Crown-Ether Coordination Compounds of Zirconium, Hafnium and Scandium Using Metal Nanoparticles

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–SUPPORTING INFORMATION–

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1. Analytical Techniques

Transmission electron microscopy (TEM). TEM and high-resolution (HR)TEM analyses were performed on an aberration-corrected FEI Titan^3 80-300 microscope at 300 keV electron energy. For sample preparation, diluted suspensions of the as-prepared Zr(0), Hf(0), Sc(0) nanoparticles in toluene were deposited and evaporated on commercial 400 µm mesh Cu-grids (Plano) covered by amorphous holey carbon film with a nominal thickness of 3 nm. The deposition was performed in a glove box (MBraun, Germany) under argon atmosphere to avoid any oxidation. With a suitable vacuum/inert gas transfer module (GATAN, USA), the sample grids were finally transferred into the microscope without any contact to air. (HR)TEM images were evaluated by calculating the two-dimensional Fourier transform (FT), which yields information on the crystal structure (lattice parameters and crystal symmetry) of single nanoparticles. The analysis was performed by comparing the experimental FT and the calculated diffraction patterns with Miller indices, where the latter were obtained by using the Jems (Java version of the electron microscopy simulation) software.[S1] The zero-order beam (ZB) is indicated by using a white circle.

X-ray data collection and structure solution. Selected single crystals of the title compounds were covered with inert oil (perfluorpolyalkylether, ABCR) and deposited on a microgripper (MiTeGen). Data collection for **1**, **3** and **4** was performed at 213 K (**1**), 293 K (**3**), and 150 K (**4**) on an IPDS II image plate diffractometer (Stoe) using Mo-K_α radiation ($\lambda = 71.073$ pm, graphite monochromator). Data collection for **2** was carried out at 100 K on a Stadivari diffractometer (Stoe) with a hybrid pixel detector using Mo-K_α radiation ($\lambda = 71.073$ pm, microfocus source with graded multilayer mirror as monochromator). Data reduction and absorption correction were performed by the X-AREA software package (version 1.75, Stoe) and STOE LANA (version 1.63.1, Stoe).[S2] For structure solution and refinement, SHELXT and SHELXL were used.[S3] All non-hydrogen atoms were refined anisotropically. The position of the hydrogen atoms were modelled by idealized C–H bonds. Images were illustrated with DIAMOND.[S4] Further details related to the crystal structures may be obtained from the joint CCDC/FIZ Karlsruhe deposition service on quoting the depository numbers: 2443621 (**1**), 2443622 (**2**), 2443623 (**3**), 2443624 (**4**).

Fourier-transformed infrared (FT-IR) spectra were recorded on a Bruker Vertex 70 FT-IR spectrometer (Bruker). The samples were measured as pellets in KBr. Thus, 300 mg of dried KBr and 0.5-1.0 mg of the sample were carefully pestled and pressed to a thin pellet.

Second harmonic generation (SHG). SHG measurements were performed using the Kurtz-Perry approach[S5] on microcrystalline powder samples clamped between two glass slides in order to avoid any exposure to air. Quartz, Al_2O_3 and KH_2PO_4 (KDP) were used as reference materials. A Q-switched Nd:YAG laser (1064 nm, 5-6 ns, 2 kHz) was used for the generation of the fundamental pump wave. The fundamental infrared light was focused into the sample and the generated second harmonic (532 nm) was separated from 1064 nm using a harmonic separator, a short-pass filter, and an interference filter. The SHG signal was collected with a photomultiplier and an oscilloscope from eight different areas of the sample. On each position, 64 pulses were measured and averaged. Background signals between the laser pulses were used to correct the measured intensities. The SHG measurements were performed under ambient conditions in transmission geometry.

2. Details of Single-Crystal Structure Analysis

The data and refinement details of the title compounds **1-4** are listed in Tables S1 to S4. The unit cells of the compounds **1-4** are shown in Figures S1-S4.

Table S1. Crystallographic data and refinement details of $[AlCl_2(12c4)][NaAl_2Cl_8]$ (**1**).

Data	**$[AlCl_2(12c4)][NaAl_2Cl_8]$**
Empirical formula	$C_8H_{16}Al_3Cl_{10}NaO_4$
Formula weight	634.64 g mol^{-1}
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Lattice parameters	a = 698.73(8) pm
	b = 1268.13(13) pm
	c = 2742.6(3) pm
Cell volume	$V = 2430.1(4)\times10^6$ pm^3
Formula units per cell	Z = 4
Calculated density	$\rho = 1.735$ g cm^{-3}
Measurement limits	$-8 \leq h \leq 8$, $-15 \leq k \leq 13$, $-28 \leq l \leq 32$
Theta range for data collection	1.49 to 24.99°
Measurement conditions	IPDS II (Stoe)
	λ(Mo-Kα) = 71.073 pm
	T = 213 K
Linear absorption coefficient	$\mu = 1.286$ mm^{-1}
Number of reflections	10527 (4276 independent)
Refinement methode	Full-matrix least-squares on F^2
Merging	$R_{int} = 0.0191$
Number of parameters	236
Residual electron density	1.36 to -0.68 e^- 10^{-6} pm^{-3}
Figures of merit	R1 ($I \geq 2\sigma_I$) = 0.0860
	R1 (all data) = 0.0988
	wR2 (all data) = 0.2687
	GooF = 1.077
Flack parameter	0.5(4)

The crystal structure was refined in the non-centrosymmetric space group $P2_12_12_1$ as an inversion twin with a relative batch scale factor of 0.455.

Table S2. Crystallographic data and refinement details of [$ZrCl_2$(15c5)][$Na_2Al_4Cl_{16}$] (**2**).

Data	**[$ZrCl_2$(15c5)][$Na_2Al_4Cl_{16}$]**
Empirical formula	$C_{10}H_{20}Al_4Cl_{18}Na_2O_5Zr$
Formula weight	1103.48 g mol^{-1}
Crystal system	monoclinic
Space group	*P2₁*
Lattice parameters	a = 1082.77(8) pm b = 1455.95(9) pm c = 1225.38(11) pm β = 102.298(7) °
Cell volume	V = 1887.4(3)×10^6 pm^3
Formula units per cell	Z = 2
Calculated density	ρ = 1.942 g cm^{-3}
Measurement limits	$-13 \leq h \leq 13, -18 \leq k \leq 18, -15 \leq l \leq 15$
Theta range for data collection	2.20 to 26.50°
Measurement conditions	Stadivari (Stoe) λ(Mo-Kα) = 71.073 pm T = 100 K
Linear absorption coefficient	μ = 1.707 mm^{-1}
Number of reflections	26442 (7713 independent)
Refinement methode	Full-matrix least-squares on F^2
Merging	R_{int} = 0.0558
Number of parameters	362
Residual electron density	0.68 to -0.73 e^- 10^{-6} pm^{-3}
Figures of merit	R1 ($I \geq 2\sigma_I$) = 0.0495 R1 (all data) = 0.0656 wR2 (all data) = 0.1396 GooF = 1.094
Flack parameter	0.43(11)

The crystal structure was refined in the non-centrosymmetric space group $P2_1$ and as an inversion twin with a relative batch scale factor of 0.434.

Table S3. Crystallographic data and refinement details of $[HfCl_2(15c5)][Na_2Al_4Cl_{16}]$ (**3**).

Data	$\mathbf{[HfCl_2(15c5)][Na_2Al_4Cl_{16}]}$
Empirical formula	$C_{10}H_{20}Al_4Cl_{18}Na_2O_5Hf$
Formula weight	1190.75 g mol^{-1}
Crystal system	monoclinic
Space group	$P2_1$
Lattice parameters	a = 1099.75(11) pm b = 1490.9(5) pm c = 1251.59(13) pm β = 102.438(8) °
Cell volume	$V = 2004.0(4)\times10^6$ pm^3
Formula units per cell	Z = 2
Calculated density	$\rho = 1.973$ g cm^{-3}
Measurement limits	$-14 \leq h \leq 13, -19 \leq k \leq 19, -16 \leq l \leq 16$
Theta range for data collection	1.67 to 27.50°
Measurement conditions	IPDS II (Stoe) λ(Mo-Kα) = 71.073 pm T = 293 K
Linear absorption coefficient	$\mu = 3.936$ mm^{-1}
Number of reflections	25099 (9231 independent)
Refinement methode	Full-matrix least-squares on F^2
Merging	$R_{int} = 0.0510$
Number of parameters	497
Residual electron density	0.83 to -0.55 $e^- 10^{-6} pm^{-3}$
Figures of merit	R1 ($I \geq 2\sigma_I$) = 0.0379 R1 (all data) = 0.0896 wR2 (all data) = 0.0804 GooF = 0.816
Flack parameter	0.54(3)

The crystal structure was refined in the non-centrosymmetric space group $P2_1$ and as an inversion twin with a relative batch scale factor of 0.540. The 15c5 ligand show rotational disorder around the Cl–Hf–Cl axis with two positions. Occupation factors of the disordered parts were freely refined, resulting in occupancies of 62% and 38%. Modelling of distinct split atom positions was hindered due to the fact that all atoms of the disordered parts occupy a tight torus shaped volume. Therefore, all C and O atoms of the crown ether were refined using

SAME, SIMU and RIGU restraints. This enabled a stable disorder refinement with typical distances and angles of 15c5 as a ligand.

Table S4. Crystallographic data and refinement details of [$ScCl_2$(18c6)][$AlCl_4$] **(4).**

Data	**[$ScCl_2$(18c6)][$AlCl_4$]**
Empirical formula	$C_{12}H_{24}AlCl_6O_6Sc$
Formula weight	548.95 g mol^{-1}
Crystal system	orthorhombic
Space group	$Pna2_1$
Lattice parameters	a = 1941.3(9) pm
	b = 1123.7(3) pm
	c = 2109.2(7) pm
Cell volume	V = 4601(3)×10^6 pm^3
Formula units per cell	Z = 8
Calculated density	ρ = 1.585 g cm^{-3}
Measurement limits	$-23 \leq h \leq 23, -13 \leq k \leq 12, -26 \leq l \leq 24$
Theta range for data collection	2.05 to 26.00°
Measurement conditions	IPDS II (Stoe)
	λ(Mo-Kα) = 71.073 pm
	T = 150 K
Linear absorption coefficient	μ = 1.079 mm^{-1}
Number of reflections	27973 (8465 independent)
Refinement methode	Full-matrix least-squares on F^2
Merging	R_{int} = 0.0587
Number of parameters	480
Residual electron density	0.51 to -0.50 e^- 10^{-6} pm^{-3}
Figures of merit	R1 ($I \geq 2\sigma_I$) = 0.0428
	R1 (all data) = 0.0867
	wR2 (all data) = 0.0857
	GooF = 0.818
Flack parameter	0.60(6)

The crystal structure was refined in the non-centrosymmetric space group $Pna2_1$ as an inversion twin with a relative batch scale factor of 0.575. The non-coordinating O atom (O12) of one of the two 18c6 ligands in the asymmetric unit turned out to be disordered over two positions. Occupation factors of the disordered O atom were freely refined, resulting in occupancies of 83% and 17%. Refinement of the disordered O atom was performed using SADI restraints on the C–O bonds as wells as SIMU restraints of O12 and its neighboring C atoms to ensure suitable C–O distances.

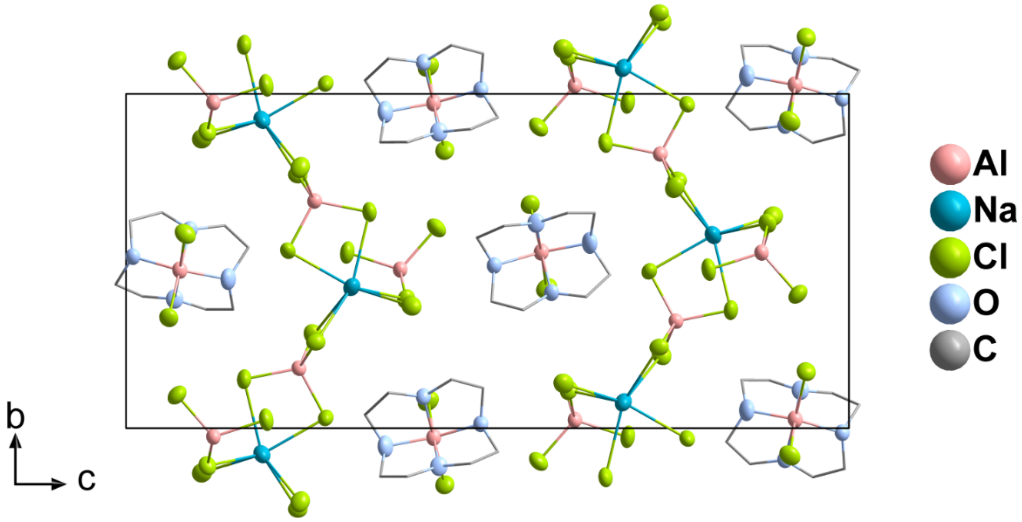

Figure S1. Unit cell of $[AlCl_2(12c4)][NaAl_2Cl_8]$ (**1**).

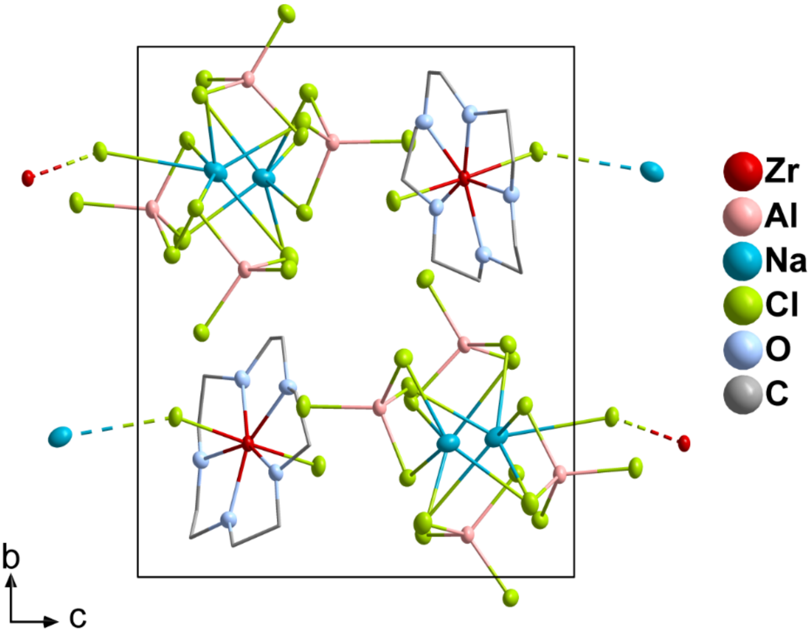

Figure S2. Unit cell of $[ZrCl_2(15c5)][Na_2Al_4Cl_{16}]$ (**2**).

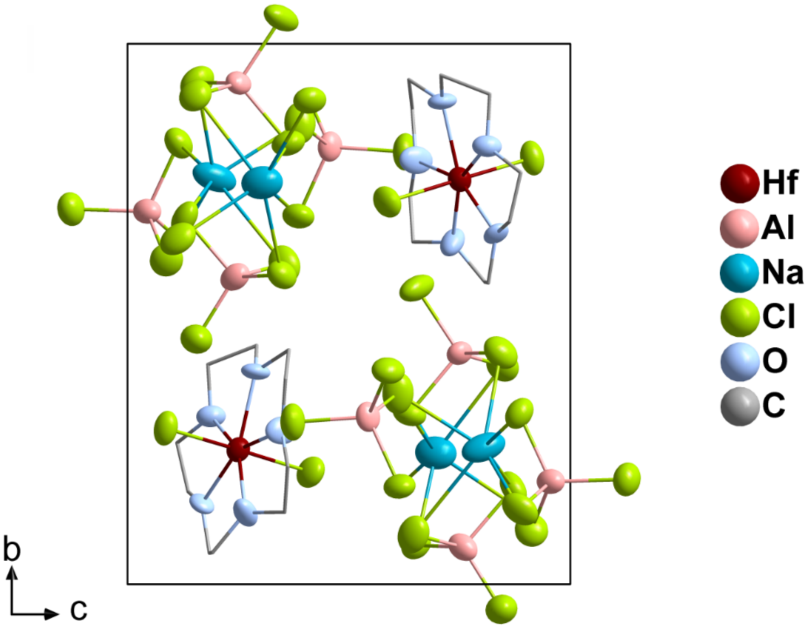

Figure S3. Unit cell of [HfCl$_2$(15c5)][Na$_2$Al$_4$Cl$_{16}$] (**3**).

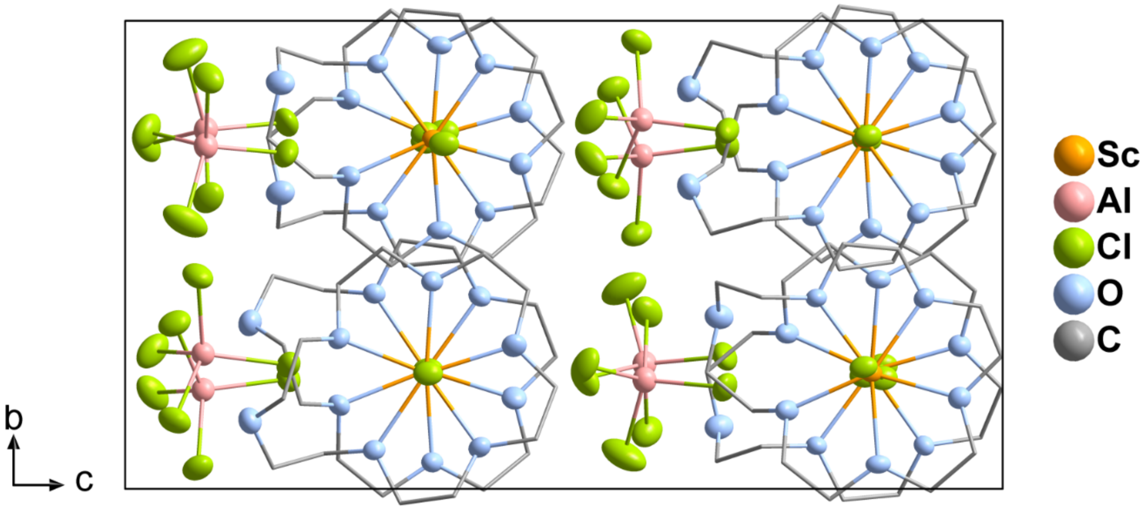

Figure S4. Unit cell of [ScCl$_2$(18c6)][AlCl$_4$] (**4**).

3. Characterization of Crown-Ether Compounds

Fourier-transform infrared (FT-IR) spectra of the compounds **1-4** are shown in Figures S5-S7. The results are discussed in the main paper.

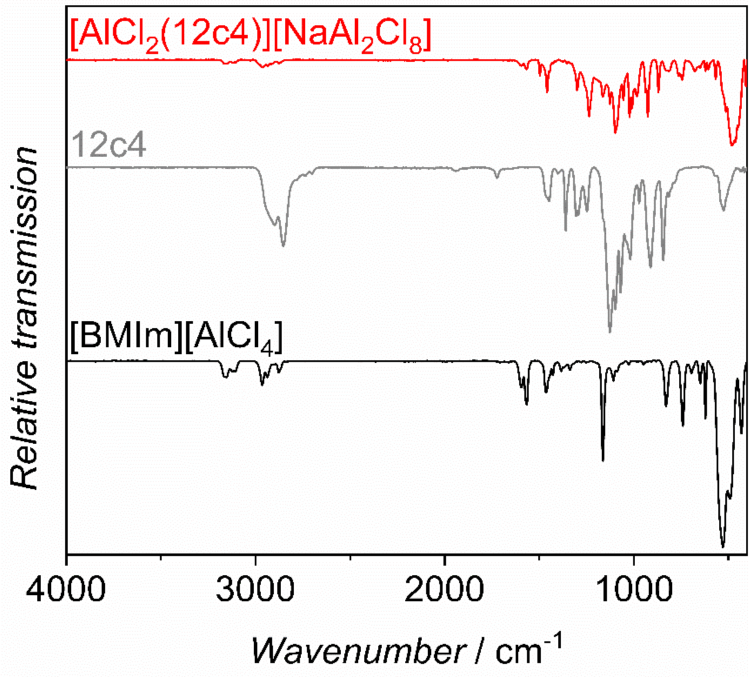

Figure S5. FT-IR spectrum of [AlCl$_2$(12c4)][NaAl$_2$Cl$_8$] (**1**) (with 12c4 and [BMIm][AlCl$_4$] as references).

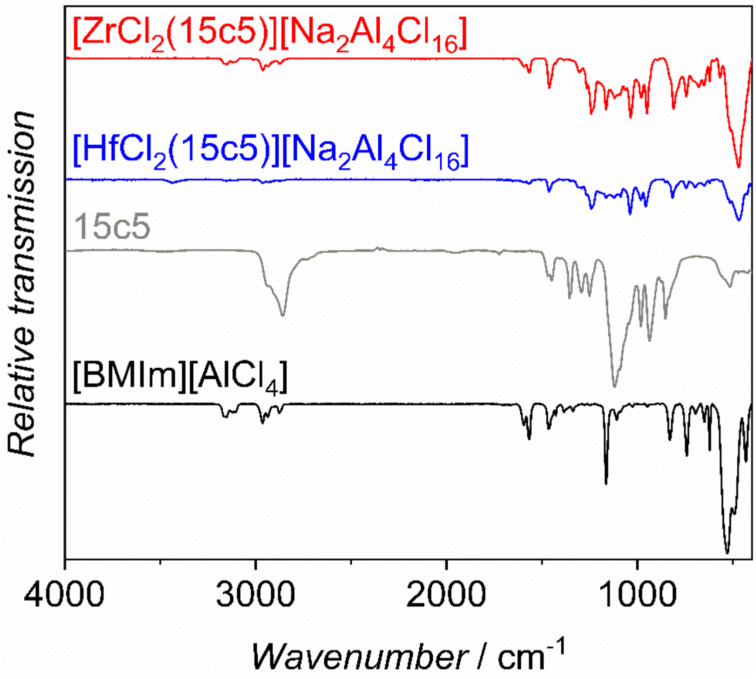

Figure S6. FT-IR spectrum of [ZrCl$_2$(15c5)][Na$_2$Al$_4$Cl$_{16}$] (**2**) and [HfCl$_2$(15c5)][Na$_2$Al$_4$Cl$_{16}$] (**3**) (with 15c5 and [BMIm][AlCl$_4$] as references).

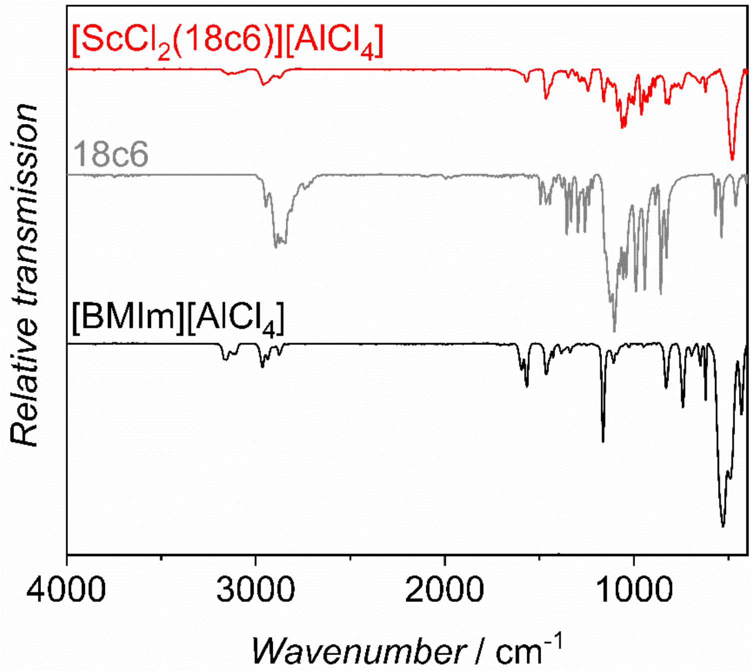

Figure S7. FT-IR spectrum of [ScCl$_2$(18c6)][AlCl$_4$] (**4**) (with 18c6 and [BMIm][AlCl$_4$] as references).

The tensor surfaces of [ScCl$_2$(18c6)][AlCl$_4$] (4) were calculated and displayed as two-dimensional projections (Figure S8) and three-dimensional projection (*see main paper: Figure 6*).

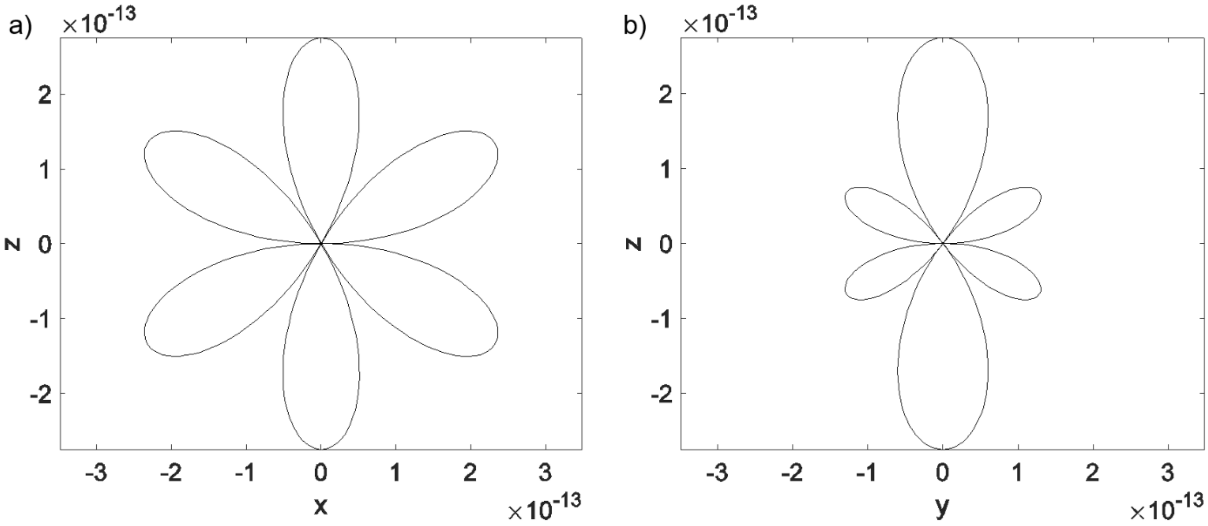

Figure S8. Two-dimensional projections of the representation surfaces of tensor $d'_{333} = \alpha_{3i}\alpha_{3j}\alpha_{3k}d_{ijk}$ of [ScCl$_2$(18c6)][AlCl$_4$] (**4**): a) *x,z* plane, b) *y,z* plane.

4. References

S1 P. A. Stadelmann, https://www.jems-swiss.ch/.

S2 X-RED32, *Data Reduction Program*, Stoe, Darmstadt **2001**.

S3 G. M. Sheldrick, *SHELXT – Integrated space-group and crystal-structure determination. Acta Crystallogr.* **2015**, *71*, 3.

S4 DIAMOND, *Crystal and Molecular Structure Visualization*, Crystal Impact GbR, Bonn **2016**.

S5 S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3789-3818.