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_2O) 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 $C_{28}H_{56}Al_2F_{12}O_{26}S_4$: 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.

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

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.[1] 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.[2] 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; $\Delta E_{int} = \Delta E_{complex} - \Sigma(\Delta E_{building\ blocks})$. All calculations were made using Gaussian09 RevB.01.[4]

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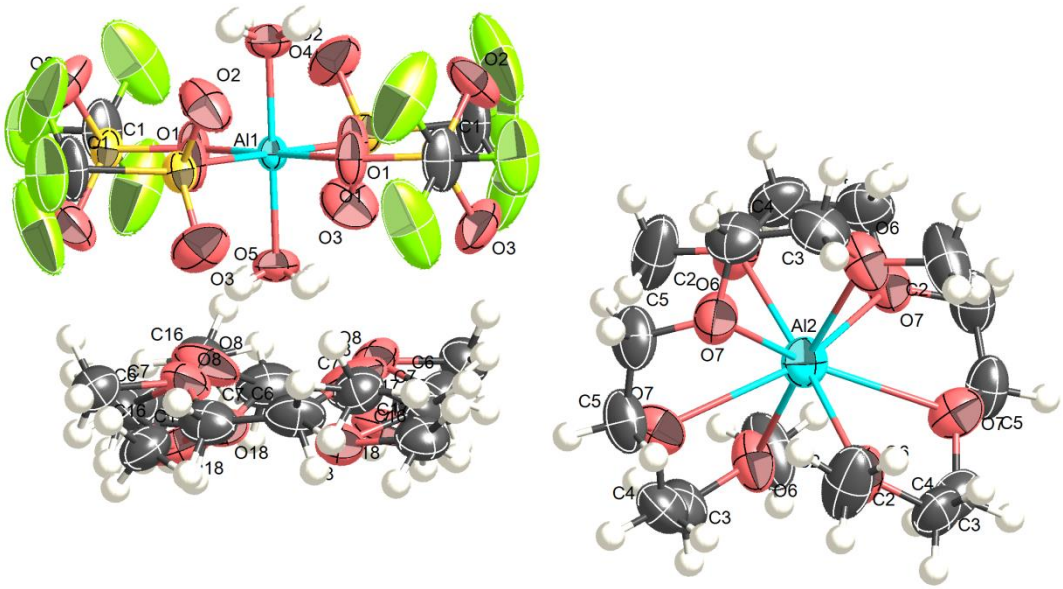

Figure S1. Thermal ellipsoid model of the crystal of DCS **1**. Disordered structures (a G3 molecule and hydrogen atoms of hydroxy groups) are indicated in the model. The ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level, while isotropic hydrogen atoms are represented by spheres of arbitrary size.

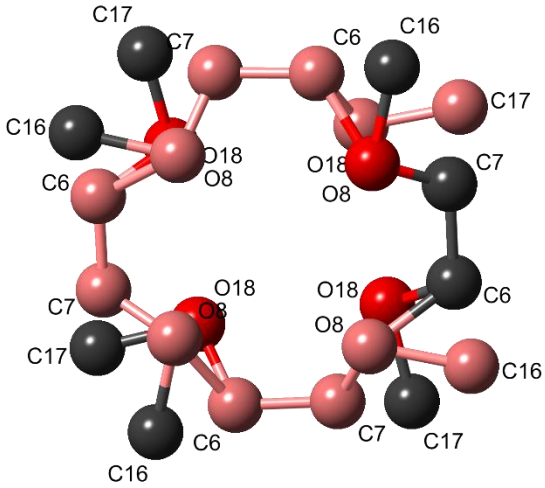

Figure S2. Atom assignment of the G3 molecule co-crystallized with the ionic species in DCS **1**. Four different arrangements are disordered. One example was extracted and colorized as pink. H atoms on each carbon atom are omitted for clarity. Gray, C; red, O.

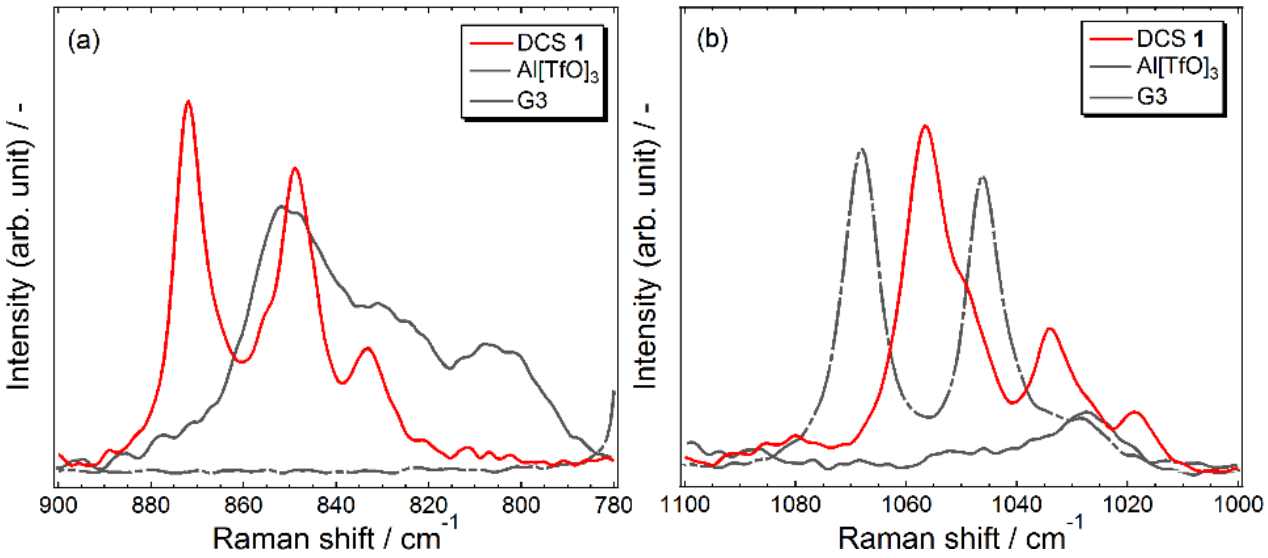

Figure S3. Raman spectra for DCS **1**, $Al[TfO]_3$, and G3 in the spectral ranges (a) 900–780 cm^{-1} and (b) 1100–1000 cm^{-1}.

Full publication list of reference [14] in the manuscript

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