Building blocks for the chemistry of perfluorinated alkoxyaluminates [Al{OC(CF₃)₃}₄]⁻: simplified preparation and characterization of Li⁺–Cs⁺, Ag⁺, NH₄⁺, N₂H₅⁺ and N₂H₇⁺ salts

Electronic Supplementary Information

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1. Experimental methods

1.1. Synthetic procedures

Typically, all manipulations have been performed in argon atmosphere in MBraun gloveboxes (typically <1 ppm O_2 and <1 ppm H_2O) or in Schlenk-type glassware. The previously described H-shaped vessels with P4 frit were used as reactors in all solvent-mediated processes¹ Unless stated otherwise, all the solvents were dried over P_2O_5 prior to use. We want to stress, that it may happen that the time of pumping of the samples under high vacuum given here may vary depending on the vacuum achieved in the vacuum line, which is difficult to control in the region below 10^{-3} mbar, especially when the sensor is exposed to various chemicals present in the line. Therefore we suggest to treat these values only as suggestion.

1.1.1. $Li[Al(OR^F)_4]$ from $LiAlH_4$ – improved protocol

A vital improvement of synthesis of $Li[Al(OR^F)_4]$ includes a reaction between excess (1.5 times) of $LiAlH_4$ and $(CF_3)_3COH$ performed in **perfluorohexane** directly in the extractor. Such synthesis, which can be conducted in the apparatus presented in Fig. S1, results in pure product obtained in single step, and ensures economical use of expensive $(CF_3)_3COH$.

The following reagents have been successfully used: $LiAIH_4 - both$ Sigma-Aldrich 95% (grey) and Alfa Aesar 97% (almost white) work, but the latter is recommended; $(CF_3)_3COH - Fluorochem$; perfluorohexane – mostly branched, Fluorochem – a mixture of isomers.

The method does not require purification of substrates, since i) perfluorocarbons dissolve only traces of water (in order of ppm)⁵² ii) (CF₃)₃COH is dried with excessive LiAlH₄ on the frit iii) if any hydrated Li compounds were formed, as ionic compounds, they would not dissolve in C_6F_{14} and would remain on the frit; Li[An] is the only product which is soluble in perfluorocarbons ([LiOC(CF₃)₃]₄ has not been detected in our tests). Another advantage of the method is that an excessⁱ of the (inexpensive) alanate can be used resulting in virtually complete consumption of the alcohol. The oxygen dissolved in C_6F_{14} does not distract the reaction when this solvent is used in small amount, which can be achieved when the alcohol is added dropwise (!). Generally, it is recommended to introduce only as much of perfluorocarbon as needed to soak the LiAlH4 left on the frit and keep some of it circulating in the system. In our tests, we were able to obtain as much as 80 g of $Li[AI(OR^{F})_{4}]$ using only 10 ml of $C_{6}F_{14}$, although this requires very slow addition of the alcohol. Large portion of (CF₃)₃COH may result in very vigorous reaction and rapid formation of considerable amount of $Li[Al(OR^F)_4]$ on the frit which may hamper the circulation of perfluorohexane. We have also observed, that some samples of LiAlH₄ (grey from Sigma-Aldrich) started to react with the alcohol only after induction period of several minutes, probably due to surface inactivation. In such case, if a large portion of the alcohol is added, the reaction may become very vigorous upon initiation and the whole reaction mixture may get hot posing danger (note instability of LiAlH₄ above 120°C).

ⁱ Our experience shows that some vendors supply LiAlH₄ which is very contaminated. One of the batches (we do not name the vendor) yielded only <1 g of pure LiAlH₄ in extraction from the 25 g of crude chemical with the reported assay of 95% (!). Therefore the method relies on the quality of the starting alanate. Our recommendation is to use >97% purity and at least 1.5 molar excess of LiAlH₄ to minimize loses of the alcohol.

The temperature of the hot bath should be *ca*. 70–80°C to boil C_6F_{14} off. To obtain higher yields, it is vital to use an efficient condenser keeping the alcohol in the system, similarly to the previously reported protocols.^{S1} The **typical yield** with a highly efficient condenser kept at 0°C (temperature of the condenser and not the oil in the circulation cryostat) is >97%, as based on the amount of the alcohol used and the weight of recovered product.

Upon complete removal of perfluorohexane (under dynamic vacuum, 30 minutes at 10^{-2} mbar for a flask kept in still warm bath used during the synthesis) the product is obtained in the form of large grains, and ready to use without further purification, according to FTIR, NMR and XRDP results.



Figure S1. The experimental setup for one-pot synthesis of Li[An].

1.1.2. Li[Al(OR^F)4] from LiAlH4 – previous optimized protocol ^{S3}

The synthesis uses purified and very finely ground LiAlH₄ (=> Dissolution of crude LiAlH₄ in Et₂O, filtration and removal of the solvent of the filtrate to constant weight at 100 °C. Care has to be taken, as LiAlH₄ decomposes above 120 °C. Thus, a water bath is to be recommended for heating, as this prevents temperatures to get higher than 100 °C.). This purified and very finely ground LiAlH₄ is placed in a two-necked Schlenk flask and suspended in petroleum ether (boiling fraction 80 to 100 °C; *ca*. 50

mL per 1 g of LiAlH₄). The reaction is routinely done in 100 g product scale with isolated yields around 99 %. One neck is used to connect a pressure-equalizing dropping funnel, while the second is to attach an intensive gas cooler set to -25° C by an external thermostat) with a bubbler at its top. It is extremely important to use the gas cooler instead of a conventional reflux condenser and to cool the gas cooler to low temperature as the evolving H_2 evaporates the very volatile (CF₃)₃COH and one loses yield, if not sticking to this protocol. In addition, the product then contains unreacted LiAlH₄, which is detrimental to follow-up chemistry. Thus, 4.1 equivalents of $(CF_3)_3COH$ are added dropwise to the stirred suspension. After all alcohol is consumed, the mixture is heated under reflux for about 3 h. After that time, the Schlenk vessel is cooled down to -25°C to allow complete precipitation of the product. The solvent is decanted off and its remnants are removed under dynamic vacuum (10⁻³ mbar) until constant weight of the sample. This material is completely colorless and may be used directly without further purification. A simple test, if unreacted LiAlH₄ is present, is to add a small quantity of the $Li[Al(OR^{F})_{4}]$ to water. If there is no humming sound at all and if it is a clear solution it is clean. If some humming (reaction of LiAlH₄ with water) is present or the solution is turbid, one should grind the $Li[Al(OR^{F})_{4}]$ inside a glovebox, suspend it again with petroleum ether and reflux it with addition of extra alcohol similar to the procedure described above. However, with the process described above this is typically not necessary.

1.1.3. $M[Al(OR^F)_4]$, M = Na, K, from MAlH₄

The suspension of MAlH₄ (NaAlH₄ – Sigma-Aldrich, purified by extraction by THF, filtration and evaporation of the solvent, KAlH₄ – prepared from KH and LiAlH₄ in diglyme/THF^{S4,S5}) in hexane was cooled to 0 °C and (CF₃)₃COH (Fluorochem) was slowly added with an excess (*ca.* 150%). The reaction mixture was refluxed for several hours. The solvent has been evaporated and the white solid product has been extracted in Soxhlet extractor using dichloromethane (Sigma-Aldrich, dried over P₂O₅) for M=Na and K, which yield pure products as evaluated by FTIR, NMR and XRDP analyses. Typical yield: >80%.

1.1.4. Ultrasound-induced synthesis of M[Al(OR^F)₄], M = K – Cs, NH₄, N₂H₅

Li[Al(OR^F)₄] and an excess (200%) of ground anhydrous MCl were placed in a reactor together with anhydrous CH_2Cl_2 (*ca.* 5 ml per 1 g of the expected product) and sonicated overnight using a Bandelin DL 156 BH ultrasonic bath with 60% of the maximum output power to reduce heating and loss of water in the bath during the long process. The products were extracted with dichloromethane. Typical yield of the recovered products: M = K *ca.* 40%, Rb *ca.* 65%, Cs *ca.* 85%. Tests with KBr and KF have shown that these halides give much lower yields (30% and 25% respectively). However, with CsF it was already above 80%.

This method is not recommended for the synthesis of Na[An] due to very slow reaction and low conversion rate.

1.1.5. Mechanochemical synthesis of M[Al(OR^F)₄], M = K, Rb, Cs, NH₄

Li[Al(OR^F)₄] and an excess of MCl (*ca.* 200%) were mixed and milled for 30 min in 5 min cycles at 1400 rpm using a stainless steel vessel containing a stainless steel milling disc and a LMW-S laboratory vibrating mill (Testchem), Figure S2. Between the milling cycles the vessel was cooled with liquid

nitrogen to maintain room temperature. The product was then extracted using anhydrous dichloromethane. Typical yield: >80%.

A similar procedure has been applied initially for synthesis of $NH_4[Al(OR^F)_4]$, however, it resulted in the product contaminated by $[N_2H_7][Al(OR^F)_4]$, probably due to a significant excess of NH_4Cl .

While this is a very convenient and fast method, the samples prepared this way may be slightly contaminated with small amount of metal halides which may be transferred through the glass frit due to very small grain size.



Figure S2. The LMW-S vibrational mill (left) and a stainless steel disc bowls (right) used for mechanochemical synthesis.

1.1.6. Synthesis of Ag[Al(OR^F)₄]

The synthesis starts from purified Li[Al(OR^F)₄] and *ca*. 40% molar excess of AgF (Fluorochem – we have found the compound of very good quality and used it with success despite previous suggestions to use another vendor of the chemical). The excess of AgF can be also at the level of 15-20%, but since AgF can be in the state of fine powder mixed with larger chunks, to provide its higher surface area we recommend the higher value. For each gram of Li[Al(OR^F)₄] we recommend at least 2 ml of SO₂, what facilitates extraction of Ag[Al(OR^F)₄]. The reaction mixture is left on vigorous stirring. Complete conversion is achieved after 7-10 days. The typical yield of isolated product is *ca*. 85%, i.e. similar for the route with perfluorohexane used as reaction medium.^{S6}

1.1.7. $M[Al(OR^{F})_{4}], M = NO$

The compound was synthesized according to the previously reported method.⁵⁷

1.1.8. Ag[*alfal*] and Cu[*alfal*]

The silver salt was obtained according to literature protocol^{S8} and was crystallized from C_6F_6 (though the compound is also soluble in C_6F_{14}).

Route to crystals of Cu[*alfal*] is described in the main manuscript. Note, that heating to *ca*. 45°C of dry Cu[Al(OR^F)₄] leads to amorphous solid. Slight contamination with Ag visible in the crystal structure is the result of presence of silver salt (most probably AgI, but presence of minor amounts of Ag[Al(OR^F)₄] cannot be overruled) during heating of Cu[Al(OR^F)₄].

1.2. Analytical procedures

1.2.1. FTIR spectroscopy

The FTIR spectra of the solid samples were measured either in transmission or in reflection geometry. For the measurements in transmission mode a Vertex 80v FTIR spectrometer (Bruker) has been used. The samples were placed between the windows made of AgCl. The measurements in reflection geometry were conducted using Nicolet Magna-IR spectrometer with a Diamond-ATR module with ATR corrections applied.

1.2.2. Raman spectroscopy

Raman spectra have been recorded on a Bruker VERTEX 70 spectrometer with RAM II module at 1064 nm (Nd-YAG laser). Samples were closed in a flame-sealed glass capillaries.

1.2.3. Powder X-ray diffraction

Powder X-ray diffraction (XRDP) patterns of the samples sealed inside quartz capillaries (diameter of 0.5–1 mm) were measured on three diffractometers: Bruker D8 Discover diffractometer (parallel beam; the CuK_{$\alpha1$} and CuK_{$\alpha2$} radiation), Panalytical X'Pert Pro diffractometer (parallel beam; the CoK_{$\alpha1$} and CoK_{$\alpha2$} radiation) and Stoe Stadi P powder diffractometer using monochromated Mo K_{$\alpha1$} radiation and PSD or Mythen 1K microstrip X-ray detector. They are marked according to the radiation used.

1.2.4. Single crystal diffraction

The single crystals suitable for structure determination of $M[Al(OR^F)_4]$ were grown in various ways. Good quality crystals of the salts containing larger cations, M = K, Rb, NH_4 , N_2H_5 , were easily obtained from the saturated solutions in dichloromethane. For M=Na a prolonged (days) crystallization from slowly cooled (from 25°C down to -40°C in *ca.* 24 h) FC-770 solution was required to obtain crystals of sufficient quality. During the measurements the crystals were immersed in the protective perfluorinated oil (Krytox 1531).

Data collection and reduction was performed with one of the two setups: Agilent Supernova X-ray diffractometer with K α -Cu radiation (microsource) with data reduction performed by CrysAlisPro software (v. 38.43)⁵⁹ or Bruker Smart Apex II Quazar single crystal diffractometer, graphite-monochromated Mo-K α radiation from microsource, data collection and reduction: APEX v2013.10-0 and SAINT V8.34A; absorption correction: TWINABS 2012/1. Structure solution: SHELXT^{S10}, refinement against F² in ShelxI-2013,^{S10} with ShelXIe as GUI software.^{S11} The disorder of the $-OC(CF_3)_3$ groups was resolved using DSR.^{S12} Graphical presentation of crystal structures has been performed with Vesta.^{S13}

1.2.5. TGA/DSC

Thermal decomposition was investigated using a combined thermogravimeter (TGA) and differential scanning calorimeter (DSC) from Netzsch – STA 409 PG. The samples were placed inside Al_2O_3 crucibles, and were heated at 5°C min⁻¹ rate under a constant Ar (99.9999%) flow. The evolved gases were analyzed with a quadrupole mass spectrometer (MS) QMS 403 C (Pfeiffer Vacuum), connected to the TGA/DSC device by a quartz capillary preheated to 200°C to avoid condensation of low-boiling volatiles. Range of M/Z from 1 to at least 120 was studied.

1.2.6. NMR spectra

NMR spectra were recorded on Bruker AVANCE III HD 300 MHz or 500 MHz. Samples highly susceptible to traces of water (Li, Na, N-compounds, Cl_3CCN solvates) were placed in 4mm air-tight NMR tubes equipped with PTFE valve and dissolved in SO₂. Deuterated solvents (acetone, CDCl₃ or CD₂Cl₂) for these compounds were placed in outer, 5mm tube. K-Cs salts were dissolved in CD_2Cl_2 (not dried) in air.

It was observed, that in every ¹⁹F measurement there is a weak signal ca. 0.8 ppm less negative the main one. This is the signal from the free HOC(CF₃)₃, which is commonly found in the spectra of $[Al(ORF)_4]^-$ salts. For ¹H spectra, the signals from NH₄ and N₂H₅ are not very strong as compared to impurities present in deuterated (CD₃)₂CO (H₂O and not perdeuterated acetone).

2. Supplementary analytical results



Figure S3. The Rietveld fit for the sample of Li[Al(OR^F)₄] prepared according to the procedure described in the section 1.1.1. The measured powder pattern (black line), the calculated powder pattern (red line), the Bragg reflections and the difference plot (bottom) have been shown. wRp = 3.95%, T = *ca*. 295 K, a = 10.104(4) Å, b = 13.886(6) Å, c = 21.504(8) Å, V = 3017(2) Å³ (*ca*. 6.8% expansion as compared to 100 K). Co K α .



Figure S4. XRDP patterns of Na[Al(OR^F)₄]: experimental (RT, bottom – red curve; **prepared as described in 1.1.3**) and generated from the crystal structure (data for 100 K, top – black curve). The shift in positions of reflexes and differences in intensities are the result of different measurement temperatures. Cu K α .



Figure S5. XRDP patterns of K[Al(OR^F)₄]: experimental (RT, bottom – red curve; **prepared as described in 1.1.4**) and generated from the crystal structure (data for 100 K, top – black curve). The shift in positions of reflexes and differences in intensities are the result of different measurement temperatures. Cu K α .



Figure S6. XRDP patterns of Rb[Al(OR^F)₄]: (a) generated from the crystal structure (data for 100 K); (b) experimental (RT, **prepared as described in 1.1.5 – extracted with dichloromethane and precipitated with hexane**ⁱⁱ); (c) experimental (RT, **prepared as described in 1.1.5 – before extraction**). The patterns generated for LiCl and RbCl were included for comparison. The shift in positions of reflexes and differences in intensities are the result of different measurement temperatures. Cu K α .

ⁱⁱ Precipitation with hexane instead of evaporation has been applied as Li[Al(OR^F)₄] of low purity was used in this particular synthesis.



Figure S7. XRDP patterns of Cs[Al(OR^F)₄]: (a) experimental (RT), **prepared as described in 1.1.5** – **extracted with dichloromethane and precipitated with hexane**ⁱⁱⁱ); (b) generated from the **P1** crystal structure (data for 100 K); generated from the **Cc** crystal structure (data for 223 K).⁵¹⁴ The pattern generated for CsCl was also included for comparison. The shift in positions of reflexes and differences in intensities are the result of different measurement temperatures. Cu K α .



Figure S8. XRDP patterns of NH₄[Al(OR^F)₄]: top – generated from the crystal structure (data for 100 K); bottom – experimental (RT), the sample **prepared as described in 1.1.4, extracted with dichloromethane**. The shift in positions of reflexes and differences in intensities are the result of different measurement temperatures – possibly a polymorphic transition occurs. Cu K α .

ⁱⁱⁱ Precipitation with hexane instead of evaporation has been applied as Li[Al(OR^F)₄] of low purity was used in this particular synthesis.



Figure S9. XRDP patterns of: (a) the sample of $NH_4[Al(OR^F)_4]$ prepared as described in 1.1.5 – extracted with dichloromethane, the characteristic peaks from $N_2H_7[Al(OR^F)_4]$ have been marked with an asterisk; (b) generated from the crystal structure of $N_2H_7[Al(OR^F)_4]$ (data for 100 K); (c) generated from the crystal structure of $NH_4[Al(OR^F)_4]$ (data for 100 K); (c) generated from the result of different measurement temperatures – possibly a polymorphic transition occurs for $NH_4[Al(OR^F)_4]$. Cu K α .



Figure S10. XRDP patterns of: the sample of $N_2H_5[Al(OR^F)_4]$ **prepared as described in 1.1.4 – extracted with dichloromethane** (top); generated from the crystal structure of $N_2H_5[Al(OR^F)_4]$ (data for 100 K). The shift in positions of reflexes and differences in intensities are the result of different measurement temperatures – possibly a polymorphic transition occurs. Cu K α .

| Li | Na | Ag | к | Rb | Cs | NH₄ * | N2H5 * | NO | TAA ^{S15} |
|---------|---------|---------|---------|---------|---------|-------------|-------------|---------|---------------------------|
| 456 vw | 455 vw | 439 vw | 447 vw | 448 w | 447 w | 448 s | 448 s, sh | 447 vw | 446–449 |
| 481 vw | 480 vw | 468 vw | - | - | | - | - | - | |
| 538 vw | 538 vw | 537 vw | 535 w | 536 w | 537 w | 537 m | 536 w | 535 vw | 536-538 |
| 550 vw | 550 vw | 554 vw | - | - | | - | - | - | |
| 565 vw | 565 vw | 568 vw | 562 vw | 561 w | 561 vw | 562 m | 560 w | 560 vw | 559–562 |
| 572 vw | 573 vw | 578 vw | 573 vw | 572 vw | 572 vw | 571 w | 572 vw | 573 vw | 571–573 |
| 581 vw | 581 vw | | - | - | | - | | - | |
| 726 m | 726 m | 728 m | 726 s | 726 m | 727 s | 727 vs | 727 s | 726 s | 726–727 |
| 729 m | 729 sh | - | - | - | | - | | - | |
| 745 vw | 745 vw | 745 vw | - | - | | - | | - | 744–747 R |
| 756 vw | 756 vw | | 757 vw | 755 vw | 756 vw | 756 w | 755 w | 757 vw | 755–756 |
| 760 vw | 759 vw | 760 vw | - | - | | - | | - | |
| 799 vw | 800 vw | 800 vw | | | | | | | 794–799 R |
| | | | - | - | | | | - | |
| 844 vw | 844 vw | - | 833 vw | 834 vw | 834 vw | 834 w | 836 w | 832 vw | 830–833 |
| 864 vw | 866 vw | 864 vw | - | | | | 878 vw | - | |
| | | | | | | | | | |
| 963 sh | 961 sh | | 967 sh | 963 s | 964 vs | 962 vs | 971 vs | | 967 sh |
| 976 s | 976 vs | 974 s | 972 vs | 975 m | 976 s | 975 vs | | 972 s | 973–976 |
| | | | | | | 1022 vw, sh | 1021 | | |
| | | | | | | | 1050 vw | | |
| 1108 vw | 1115 vw | 1129 vw | 1122 w | 1125w | 1130 vw | 1120 w | 1127 vw, sh | 1119 vw | 1133–1139 R |
| - | - | 1155 vw | 1155 w | - | | | | - | |
| 1175 m | 1175 w | 1176 vw | 1173 m | 1185 m | 1183 m | 1177 w | 1183 m, sh | 1171 w | 1163–1176 |
| 1216 s | 1216 s | 1215 s | 1208 vs | 1225 vs | 1224 vs | 1224 vs | 1220 vs | 1208 vs | 1217–1223 |
| 1230 sh | | | 1218 sh | | | | | | |
| 1249 vs | 1251 vs | 1253 vs | 1253 vs | 1247 vs | 1247 vs | 1245 vs | 1249 vs | 1252 vs | 1236–1240 |
| | | | | 1265 s | 1266 vs | 1266 s | | | |
| 1277 s | 1272 vs | 1272 vs | 1278 vs | | 1276 vs | 1276 s | 1273 vs | 1279 vs | 1271–1274 |
| 1302 sh | 1301 sh | 1302 w | 1298 s | 1297 m | 1306 s | 1301 s | 1300 s | 1298 s | 1296–1299 |
| 1352 vw | 1355 vw | 1367 vw | 1355 m | 1354 w | 1357 m | 1354 m | 1355 m | 1354 w | 1349–1353 |
| | | | | | | | 1517 w | | |
| | | | | | | 1434 m | 1540 vw | | |
| | | | | | | | 1604 w, br | | |
| | | | | | | | 3186 vw | | |
| | | | | | | 3236 sh. br | 3205 w | | |
| | | | | | | 3324 m. br | 3246 w | | |
| | | | | | | 3434 sh. br | 3300 m | | |
| | | | | | | | 3327 sh | | |
| | | | | | | | 3413 w | | |

Table S1. The absorption bands observed in the FTIR spectra of $M[Al(OC(CF_3)_3)_4]$ salts, $[cm^{-1}]$. The values reported for tetraalkylammonium salts (TAA), i.e. $[Me_4N]$, $[Et_4N]$ and $[Bu_4N]$, are listed for comparison . vw – very weak, w – weak, m – medium, s – strong, vs – very strong, sh – shoulder, br – broad, R – Raman active mode for the anions of higher symmetry.

* samples measured on AgCl windows

Raman spectra with the most important bands marked



NMR spectra

NH₄[Al(OR^F)₄]

19F



27Al

| 6544.3.fid 6544-27Al NH4PF_MD030B | | | | | | | | | | 5 5 1 | | | | |
|---|---------------|----------|-----|----|----|-------------|------------|----|----|-------------|----|----|---|-----|
| Parameter | Value | 9 | | | | | | | | | | | | |
| 1 Origin | Bruker BioSpi | n GmbH | | | | | | | | | | | | |
| 2 Owner | felix | | | | | | | | | | | | | |
| 3 Instrument | spect | | | | | | | | | | | | | |
| 4 Solvent | Acetone | | | | | | | | | | | | | |
| 5 Temperature | 298.2 | | | | | | | | | | | | | |
| 6 Pulse Sequence | zg_pi_CPD | | | | | | | | | | | | | |
| 7 Experiment | 1D | | | | | | | | | | | | | |
| 8 Number of Scans | 8 | | | | | | | | | | | | | |
| 9 Relaxation Delay | 1.5000 | | | | | | | | | | | | | |
| 10 Pulse Width | 16.0000 | | | | | | | | | | | | | |
| 11 Acquisition Time | 1.6078 | | | | | | | | | | | | | |
| 12 Acquisition Date | 2019-10-11T | 09:27:16 | | | | | | | | | | | | |
| 13 Spectrometer Frequ | ency 130.34 | | | | | | | | | | | | | |
| 14 Spectral Width | 20380.4 | | | | | | | | | | | | | |
| 15 Nucleus | 27AI | | | | | | | | | | | | | |
| 16 Acquired Size | 32768 | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | |
| 140 130 | 120 | 110 | 100 | 90 | 80 | 70 f1 (p | 60 opm) | 50 | 40 | 30 | 20 | 10 | 0 | -10 |



The signals between 2 and 3 ppm come from impurities of $(CD_3)_2CO$. The origin of the weak signal at 5.014 ppm remains unknown.

1H

$N_2H_5[AI(OR^F)_4]$



27Al

| 6545.3.fid 6545-27Al N2H5PF_N | I MD042B | | | | | | | | 34.531 | | | | |
|-------------------------------------|-----------------|------------------------------|-----|-----|----|-------------------|----|----|--------|----|----|---|-----|
| P | arameter | Value | | | | | | | | | | | |
| 1 Origin 2 Owner | | Bruker BioSpin GmbH felix | | | | | | | | | | | |
| 3 Instrume | ent | spect | | | | | | | | | | | |
| 4 Solvent | | Acetone | | | | | | | | | | | |
| 5 Tempera | iture | 298.1 | | | | | | | | | | | |
| 6 Pulse Se | quence | zg_pi_CPD | | | | | | | | | | | |
| 7 Experime | ent of Coord | 10 | | | | | | | 1 | | | | |
| 8 Number | or Scans | 4 | | | | | | | | | | | |
| 10 Pulco Wi | off Delay | 1.5000 | | | | | | | | | | | |
| 11 Acquisitio | on Time | 1 6078 | | | | | | | | | | | |
| 12 Acquisitio | on Date | 2019-10-11T11-19-02 | | | | | | | | | | | |
| 13 Spectron | meter Frequenc | v 130.34 | | | | | | | | | | | |
| 14 Spectral | Width | 20380.4 | | | | | | | | | | | |
| 15 Nucleus | | 27AI | | | | | | | | | | | |
| 16 Acquired | l Size | 32768 | | | | | | | | | | | |
| 17 Spectral | Size | 65536 | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| 140 | 120 | 120 | | , , | | 70 | | | | | 10 | | 10 |
| 140 | 130 | 120 110 | 100 | 90 | 80 | 70 60 f1 (ppm) | 50 | 40 | 30 | 20 | 10 | U | -10 |

Li[Al(OR^F)₄]

19F



27AI

| Г | Parameter | Value |
|----|------------------------|-----------------------------|
| 1 | Comment | 23903-127Al LiPF_09.2019 |
| 2 | Origin | Bruker BioSpin GmbH |
| 3 | Solvent | CDCI3 |
| 4 | Temperature | 298.2 |
| 5 | Pulse Sequence | zg_pi_CPD |
| 6 | Number of Scans | 12 |
| 7 | Receiver Gain | 179 |
| 8 | Relaxation Delay | 1.5000 |
| 9 | Pulse Width | 20.5500 |
| 10 | Acquisition Time | 1.3981 |
| 11 | Acquisition Date | 2019-10-10T14:40:18 |
| 12 | 2 Modification Date | 2019-10-10T14:40:27 |
| 13 | G to G' | 1.00000000 |
| 14 | Echo Delay | 0.0000 |
| 15 | Gradient Duration | 0.0000 |
| 16 | Spectrometer Frequency | 78.22 |
| 17 | Spectral Width | 23437.5 |
| 18 | B Lowest Frequency | -3896.5 |
| 19 | Nucleus | |
| 20 | Acquired Size | 32768 |
| 21 | Spectral Size | 65536 |
| | | |

----35.798



Na[Al(OR^F)₄]

19F



| Parameter | Value | 1 | | | | | .803 | | | | | | |
|---|--|--|------|------|---------------------------------|--|------|----------------------|-------------|--|------|-------------|----------------------------------|
| 1 Comment | 23904-127Al NaPF | | | | | | 35 | | | | | | |
| 2 Origin | Bruker BioSpin GmbH | | | | | | | | | | | | |
| 3 Solvent | CDCI3 | | | | | | | | | | | | |
| 4 Temperature | 298.2 | | | | | | | | | | | | |
| 5 Pulse Sequence | zg_pi_CPD | | | | | | | | | | | | |
| 6 Number of Scans | 24 | | | | | | 1 | | | | | | |
| 7 Receiver Gain | 200 | | | | | | | | | | | | |
| 8 Relaxation Delay | 1.5000 | | | | | | | | | | | | |
| 9 Pulse Width | 20.5500 | | | | | | | | | | | | |
| 10 Acquisition Time | 1.3981 | | | | | | | | | | | | |
| 11 Acquisition Date | 2019-10-10T14:42:15 | | | | | | | | | | | | |
| 12 Modification Date | 2019-10-10T14:42:48 | | | | | | | | | | | | |
| 13 G to G' | 1.00000000 | | | | | | | | | | | | |
| 14 Echo Delay | 0.0000 | | | | | | | | | | | | |
| 15 Gradient Duration | 0.0000 | | | | | | | | | | | | |
| 16 Spectrometer Frequency | / 78.22 | | | | | | | | | | | | |
| 17 Spectral Width | 23437.5 | | | | | | | | | | | | |
| 18 Lowest Frequency | -3896.5 | | | | | | | | | | | | |
| 19 Nucleus | | | | | | | | | | | | | |
| 20 Acquired Size | 32768 | | | | | | | | | | | | |
| 21 Spectral Size | 65536 | | | | | | | | | | | | |
| | | 1 | | | | | | | | | | | |
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K[AI(OR^F)₄]

19F

| | Parameter | Value |
|----|------------------------|---------------------|
| 1 | Comment | 23905-19F KPF |
| 2 | Origin | Bruker BioSpin GmbH |
| 3 | Solvent | CD2Cl2 |
| 4 | Temperature | 298.2 |
| 5 | Pulse Sequence | zg_pi |
| 6 | Number of Scans | 32 |
| 7 | Receiver Gain | 200 |
| 8 | Relaxation Delay | 0.0000 |
| 9 | Pulse Width | 15.0000 |
| 10 | Acquisition Time | 0.9787 |
| 11 | Acquisition Date | 2019-10-10T14:25:12 |
| 12 | Modification Date | 2019-10-10T14:25:40 |
| 13 | G to G' | 1.00000000 |
| 14 | Echo Delay | 0.0000 |
| 15 | Gradient Duration | 0.0000 |
| 16 | Spectrometer Frequency | 282.47 |
| 17 | Spectral Width | 66964.3 |
| 18 | Lowest Frequency | -61729.2 |
| 19 | Nucleus | 19F |
| 20 | Acquired Size | 65536 |
| 21 | Spectral Size | 131072 |

-54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96 -98 -100 -104 f1 (ppm)

27Al

| | | | | | | | | | | | - | | | | | | |
|-------------------------|---------------------|-----|-----|-----|----|----|----------|----|----|----|------|----|----|---|-----|-----|---|
| Parameter | Value | | | | | | | | | | 1.68 | | | | | | |
| L Comment | 23905-27AI KPF | | | | | | | | | | Ĩ | | | | | | |
| 2 Origin | Bruker BioSpin GmbH | | | | | | | | | | | | | | | | |
| 3 Solvent | CD2Cl2 | | | | | | | | | | | | | | | | |
| 4 Temperature | 298.2 | | | | | | | | | | | | | | | | |
| 5 Pulse Sequence | zg_pi_CPD | | | | | | | | | | | | | | | | |
| 5 Number of Scans | 12 | | | | | | | | | | | | | | | | |
| 7 Receiver Gain | 200 | | | | | | | | | | | | | | | | |
| 8 Relaxation Delay | 1.5000 | | | | | | | | | | | | | | | | |
| 9 Pulse Width | 20.5500 | | | | | | | | | | | | | | | | |
| 10 Acquisition Time | 1.3981 | | | | | | | | | | | | | | | | |
| 11 Acquisition Date | 2019-10-10T14:43:5 | 7 | | | | | | | | | 1 | | | | | | |
| 12 Modification Date | 2019-10-10T14:44:2 | 7 | | | | | | | | | | | | | | | |
| 13 G to G' | 1.00000000 | | | | | | | | | | | | | | | | |
| 14 Echo Delay | 0.0000 | | | | | | | | | | | | | | | | |
| 15 Gradient Duration | 0.0000 | | | | | | | | | | | | | | | | |
| 16 Spectrometer Frequer | ncy 78.22 | | | | | | | | | | | | | | | | |
| 17 Spectral Width | 23437.5 | | | | | | | | | | | | | | | | |
| 18 Lowest Frequency | -3896.5 | | | | | | | | | | | | | | | | |
| 19 Nucleus | | | | | | | | | | | | | | | | | |
| 20 Acquired Size | 32768 | | | | | | | | | | | | | | | | |
| 21 Spectral Size | 65536 | | | | | | | | | | | | | | | | |
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| 70 160 150 | 140 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | | -10 | -20 | - |
| 0 100 150 | 150 | 120 | 110 | 100 | 50 | 80 | f1 (ppm) | 00 | 50 | 40 | 50 | 20 | 10 | U | -10 | -20 | |

Rb[Al(OR^F)₄]

19F

| Г | Parameter | Value |
|----|------------------------|---------------------|
| 1 | Comment | 23906-19F RbPF |
| 2 | Origin | Bruker BioSpin GmbH |
| 3 | Solvent | CD2Cl2 |
| 4 | Temperature | 298.1 |
| 5 | Pulse Sequence | zg_pi |
| 6 | Number of Scans | 32 |
| 7 | Receiver Gain | 200 |
| 8 | Relaxation Delay | 0.0000 |
| 9 | Pulse Width | 15.0000 |
| 10 | Acquisition Time | 0.9787 |
| 11 | Acquisition Date | 2019-10-10T14:30:10 |
| 12 | Modification Date | 2019-10-10T14:30:11 |
| 13 | G to G' | 1.00000000 |
| 14 | Echo Delay | 0.0000 |
| 15 | Gradient Duration | 0.0000 |
| 16 | Spectrometer Frequency | 282.44 |
| 17 | Spectral Width | 66964.3 |
| 18 | Lowest Frequency | -61729.2 |
| 19 | Nucleus | 19F |
| 20 | Acquired Size | 65536 |
| 21 | Spectral Size | 131072 |

| -30 | -35 | -40 | -45 | -50 | -55 | -60 | -65 | -70 f1 (ppm) | -75 | -80 | -85 | -90 | -95 | -100 | -105 | -110 | -115 |
|------|-----|-----|-----|-----|-----|-----|-----|-----------------|-----|-----|-----|-----|-----|------|------|------|------|
| 27AI | | | | | | | | | | | | | | | | | |

| Comment Origin Solvent Temperature Pulse Sequence Number of Scans Receiver Gain Repeation Delay | 23906-27Al RbPF Bruker BioSpin GmbH CD2CI2 298.2 zg_pi_CPD 9 |
|---|--|
| 2 Origin 3 Solvent 4 Temperature 5 Pulse Sequence 6 Number of Scans 7 Receiver Gain 8 Pelavation Delay | Bruker BioSpin GmbH CD2CI2 298.2 zg_pi_CPD 9 |
| 3 Solvent Temperature Vulse Sequence Number of Scans Receiver Gain Receivation Delay | CD2Cl2 298.2 zg_pi_CPD 9 |
| 4 Temperature 5 Pulse Sequence 6 Number of Scans 7 Receiver Gain 8 Relevation Delay | 298.2 zg_pi_CPD 9 |
| 5 Pulse Sequence 6 Number of Scans 7 Receiver Gain 8 Relaxation Delay | zg_pi_CPD 9 |
| 6 Number of Scans 7 Receiver Gain 8 Relayation Delay | 9 |
| 7 Receiver Gain 8 Relaxation Delay | - |
| 8 Relayation Delay | 200 |
| C Reason Delay | 1.5000 |
| 9 Pulse Width | 20.5500 |
| 10 Acquisition Time | 1.3981 |
| 11 Acquisition Date | 2019-10-10T14:46:50 |
| 12 Modification Date | 2019-10-10T14:47:05 |
| 13 G to G' | 1.0000000 |
| 14 Echo Delay | 0.0000 |
| 15 Gradient Duration | 0.0000 |
| 16 Spectrometer Frequency | / 78.22 |
| 17 Spectral Width | 23437.5 |
| 18 Lowest Frequency | -3896.5 |
| 19 Nucleus | |
| 20 Acquired Size | 32768 |
| 21 Spectral Size | 65536 |
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| 90 85 80 75 | 5 70 65 |

Cs[Al(OR^F)₄]

19F

| | Parameter | Value |
|--------|------------------------|-------------------------------|
| 1 | Comment | 23907-19F |
| 2 | Oxisia | CSPF Bruker BioCoin Conhid |
| 2 | Solvent | CD2CI2 |
| 3 | Tormorature | 202.1 |
| 4 | Ruko Soguonso | 298.1 |
| 5 | Puise Sequence | 2g_pi |
| - | Number of Scans | 32 |
| , , | Receiver Gain | 200 |
| 8 | Relaxation Delay | 15,0000 |
| 9 | Pulse Width | 15.0000 |
| 10 | Acquisition Time | 0.9787 |
| 11 | Acquisition Date | 2019-10-10114:33:21 |
| 12 | Modification Date | 2019-10-10114:33:21 |
| 13 | G to G | 1.0000000 |
| 14 | Echo Delay | 0.0000 |
| 15 | Gradient Duration | 0.0000 |
| 16 | Spectrometer Frequency | 282.47 |
| 17 | Spectral Width | 66964.3 |
| 18 | Lowest Frequency | -61729.2 |
| 19 | Nucleus | 19F |
| 20 | Acquired Size | 65536 |
| 21 | Spectral Size | 131072 |
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|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----------------|-----|-----|-----|-----|-----|------|------|------|------|
| -25 | -30 | -35 | -40 | -45 | -50 | -55 | -60 | -65 | -70 f1 (ppm) | -75 | -80 | -85 | -90 | -95 | -100 | -105 | -110 | -115 |

27Al

| Formet 2307-27AI CSPF 2 Origin Bruker BloSpin GmbH 3 Solvent CD2CI2 4 Temperature 298.2 5 Pube Sequence 2q_pl_CPD 6 Number of Scans 13 7 Receiver Gain 200 8 Relaxation Delay 1.5000 9 Pube Width 20.5500 10 Acquistion Time 1.3981 11 Acquistion Tate 2019-10-10T14:49:32 12 Modification Date 2019-10-10T14:49:50 13 G G' 1.0000000 14 Echo Delay 0.0000 15 Gradient Duration 0.0000 14 Echo Delay 0.0000 15 Gradient Duration 0.0000 16 Spectrometer Frequency 78.22 17 Spectral Width 23437.5 18 Lowest Frequency -3896.5 19 Nucleus 20 20 Acquired Size |
|---|
| 1 Comment 239/7-2/AI CoFF Corigin Bruker BioSpin GmbH 3 Solvent CD2CI2 4 Temperature 298.2 5 Pulse Sequence 2g_pL_CPD 5 Nurber of Scans 13 7 Receiver Gain 200 8 Relaxation Delay 1.5000 9 Pulse Width 20.5500 10 Acquisition Time 1.3981 11 Acquisition Date 2019-10-10T14:49:52 12 Modification Date 2019-10-10T14:49:50 13 G to G' 1.000000 14 Echo Delay 0.0000 15 Gradient Duration 0.0000 16 Spectral Width 23475.5 18 Lowest Frequency 3896.5 19 Nucleus 32768 11 Spectral Size 65536 |
| 2 Origin Bruker BioSpin GmbH 3 Solvent CD2CL2 4 Temperature 298.2 5 Pulse Sequence rg.p.LCPD 6 Number of Scans 13 7 Reclavation Delay 1.5000 9 Pulse Width 20.5500 10 Acquistion Time 1.3981 11 Acquistion Time 2019-10-10714:49:32 12 Modification Date 2019-10-10714:49:32 13 Gto G' 1.00000000 14 Echo Xelay 0.0000 15 Gradient Duration 0.0000 15 Soratomet Frequency 78.22 17 Spectranet Frequency 78.24 18 Lowest Frequency 389.6.5 19 Nucleus 2768 21 Spectral Size 5536 |
| 3 Solvent CD2CI2 4 Temperature 298.2 4 Temperature 298.2 5 Pulse Sequence zg_D_CPD 6 Number of Scans 13 7 Recelver Gain 20 8 Relaxation Delay 1.5000 9 Pulse Width 20.5500 10 Acquisition Time 1.3981 11 Acquisition Time 2019-10-10T14:49:32 12 Modification Deta 2019-10-10T14:49:50 13 Gt G' 1.0000000 14 Echo Delay 0.0000 15 Spectraneter Frequency 78.22 17 Spectraneter Frequency 78.23 19 Nucleus 23437.5 19 Nucleus 22768 20 Acquired Size 32768 21 Spectral Size 6536 |
| 4 Temperature 298.2 5 Pulse Sequence 2g_pl_CPD 6 Number of Scans 13 7 Receiver Gain 200 8 Relaxition Delay 1.5000 9 Pulse Width 20.5500 10 Acquisition Time 1.3981 11 Acquisition Toate 2019-10-10714:49:32 12 Modification Date 2019-10-10714:49:50 13 G to G* 1.00000000 14 Echo Delay 0.0000 15 Gradient Duration 0.0000 15 Spectravitity 78.22 17 Spectravitity 389.5 18 Lowest Frequency -3896.5 19 Nucleus 32768 21 Spectravitity 32768 |
| 5 Pulse Sequence zg_pl_CPD 6 Number of Scans 13 7 Receiver Gamma 200 8 Relaxation Delay 1.5000 9 Pulse Width 20.5500 10 Acquisition Time 1.3981 11 Acquisition Tate 2019-10-10T14:49:32 12 Modification Date 2019-10-10T14:49:50 13 G to G' 1.000000 14 Echo Delay 0.0000 15 Gradient Duration 0.0000 15 Spectrant Width 23437.5 18 Lowest Frequency 3896.5 19 Nucleus 32768 21 Spectral Size 6536 |
| 6 Number of Scans 13 7 Receiver Gain 200 8 Rebation Delay 1.5000 9 Pulse Width 20.5500 10 Acquisition Time 1.3981 11 Acquisition Date 2019-10-101714:49:32 12 Modification Date 2019-10-101714:49:32 13 G to G' 1.0000000 14 Echo Delay 0.0000 15 Gradient Duration 0.0000 15 SpectranWidth 23437.5 18 Lowest Frequency 7.396.5 19 Nucleus 32768 21 Spectral Size 325.6 |
| 7 Receiver Gain 200 8 Rekaxtion Delay 1.5000 9 Pulse Width 20.5500 10 Acquisition Time 1.3981 11 Acquisition Tame 2019-10-10T14:49:32 12 Modification Date 2019-10-10T14:49:32 13 G to G* 1.0000000 14 Echo Delay 0.0000 15 Gradient Duration 0.0000 15 Gradient Duration 0.0000 16 Spectranet Width 23437.5 18 Lowest Frequency -3896.5 19 Nucleus 32768 21 Spectral Size 65536 |
| 8 Relaxation Delay 1.5000 9 Pube Width 20.5500 10 Acquisition Time 1.3981 11 Acquisition Date 2019-10-10T14:49:32 12 Modification Date 2019-10-10T14:49:50 13 G to G' 1.00000001 14 Echo Delay 0.0000 15 Gradient Duration 0.0000 15 Gradient Duration 0.0000 15 Spectrankter Frequency 78.22 17 Spectrankter 3434.75 18 Lowest Frequency -3896.5 19 Nucleus 2 20 Acquired Size 32768 21 Spectrankter 65536 |
| 9 Pulse Width 20.5500 10 Acquisition Time 1.3981 11 Acquisition Date 2019-10-10T14-49:32 12 Modification Date 2019-10-10T14-49:32 13 G to G" 1.0000000 14 Echo Delay 0.0000 15 Goetrantomoto 0.0000 15 Goetrantomoto 0.0000 15 Spectrometer Frequency 78.22 17 SpectrantWidth 23437.5 18 Lowest Frequency -3395.5 19 Nucleus 2 20 Acquired Size 32768 21 SpectrantSize 65536 |
| 10 Acquisition Time 1.3981 11 Acquisition Date 2019-101114:49:32 12 Modification Date 2019-10-10T14:49:50 13 G to G' 0.00000 13 G to G' 0.00000 14 Echo Delay 0.0000 15 Gradient Duration 0.0000 16 Spectrometer Frequency 78.22 17 Spectral Width 2343.75 18 Lowest Frequency -3896.5 19 Nucleus |
| 11 Acquisition Date 2019-10-10T14:49:32 12 Modification Date 2019-10-10T14:49:50 13 G to G' 1.00000000 14 Echo Delay 0.0000 15 Gradient Duration 0.0000 16 Spectrometer Frequency 78.22 17 Spectral Width 23437.5 18 Lowest Frequency -3896.5 19 Nucleus |
| 12 Modification Date 2019-10-10T14:49:50 13 G to G' 1.00000001 14 Echo Delay 0.0000 15 Gradient Duration 0.0000 16 Spectrometer Frequency 78.22 17 Spectral Width 23437.5 18 Lowest Frequency 3985.5 19 Nucleus 20 20 Acquired Size 32768 21 Spectral Size 65536 |
| 13 G to G' 1.0000000 14 Echo Delay 0.0000 15 Gradient Duration 0.0000 15 Spectrometer Frequency 78.22 17 Spectral Width 23437.5 18 Lowest Frequency -3896.5 19 Nucleus |
| 14 Echo Delay 0.0000 15 Gradient Duration 0.0000 16 Spectrometer Frequency 78.22 17 Spectral Width 23437.5 18 Lowest Frequency -3896.5 19 Nucleus |
| 15 Gradient Duration 0.0000 16 Spectrometer Frequency 78.22 17 Spectral Width 23437.5 18 Lowest Frequency -3896.5 19 Nucleus |
| 16 Spectrometer Frequency78.2217 Spectral Width23437.518 Lowest Frequency-3896.519 Nucleus |
| 17 Spectral Width 23437.5 18 Lowest Frequency -3896.5 19 Nucleus |
| 18 Lowest Frequency -3896.5 19 Nucleus |
| 19 Nucleus 32768 20 Acquired Size 32768 21 Spectral Size 65536 |
| 20 Acquired Size 32768 21 Spectral Size 65536 |
| 21 Spectral Size 65536 |
| 21 Spectral Size 05530 |
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| 130 120 110 100 90 80 70 60 50 40 |
| 100 100 100 00 100 f1 (ppm) |

3. Crystallographic data

| Table S2 | . Crystallographic | data for | refined | structures. |
|----------|--------------------|----------|---------|-------------|
|----------|--------------------|----------|---------|-------------|

| Compound | Li[Al(OR ^F)₄] | Na[Al(OR ^F) ₄] | K[Al(OR ^F) ₄] | Rb[Al(OR ^F) ₄] | Cs[Al(OR ^F) ₄] | NH ₄ [Al(OR ^F) ₄] | $N_2H_5[AI(OR^F)_4]$ | $N_2H_7[AI(OR^F)_4]$ | Ag[alfal] | Cu[alfal] |
|--------------------------------------|---------------------------|--|---------------------------------------|--|--|--|----------------------|----------------------|--------------------|--------------------|
| Kα | 0.71073 (Mo) | 0.71073 (Mo) | 0.71073 (Mo) | 0.71073 (Mo) | 0.71073 (Mo) | 1.54184 (Cu) | 1.54184 (Cu) | 0.71073 (Mo) | 0.71073 (Mo) | 1.54184 (Cu) |
| Temperature (K) | 100 | 190 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Space group | P212121 | P21/c | P21/c | P1 | P1 | P1 | P1 | ΡĪ | P21/c | ΡĪ |
| Ζ | 4 | 4 | 8 | 2 | 4 | 2 | 2 | 8 | 4 | 2 |
| a (Å) | 9.9680(5) | 13.6410(8) | 23.8816(11) | 9.6213(7) | 17.1845(18) | 9.6278(4) | 9.6450(4) | 17.4972(8) | 21.151(2) | 10.5661(5) |
| b (Å) | 13.4495(6) | 10.1222(6) | 12.9259(6) | 10.4768(7) | 17.4964(18) | 10.5021(4) | 10.6675(5) | 17.5074(7) | 10.2666(10) | 10.7463(4) |
| <i>c</i> (Å) | 21.0791(10) | 21.3566(13) | 20.6284(10) | 16.8127(12) | 18.6544(19) | 16.8670(4) | 17.0803(8) | 20.3760(9) | 21.257(2) | 22.2844(8) |
| α (°) | 90 | 90 | 90 | 81.079(4) | 105.940(2) | 81.237(3) | 82.791(4) | 91.583(2) | 90 | 82.600(3) |
| β (°) | 90 | 89.957(3) | 115.546(2) | 73.385(3) | 105.366(2) | 73.421(3) | 73.622(4) | 91.488(2) | 112.868(3) | 87.100(3) |
| γ (°) | 90 | 90 | 90 | 62.701(3) | 113.601(2) | 62.778(4) | 63.240(4) | 105.979(2) | 90 | 61.460(4) |
| V (ų) | 2826.0(2) | 2948.9(3) | 5745.3(5) | 1442.53(18) | 4472.2(8) | 1453.04(10) | 1505.47(13) | 5994.7(5) | 4253.3(7) | 2204.15(17) |
| $\rho_{calc.}$ (g cm ⁻³) | 2.290 | 2.230 | 2.327 | 2.423 | 2.451 | 2.243 | 2.201 | 2.221 | 2.485 | 2.333 |
| μ _{exp.} (mm⁻¹) | 0.340 | 0.341 | 0.480 | 2.010 | 1.526 | 3.163 | 3.075 | 0.326 | 0.801 | 3.877 |
| ϑ _{max} (°) | 27.517 | 23.2155 | 26.667 | 27.658 | 30.768 | 72.051 | 75.288 | 26.097 | 28.740 | 68.252 |
| <i>R</i> ₁ | 2.83% | 3.78% | 3.30% | 2.23% | 4.62% | 5.64% | 4.55% | 4.95% | 2.90% | 7.19% |
| wR ₂ | 7.37% | 10.25% | 8.20% | 4.77% | 10.71% | 15.06% | 12.08% | 12.90% | 6.50% | 19.46% |
| GooF | 1.156 | 1.052 | 1.034 | 1.036 | 1.043 | 1.056 | 1.039 | 1.033 | 1.134 | 1.026 |
| Crystal size (mm×mm×mm) | 0.20x0.30x0.38 | 0.08x0.08x0.25 | 0.07x0.15x0.15 | 0.10x0.12x0.13 | 0.08x0.10x0.20 | 0.08x0.14x0.19 | 0.21x0.28x0.35 | 0.20x0.23x0.24 | 0.10x0.25x0.40 | 0.05x0.12x0.15 |
| Crystal color | colorless | colorless | colorless | colorless | colorless | colorless | colorless | colorless | colorless | colorless |
| CCDC No. | 1960194 | 1960196 | 1960195 | 1960197 | 1960198 | 1960459 | 1960205 | 1960204 | 1960514 | 1960199 |

4. Supplementary data and figures for description of the crystal structures



Figure S11. The minimal M–Al distances [Å] observed in the crystals in the function of crystallographic octahedral radii [Å].



Figure S12. View of KAI sublattice in the crystal structure of K[Al(OR^F)₄]. Purple: K, blue: Al. Black solid line: the shortest K-Al distance (*ca*. 5.2 Å), dashed grey lines: K-Al distances in the range of 7 - 8 Å.



Figure S13. View of RbAl sublattice in the crystal structure of Rb[Al(OR^F)₄]. Pink: Rb, blue: Al. Similar arrangement has also been observed for M = Cs and NH_4 .



Figure S14. The view of CsAl sublattice in Cs[Al(OR^F)₄] at 100 K (left) and 200 K (right).^{S14} The orientation of both structures is set to see the modulation in the arrangement of Cs and Al in the former one. Celadon: Cs, blue: Al.



Figure S15. Visualization of the disorder in {M[Al(OR^F)₄]}∞ chains (M=Ag,⁵⁶ Li, Na). The atoms from main orientation are in colour, while localized atoms from the opposite orientation are in black. Disorder in -OR^F groups, thermal ellipsoids of C and F atoms are omitted for clarity.



Figure S16. Coordination spheres of K⁺ (purple) and Rb⁺ (violet) in their [Al(ORF)₄]⁻ salts. Bond lengths given in Å.

Cs[Al(OR^F)₄]- toluene adduct

Due to the weakly coordinating character and large size of $[Al(OR^F)_4]^-$, even the large Cs⁺ is able to form a fairly stable solvate with a toluene molecule. Cs coordinates in n⁶-fashion with very long Cs–C distances exceeding 3.44 Å and Cs–aromatic ring distance of ca. 3.2 Å, which are in agreement with the DFT predictions (B3LYP/def2-TZVP/D3BJ). Toluene molecules are arranged in a way that the methyl group is pointing perpendicular to the aromatic ring of its neighbor enabling a CH···π interaction at *ca*. 3.6 Å (see Figure S17), which is the most thermodynamically favored mode of bonding between two methyl-substituted aromatic molecules.⁵¹⁶ Coordination of the toluene molecules renders the structure layered, if weak toluene-toluene interactions are neglected. On the basis of the DFT calculations, the Cs⁺-toluene dissociation energy is $\Delta_r H = -50$ kJ mol⁻¹ and $\Delta_r G = -26$ kJ mol⁻¹. Based on the Jenkins equation,⁵¹⁷ the energetic cost of lattice expansion upon toluene coordination is estimated at 15 kJ mol⁻¹. For smaller anions the value is much higher, even higher than the coordination energy. *E.g.*, for the [SbF₆]⁻ anion, the lattice energy change would be 96 kJ mol⁻¹ which significantly outweighs the Cs⁺-toluene interaction energy.



Figure S17. Views of the crystal structure of $Cs(C_6H_5CH_3)[Al(OR^F)_4]$. Left: coordination sphere Cs including the neighbouring toluene molecule; right: the view of the crystal structure along a axis with one layer marked with blue rectangle.

| Compound | $Cs(C_6H_5CH_3)[Al(OR^F)_4]$ | | | |
|-------------------------------------|------------------------------|--|--|--|
| Kα | 1.54184 (Cu) | | | |
| Temperature (K) | 100 | | | |
| Space group | P21/n | | | |
| Ζ | 24 | | | |
| a (Å) | 21.7362(2) | | | |
| b (Å) | 31.2247(2) | | | |
| <i>c</i> (Å) | 33.0960(3) | | | |
| α (°) | 90 | | | |
| β (°) | 107.8910(10) | | | |
| γ (°) | 90 | | | |
| <i>V</i> (Å ³) | 21376.2(3) | | | |
| $ ho_{calc.}$ (g cm ⁻³) | 2.219 | | | |
| $\mu_{exp.}$ (mm ⁻¹) | 10.490 | | | |
| ϑ _{max} (°) | 76.378 | | | |
| <i>R</i> ₁ | 5.62% | | | |
| wR ₂ | 14.67% | | | |
| GooF | 1.040 | | | |
| Crystal size (mm×mm×mm) | 0.18x0.28x0.78 | | | |
| Crystal colour | colorless | | | |
| CCDC No. | 1960207 | | | |

Table S3. Crystallographic data for refined structure of $Cs(C_6H_5CH_3)[Al(OR^F)_4]$.

5. DFT calculations details and results

All calculations were performed with the use of Orca ^{S18} (v. 4.0.1.2) using B3LYP ^{S19} functional with def2-TZVP ^{S20} (with ECP and Cs ^{S21}) and D3BJ dispersion correction. ^{S22} or RIJCOSX ^{S23} approximation was used to increase the speed of calculations (with auxiliary basis set by Weigend ^{S24}). Thermal contributions to *ab initio* reaction energies were calculated with inclusion of zero point energy, thermal contributions to the enthalpy/entropy. Graphical presentation of the calculated structures and molecular orbitals has been performed with Avogadro ^{S25} or Vesta. ^{S13}

5.1. Coordinates of optimized structures

Cs⁺-(C₆H₅CH₃) B3LYP/def2-TZVP/D3BJ

| C | -1 5529885/709061 | 1 61/091798/2090 | -0 0/665566911667 |
|----|-------------------|-------------------|-------------------|
| 2 | -1.55258854705001 | 1.01409179842090 | -0.04003300311007 |
| С | -0.20608824339348 | 1.99356428661840 | -0.07745359924700 |
| С | 0.81100572665118 | 1.04266244038421 | -0.03557681375910 |
| С | 0.50028052650990 | -0.31405854515234 | 0.03019160427540 |
| С | -0.83573401035016 | -0.70813585173784 | 0.05143341755952 |
| С | -1.84887069630477 | 0.24739458578233 | 0.00926648900364 |
| С | -2.64714597310179 | 2.64568497121835 | -0.01375451571669 |
| Н | 0.04866579178759 | 3.04671636139091 | -0.10226829850079 |
| Н | -1.09016765041315 | -1.75796012191355 | 0.12686102378385 |
| Н | -2.88405014378278 | -0.07044744682498 | 0.05219688214897 |
| Н | 1.84537301814381 | 1.36299570339722 | -0.02784861330991 |
| Н | 1.28895384866559 | -1.05252651891820 | 0.09409778057470 |
| Н | -3.57696843451420 | 2.26222997042325 | -0.43467990409583 |
| Н | -2.36601345249387 | 3.55094939473346 | -0.55307169253033 |
| Н | -2.85751343122056 | 2.93925334442210 | 1.01795680008316 |
| Cs | -0.50082832909268 | 0.47935562775577 | -3.29031489115291 |

C₆H₅CH₃ B3LYP/def2-TZVP/D3BJ

| С | -1.56473879485697 | 1.60774051209632 | -0.0000060859449 |
|----|-------------------------------|-------------------|-------------------|
| С | -0.22104914807202 | 1.98848970594859 | -0.0000013724249 |
| С | 0.79134895610879 | 1.03881432155158 | -0.00000041596318 |
| С | 0.47872739722706 | -0.31696655760333 | 0.0000005844254 |
| С | -0.85301333439763 | -0.70996555053212 | 0.0000004087133 |
| С | -1.86344060025997 | 0.24631764384811 | -0.0000009618781 |
| С | -2.65422905045620 | 2.64634761350377 | 0.0000006854494 |
| Н | 0.03266457309567 | 3.04260278663147 | -0.00000031120099 |
| Н | -1.10868714874082 | -1.76223479471793 | -0.00000009025738 |
| Н | -2.90020905433412 | -0.06948144684968 | -0.0000026859002 |
| Н | 1.82661358237225 | 1.35648194574242 | -0.00000020332523 |
| Н | 1.26728025610395 | -1.05850675097700 | 0.00000109099985 |
| Н | -3.64184563261802 | 2.18480277117256 | -0.0000001390742 |
| Н | -2.58495116310355 | 3.29131440698536 | -0.87942732209739 |
| Н | -2.58495083806842 | 3.29131339319989 | 0.87942820850772 |
| NH | 4 ⁺ B3LYP/def2-TZV | P/D3BJ | |
| | | | |
| Ν | -0.23246307446417 | 0.29429869463271 | -0.01004821075834 |
| | 0 70000704700040 | 0.054454400050 | 0.04000050500050 |

| Ν | -0.23246307446417 | 0.29429869463271 | -0.01004821075834 |
|---|-------------------|-------------------|-------------------|
| Н | 0.79068791738210 | 0.35145441389858 | 0.01998959538056 |
| Н | -0.60507467633292 | 1.10204210931161 | -0.51978309021493 |
| Н | -0.60240885798735 | 0.29248188771124 | 0.94594013442097 |
| Н | -0.51296130859766 | -0.56897710555414 | -0.48666842882826 |
| | | | |

N₂H₇⁺ B3LYP/def2-TZVP/D3BJ

| н | 0.80705538373505 | 0.43776681029806 | -0.02046926157133 |
|---|-------------------|-------------------|-------------------|
| Н | -0.79392503946007 | 1.05049396841255 | -0.52565093785329 |
| Н | -0.68823392063696 | 0.30869378474451 | 0.95003006130973 |
| Н | -0.59608200858890 | -0.58974604736335 | -0.43640375314408 |
| Ν | 2.32231603527584 | 0.62285109196387 | -0.03738003095423 |
| Н | 2.59901548585837 | 1.56193481690543 | 0.24202493396214 |
| Н | 2.79613877813952 | -0.02034697843149 | 0.59368535997936 |
| н | 2.71711341699923 | 0.46629399078629 | -0.96269284400600 |

HCI B3LYP/def2-TZVP/D3BJ

| Cl | 1.24106490345696 | 0.000000000000000 | 0.000000000000000 |
|----|-------------------|--------------------|-------------------|
| н | -0.04106490345696 | 0.0000000000000000 | 0.000000000000000 |

NH₄Cl B3LYP/def2-TZVP/D3BJ

| Ν | -0.16900093693308 | 0.05368279604144 | 0.11435838027586 |
|----|-------------------|-------------------|-------------------|
| Н | 0.75504079510498 | -0.32742093760746 | 0.28592581935059 |
| Н | -0.04950577236071 | 1.69801426839939 | -0.50004793241511 |
| Н | -0.68273031212324 | 0.04167455378346 | 0.98848725242791 |
| Н | -0.64533956069071 | -0.55576592205614 | -0.54143649794028 |
| Cl | 0.05187578700275 | 2.95522524143931 | -0.95010702169896 |

Supplementary references

- ^{S1} I. Krossing, A. Reisinger, Coord. Chem. Rev., 2006, 250, 2721–2744.
- ⁵² M. G. Freire, L. Gomes, L. M. N. B. F. Santos, I. M. Marrucho, J. A. P. Coutinho, *J. Phys. Chem. B* **2006**, *110*, 22923–22929.
- ^{S3} I. K. I. Raabe, A. Reisinger, in *Experiments in Green and Sustainable Chemistry (Eds. H. W. Roesky, D. K. Kennepohl)*, Wiley-VCH, Weinheim, 2009, pp. 131–144.
- ^{S4} J. A. Dilts, E. C. Ashby, *Inorg. Chem.* **1972**, *11*, 1230–1236.
- ^{S5} T. Jaroń, P. A. Orłowski, W. Wegner, K. J. Fijałkowski, P. J. Leszczyński and W. Grochala, *Angew. Chem. Int. Ed.*, 2015, **54**, 1236–1239.

^{S6} P. J. Malinowski, D. Himmel and I. Krossing, Angew. Chemie Int. Ed., 2016, 55, 9259–9261.

⁵⁷ T. A. Engesser, C. Friedmann, A. Martens, D. Kratzert, P. J. Malinowski, I. Krossing, *Chem. Eur. J.* **2016**, *22*, 15085–15094.

⁵⁸ A. Martens, P. Weis, M. C. Krummer, M. Kreuzer, A. Meierhöfer, S. C. Meier, J. Bohnenberger, H. Scherer, I. Riddlestone, I. Krossing, *Chem. Sci.* **2018**, *9*, 7058–7068.

⁵⁹ Agilent (2014). *CrysAlis PRO*. Agilent Technologies Ltd, Yarnton, Oxfordshire, England.

- ^{S10} G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3–8.
- ^{S11} C. B. Hübschle, G. M. Sheldrick, B. Dittrich, J. Appl. Crystallogr. **2011**, 44, 1281–1284.
- ^{S12} D. Kratzert, J. J. Holstein, I. Krossing, J. Appl. Crystallogr. 2015, 48, 933–938.
- ^{S13} K. Momma, F. Izumi, J. Appl. Crystallogr. **2011**, 44, 1272–1276.
- ⁵¹⁴ I. Krossing, H. Brands, R. Feuerhake, S. Koenig, J. Fluorine Chem. 2001, 112, 83–90.

^{S15} I. Raabe, K. Wagner, K. Guttsche, M. Wang, M. Grätzel, G. Santiso-Quiñones, I. Krossing, *Chem. Eur. J.* **2009**, *15*, 1966–1976.

- ^{S16} C. R. Martinez and B. L. Iverson, *Chem. Sci.*, 2012, **3**, 2191.
- ^{S17} H. D. B. Jenkins, H. K. Roobottom, J. Passmore and L. Glasser, *Inorg. Chem.*, 1999, **38**, 3609–3620.
- ^{S18} F. Neese, WIREs Comput. Mol. Sci. 2018, e1327.

⁵¹⁹ a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627.

^{s20} a) F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143–152; b) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

^{S21} T. Leininger, A. Nicklass, W. Kuechle, H. Stoll, M. Dolg, A. Bergner, *Chem. Phys. Lett.* **1996**, *255*, 274–280.

^{S22} S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465.

^{S23} F. Neese, F. Wennmohs, A. Hansen, U. Becker, Chem. Phys. 2009, 356, 98–109.

^{S24} F. Weigend, Phys. Chem. Chem. Phys. 2006, 8, 1057–1065.

^{\$25} a) Avogadro: an open-source molecular builder and visualization tool. Version 1.1.1. <u>http://avogadro.cc/</u>;

b) M. D. Hanwell; D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek, G. E. Hutchison, J. Cheminform. 2012, 4:17.