Supporting Information for:

Extraordinary Aluminum Coordination in a Novel Homometallic Double Complex Salt

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The experimental details are herein described. The thermal ellipsoid model of the crystal of DCS 1 and atom assignment of the G3 molecule co-crystallized with the ionic species in DCS 1 are shown in Figures S1 and S2, respectively. Raman spectra of DCS 1, Al[TfO]$_3$, and G3 are also included, Figure S3. The full publication list of reference [14] in the manuscript is provided.
Experimental details

Materials and synthesis of DCS 1

Al[TfO]$_3$ (99.9% trace metal basis) and triglyme (G3; 99%) were purchased from Sigma-Aldrich. Al[TfO]$_3$ was dried under high vacuum at 120 ºC for 48 h, and G3 was dried over molecular sieves 4A for several days, then stored in an Al-filled glovebox prior to use. The single crystals of DCS 1 grew as colorless crystals from the G3-Al[TfO]$_3$ solution mixed in 4:1 molar ratio (2.93 g, 16.4 mmol for G3; 1.95 g, 4.11 mmol for Al[TfO]$_3$) upon storing in an Ar filled glovebox (≤ 1 ppm O$_2$ and ≤ 0.5 ppm H$_2$O) for less than one month at ambient temperature. The crystals were collected by filtration and dried under high vacuum for a week at 45 ºC, given pure DCS 1 (0.41 g, 16.2%). Elemental analysis: calculated (%) for C$_{28}$H$_{56}$Al$_2$F$_{12}$O$_{26}$S$_4$: C 27.56, H 4.59, Al 4.43, F 18.70, S 10.50; found: C 27.31, H 4.62, Al 4.14, F 18.50, S 10.39.

\[
2\text{Al[TfO]}_3 + 3\text{G3} + 2\text{OH}^- \rightarrow \text{[Al(G3)$_2$]}^{3+} \cdot \text{[Al(TfO)$_4$(OH)$_2$]}^{3-} \cdot \text{G3} + 2\text{[TfO]}^-
\]

Scheme to give the DCS 1 compound.

X-ray crystallography

DCS 1 coated with vacuum grease to avoid adsorbing moisture was mounted on a glass pin and cooled to −50 ºC using a steady flow of nitrogen gas stream. All measurements were performed on a Bruker Smart ApexII Ultra equipped with a CCD area detector using monochromated Cu Kα radiation (λ = 1.54178 Å). Empirical absorption correction was applied using a multiscan averaging of symmetry equivalent data on SADABS program. The structure was solved by the direct method SHELXS-97, and refined full-matrix least-squares in the anisotropic approximation for non-hydrogen atoms using the SHELXL-2013. All hydrogen atoms were placed in geometrically ideal position and refined using a riding model. CCDC deposited number: 1053538.

Raman spectroscopy

Raman spectra of DCS 1, Al[TfO]$_3$, and G3 were collected with a Bruker MultiRam FT-Raman spectrometer equipped with a liquid nitrogen cooled germanium detector, and 1064 nm line of an
Nd:YAG-excited laser with a resolution of 2 cm\(^{-1}\). The spectra were recorded in the range of 100–3600 cm\(^{-1}\) at ambient temperature, employing a laser power of 400 mW and 500 scans. The samples were sealed in a vial under an Ar atmosphere in the glovebox and transferred to the Raman set-up without exposure to air. To analyze the representative Raman bands, suitable spectral ranges were adopted in this study: 900–780 and 1100–1000 cm\(^{-1}\) for glyme and [TfO]\(^{-}\) anion, respectively.

**Calculations**

All DFT calculations were made in vacuum employing the M06 functional\(^3\) and the 6-311+G* basis set. The geometries of the building blocks ([TfO]\(^{-}\), G3, OH\(^{-}\)) were all relaxed, while [Al(G3)\(_2\)]\(^{3+}\) and [Al(TfO)\(_4\)(OH)\(_2\)]\(^{3-}\) geometries were taken from the crystal structure determination. As an additional measure the energies of the complexes were calculated with the central Al\(^{3+}\) ion removed. All interaction energies were subsequently calculated as the electronic energy differences upon complex formation; \(\Delta E_{\text{int}} = \Delta E_{\text{complex}} - \sum (\Delta E_{\text{building blocks}})\). All calculations were made using Gaussian09 RevB.01.\(^4\)

**References**

Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O¨. Farkas, J. B.

Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09 Revision B.01.
**Figure S1.** Thermal ellipsoid model of the crystal of DCS 1. Disordered structures (a G3 molecule and hydrogen atoms of hydroxy groups) are indicated in the model. The ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level, while isotropic hydrogen atoms are represented by spheres of arbitrary size.

**Figure S2.** Atom assignment of the G3 molecule co-crystallized with the ionic species in DCS 1. Four different arrangements are disordered. One example was extracted and colorized as pink. H atoms on each carbon atom are omitted for clarity. Gray, C; red, O.
Figure S3. Raman spectra for DCS 1, Al[TfO]$_3$, and G3 in the spectral ranges (a) 900–780 cm$^{-1}$ and (b) 1100–1000 cm$^{-1}$. 
Full publication list of reference [14] in the manuscript