX concentrations. The formation of low-valent aluminum compounds in the anodic oxidation of aluminum under high current denisty is already known.[31]

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