Electronic Supplementary Material (ESI) for CrystEngComm.
This journal is © The Royal Society of Chemistry 2015

Supporting Information for

Isomerization of a Lanthanide Complex using a Humming Top Guest Template: a Solid-to-Solid Reaction

Michelle B. Mills, Andrew G. Hollingshead, Adam C. Maahs, Dmitriy V. Soldatov, and Kathryn E. Preuss*

Department of Chemistry, University of Guelph, Guelph, ON, N1G 2W1, Canada.

Experimental Section

General Considerations

All reactions were performed under argon atmosphere using standard Schlenk line and glove box techniques. Dried and degassed solvents were obtained from an LC-SPS solvent purification system using dry packed columns containing 3 Å molecular sieves. All other reagents were purchased from Sigma Aldrich, Strem, and Acros Organics and used as received. FTIR spectra were collected on KBr pellets pressed under argon atmosphere, using a Nicolet 510-FTIR spectrometer at ambient temperature. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ, USA. Powder X-ray diffraction (PXRD) experiments were conducted on a SuperNova Agilent single crystal diffractometer equipped with a microfocus CuK_α (λ = 1.54184 Å) radiation source and Atlas CCD detector. Polycrystalline samples were sealed inside 0.5 mm thin-wall capillary tubes (Charles Supper) in a glove box. The samples were studied at 150 K (Cryojet XL low-temperature device, Oxford Instruments). Two frames were collected from different ω angular positions using 90° φ-scan and 90 s exposure time to cover the 2θ range of 5-60°. Points on the powder diffractogram were generated using CrysAlisPro software[1] from the original images with the step of 0.02° in 2θ, with each of the points representing readings from 60 to 500 pixels. Sublimations under dynamic vacuum were carried out on a multi-stage programmable temperature tube furnace. Sublimations under static vacuum atmosphere were carried out on a single-stage programmable temperature tube furnace. Ce(hfac)$_3$(DME)[2] and 5′-Br-pyDTDA[3] were prepared according to literature procedure (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato-; DME = 1,2-dimethoxyethane; 5′-Br-pyDTDA = 4-(5′-bromopyrid-2′-yl)-1,2,3,5-dithiadiazolyl).

Ce(hfac)$_3$(5′-Br-pyDTDA)$_2$

Anhydrous CH$_2$Cl$_2$ (35 mL) was added to a solid mixture of Ce(hfac)$_3$(DME) (0.3783 g, 0.4443 mmol) and 5′-Br-pyDTDA (0.2319 g, 0.8880 mmol) under argon. The resulting red solution was stirred for 3 h. The solvent was removed under reduced pressure to afford a bright red-purple solid. The solid residue was recovered and sublimed under dynamic vacuum (10^{-2} Torr) at 107 °C to yield dark red blocks suitable for X-ray crystallography; yield 0.1589 g (28%). FTIR (KBr): 3114(vw), 1649(s), 1556(m), 1528(m), 1477(s), 1401(m), 1377(m), 1347(w), 1321(w), 1254(vs), 1215(vs), 1144(vs), 1096(s), 1022(s), 950(w), 918(w), 845(m), 835(m), 799(m), 780(m), 740(m), 730(w), 660(m), 640(w), 584(m), 528(m), 519(w), 459(w) cm^{-1}. Anal. Calcd. for $CeC_{27}H_9O_6F_{18}N_6S_4Br_2$: C, 25.27; H, 0.71; N, 6.55%. Found: C, 25.31; H, 0.68; N, 6.68%.

[Ce(hfac)$_3$(5′-Br-pyDTDA)$_2$]*0.5{SbPh$_3$Cl$_2$}

A stoichiometric mixture of dark red, solid Ce(hfac)$_3$(5′-Br-pyDTDA)$_2$ (0.0743 g, 0.0579 mmol) and white, solid SbPh$_3$Cl$_2$ (0.0123g, 0.0290 mmol) was ground for 2 h with a mortar and pestle under argon atmosphere. The PXRD pattern of the resulting pale purple solid indicated an admixture of starting materials and no evidence of reaction product. The pale purple solid was then heated at 110 °C in a thick-walled glass tube, sealed under vacuum (10^{-1} Torr), for 1 week. The microcrystalline solid changed colour uniformly to red, and a small number of red prismatic crystals, suitable for single crystal X-ray diffraction, were collected from the opposite end of the sealed tube. PXRD of the microcrystalline red solid and single crystal XRD of the red crystals confirmed that both were the product [Ce(hfac)$_3$(5′-Br-pyDTDA)$_2$]*0.5{SbPh$_3$Cl$_2$}; yield ~100% by PXRD. FTIR (KBr): 3104(vw), 3061(vw), 1651(s), 1578(w), 1552(m), 1526(m), 1498(s), 1479(s), 1437(m), 1396(m), 1368(m), 1343(w), 1252(vs), 1203(vs), 1146(vs), 1095(s), 1022(s), 996(m), 948(w), 919(w), 848(m), 838(m), 795(s), 781(s), 731(s), 685(m), 659(m), 640(m), 583(m), 527(w), 518(w), 456(w) cm^{-1}.

Crystallographic Measurements

The crystals of two compounds studied in this work were extracted from vacuummated tubes used for the crystal growth by sublimation, mounted on MiTeGen MicroMounts and immediately protected with type NVH immersion oil. All measurements were conducted at low temperature (150 K) on a SuperNova Agilent single crystal diffractometer equipped with microfocus CuK_α (λ = 1.54184 Å) and MoK_α (λ = 0.71073 Å) radiation sources and an Atlas CCD detector. Diffraction intensity data were collected using ω-scan technique. The unit cell parameters were calculated and refined using the entire data sets. The unit cell refinement and data reduction were carried out using CrysAlisPro software[1]. Further details are described below.

$[Ce(hfac)_3(5'\text{-}Br\text{-}pyDTDA)_2]$ (**1**). The crystals of the complex were of poor quality, the problem being recognized as due to pseudomerohedral twinning around the [100] direction. Eight crystals from two independent preparations were screened and several attempts to collect a good dataset were made. Finally, a small red prism (0.16x0.10x0.08 mm) was studied using CuK_α radiation in order to achieve a better separation of spots from the two twin components, to the resolution of 0.795 Å.

The diffraction images were processed using two superimposed matrices to generate hkl data in the HKLF 5 format which then were used for structure solution and refinement with SHELX.[4] The ratio of twin components was 0.51:0.49 and the fraction of overlapped reflections was ~22%. The average agreement factor R_{int} was within 6.7-7.5% for separated, and 2.1% for overlapped reflections. The overall redundancy factor was >4.

The structure was solved in the monoclinic space group $P2_1/n$ and refined to the R value of 5.8%. Non-hydrogen atoms were refined anisotropically with mild restraints on the thermal ellipsoids (using DELU, SIMU and ISOR instructions). Hydrogen atoms were placed in calculated positions and refined isotropically. The residual extrema were located within 1 Å from either Ce or Br. The Alert B and most Alerts C generated by the IUCr checkCIF program resulted from large displacement parameters of F atoms implying intense rotation of the CF_3 groups and possible unresolved disorder of the hfac ligands.

$[Ce(hfac)_3(5'\text{-}Br\text{-}pyDTDA)_2]*0.5\{SbPh_3Cl_2\}$ (**2**). A red prism (0.20 x 0.10 x 0.05 mm) of the compound was studied using MoK_α radiation. Data were collected within the sphere to the resolution of 0.7 Å, with the redundancy factor of >12 and the agreement factor $R_{\text{int}} = 7.1\%$ for orthorhombic F cell.

The structure was solved in the orthorhombic space group Fdd2 and refined to the R value of 4.8%. Non-hydrogen atoms were refined anisotropically with mild restraints on the thermal ellipsoids of some C atoms of phenyl rings (DELU and SIMU instructions). Hydrogen atoms were placed in calculated positions and refined isotropically. All strong residual maxima (>2 e/Å^3) were located within 1 Å from heavy atoms (Ce, Br, Sb). One Alert A generated by the IUCr checkCIF program pointed on 5.1 e/Å^3 maximum near Ce which is likely a result of inadequate absorption correction on a poor quality crystal (the crystals obtained by sublimation grew up as clusters and the studied specimen had smaller fragments merged with the main body of the crystal). Most Alerts B and C resulted from other residual peaks or large displacement parameters of F atoms implying motion of the CF_3 groups.

The crystal data and further XRD experimental parameters are listed in the Tables. CIF files for the structures have been deposited with the Cambridge Crystallographic Data Centre; CCDC deposition numbers are 1415404 (complex **1**) and 1415405 (compound **2**). A copy of these data is available free of charge upon request from the CCDC web-site: http://www.ccdc.cam.ac.uk/data_request/cif or by e-mail: deposit@ccdc.cam.ac.uk.

Table S1. Crystal data and structure refinement for 1.

Empirical formula	C27 H9 Br2 Ce F18 N6 O6 S4
Formula weight	1283.58
Temperature	150(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	*P* 21/n
Unit cell dimensions	a = 16.7572(3) Å alpha = 90°
	b = 12.4340(2) Å beta = 91.3502(15) °
	c = 19.4838(3) Å gamma = 90°
Volume	4058.50(12) $Å^3$
Z	4
Density (calculated)	2.101 mg/m^3
Absorption coefficient	14.137 mm^{-1}
F(000)	2460
Crystal size	0.160 × 0.100 × 0.080 mm^3
Theta range for data collection	3.439 to 76.393°
Index ranges	$-21 \leq h \leq 17$, $-15 \leq k \leq 15$, $-24 \leq l \leq 24$
Reflections collected	15668
Independent reflections	15668
Completeness to theta = 67.684°	100%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.80223
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15668/954/577
Goodness-of-fit on F^2	1.071
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0580, wR2 = 0.1445
R indices (all data)	R1 = 0.0644, wR2 = 0.1486
Largest diff. peak and hole	1.549 and -2.020 e.$Å^{-3}$

Table S2. Crystal data and structure refinement for 2.

Empirical formula	C36 H16.50 Br2 Ce Cl F18 N6 O6 S4 Sb0.50
Formula weight	1495.56
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*F* d d 2
Unit cell dimensions	a = 36.8971(5) Å alpha = 90°
	b = 30.3093(4) Å beta = 90°
	c = 17.87564(19) Å gamma = 90°
Volume	19990.8(4) Å^3
Z	16
Density (calculated)	1.988 mg/m^3
Absorption coefficient	3.112 mm^{-1}
F(000)	11504
Crystal size	0.200 × 0.100 × 0.050 mm^3
Theta range for data collection	2.847 to 30.507°
Index ranges	$-52 \le h \le 52$, $-43 \le k \le 43$, $-25 \le l \le 25$
Reflections collected	99135
Independent reflections	15221 [R(int) = 0.0615]
Completeness to theta = 30.51°	99.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.86760
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15221 /49 /687
Goodness-of-fit on F^2	1.037
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0481, wR2 = 0.1189
R indices (all data)	R1 = 0.0599, wR2 = 0.1275
Largest diff. peak and hole	5.159 and -1.325 e.Å^{-3}

Table S3. Selected Close Contacts (Å) in the Structures of 1 and 2.

1		**2**	
Important *inter*molecular "pancake bond" distances			
S2…S22$^{(a)}$	2.942(3)	S2…S23$^{(d)}$	2.956(3)
N1…S23$^{(a)}$	3.017(6)	S3…S22$^{(d)}$	2.997(3)
S3…N21$^{(a)}$	3.093(6)	-	-
*Intra*molecular distances between DTDA heteroatoms$^{¥}$			
S2…S22	3.521(3)	-	-
S3…S23	4.118(3)	-	-
Important electrostatic contact distances			
Br9…S23$^{(b)}$	3.563(2)	Cl1…S2$^{(e)}$	3.185(3)
Br9…N24$^{(b)}$	3.143(6)	Cl1…S3$^{(e)}$	3.237(3)
Br29…S3$^{(c)}$	3.532(2)	Cl1…S22$^{(f)}$	3.254(3)
Br29…N4$^{(c)}$	3.397(6)	Cl1…S23$^{(f)}$	3.479(3)
Halogen-halogen contact distances			
-	-	Br29…Br29$^{(e)}$	3.646(2)

(¥)These are the closest S…S distances between the two 5′-Br-pyDTDA ligands that are coordinated to a common Ce(III) ion in **1**. In a *twisted*-cofacial "pancake bond", the S3…S23 distance should be ~3 Å. It is clear from these distances that the two ligands are *not* "pancake bonded".

Symmetry codes: (a) –x + 0.5, y - 0.5, -z + 1.5 (b) x + 0.5, -y +1.5, z + 0.5 (c) x + 0.5, -y +1.5, z – 0.5 (d) –x + 1, -y + 1.5, z + 0.5 (e) –x + 1, -y + 1, z (f) x, y – 0.5, z + 0.5

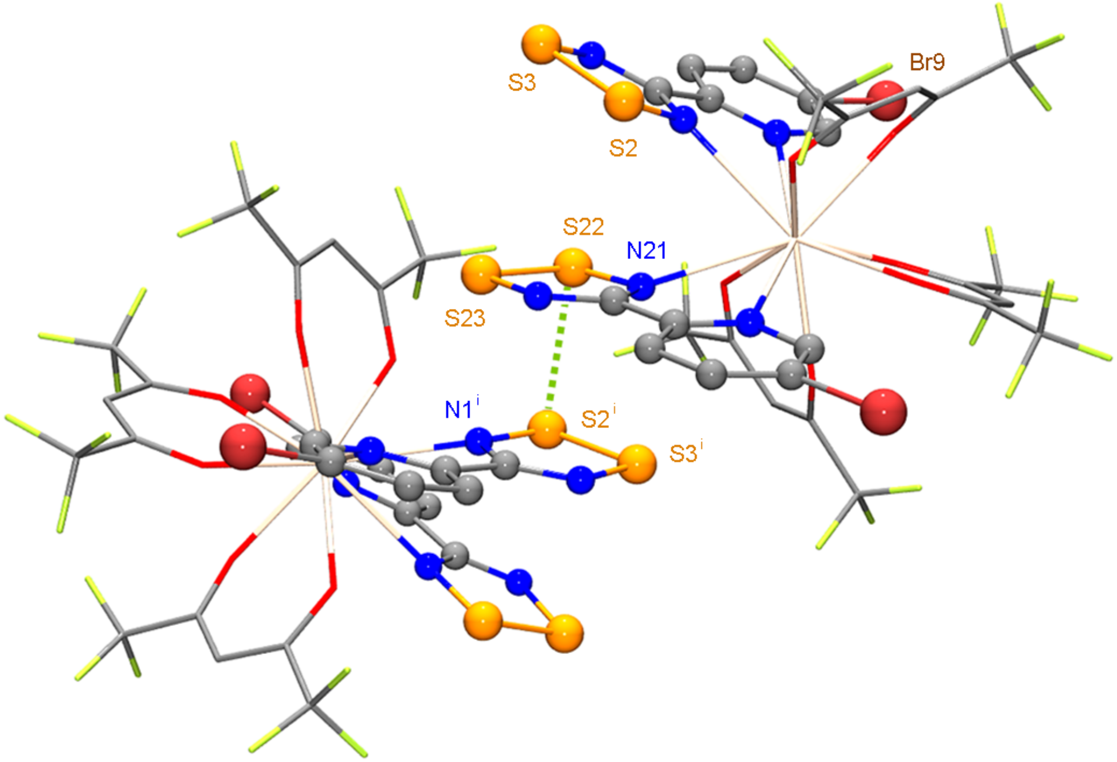

Figure S1. Excerpt from the crystal structure of **1** illustrating the close contacts, labelled with reference to Table S3. Symmetry code: (i) $1/2 - x$, $y + 1/2$, $3/2 - z$.

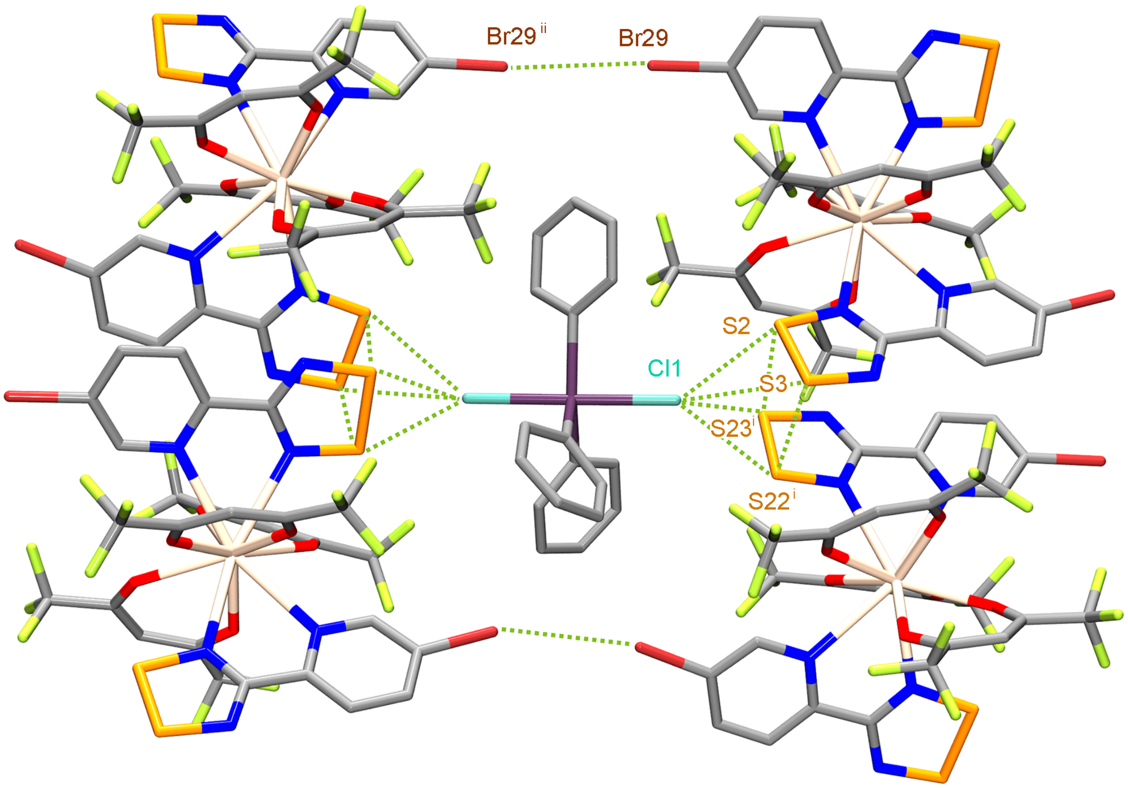

Figure S2. Excerpt from the crystal structure of **2** illustrating the close contacts, labelled with reference to Table S3. Symmetry codes: (i) 1 – *x*, 3/2 – *y*, *z* + 1/2; (ii) 1 – *x*, 1 – *y*, *z*.

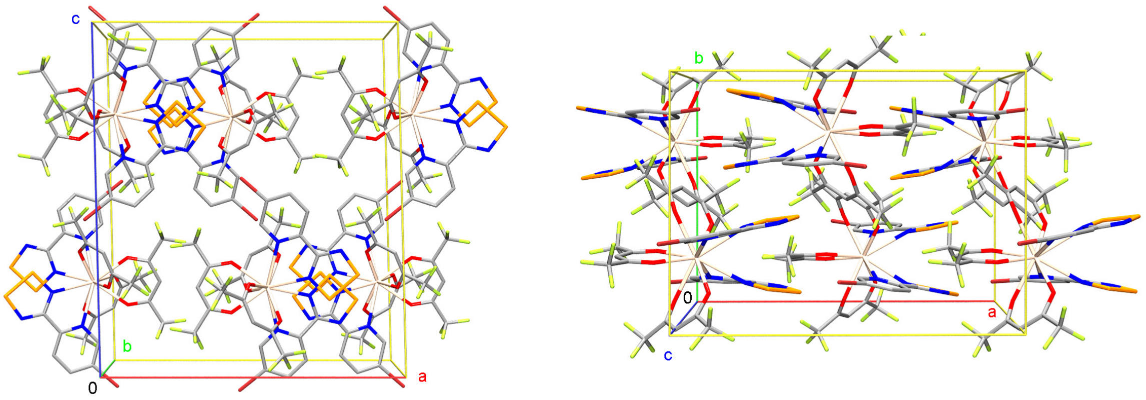

Figure S3. Excerpts from the crystal structure of **1** illustrating the crystal packing as viewed (left) normal to [010] and (right) normal to [001].

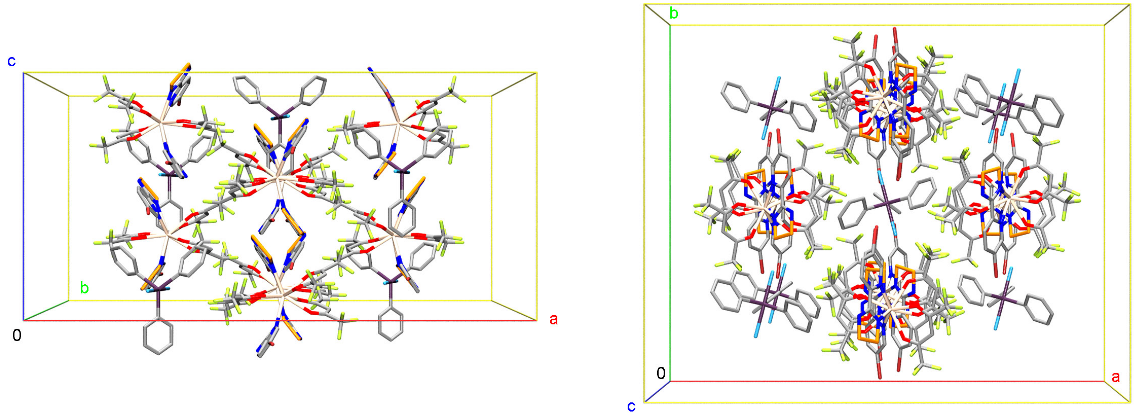

Figure S4. Excerpt from crystal structure of **2** illustrating the crystal packing as viewed (left) normal to [010] and (right) normal to [001].

References for the Supporting Information

[1] Agilent Technologies (2011) *Agilent Technologies, Xcalibur CCD system, CrysAlisPro Software system*; Version 1.171.35.8.

[2] E. M. Fatila, E. E. Hetherington, M. Jennings, A. J. Lough and K. E. Preuss, *Dalton Trans.*, 2012, **41**, 1352-1362.

[3] N. G. R. Hearns, R. Clérac, M. Jennings, and K. E. Preuss, *Dalton Trans.*, 2009, **17**, 3193-3203.

[4] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.