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From Discrete Molecule to One-Dimension Chain: Two New Nitronyl Nitroxide–Lanthanide Complexes Exhibiting Slow Magnetic Relaxation

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A mononuclear lanthanide–radical complex [Tb(hfac)$_3$(NITPhSCH$_3$)$_2$] (**1**) and a one-dimensional chain complex [Tb(hfac)$_3$(NITPhSCH$_3$)]$_n$ (**2**) {hfac = hexafluoroacetylacetonate, NITPhSCH$_3$ = 2-[4-(methylthio)phenyl]-4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide} have been synthesized. Single-crystal X-ray diffraction studies revealed that compound **1** is a mononuclear complex in which two NITPhSCH$_3$ radicals are coordinated as monodentate ligands to the Tb^{III} ion through their NO groups to form a tri-spin complex, and complex **2** is a 1D chain structure constructed of Tb(hfac)$_3$ units bridged by NITPhSCH$_3$ radicals through their NO groups. The temperature dependence of the magnetic susceptibilities of **1** and **2** indicates ferromagnetic coupling between the Tb^{III} ion and the NITPhSCH$_3$ radical. Frequency-dependent out-of-phase signals of alternating current magnetic susceptibilities were observed at low temperature for both complexes, indicative of slow magnetic relaxation.

Introduction

The design and synthesis of single-molecule and single-chain magnets (SMMs and SCMs) have attracted considerable interest in the field of molecular-based magnetic materials, because they are potential candidates for future high-density information storage materials[1–3] and quantum computations.[4] SMMs are isolated as zero-dimensional nanoparticles that exhibit slow relaxation of their magnetization, which arises from the combination of a large ground-state spin *S* and an Ising-type anisotropy. Since the SMM behavior of the famous Mn12 was discovered,[1a] various coordination compounds displaying SMM behavior have been reported in the literature, most of them bearing 3d metal centers.[1d,5–8] In addition, SCMs[9–14] have attracted considerable attention since the discovery of the first single-chain magnet [Co(hfac)$_2$(NITPhOMe)] [hfac = hexafluoroacetylacetonate, NITPhOMe = 2-(4-methoxyphenyl)-4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide].[13]

In general, SCMs possess a higher anisotropy barrier than SMMs.[2,13] Of the many characteristics required for the chemical design of SMMs and SCMs, one important factor is the strong magnetic anisotropy of clusters or chains, which provides an energy barrier for the reversal of magnetization and is of determinant importance for obtaining a convenient relaxation time. In their synthesis, magnetic anisotropy relating to magnetocrystalline and coupling anisotropy is hard to tune, but metal ions with significant anisotropy can be chosen easily. It is well known that lanthanide ions, except for gadolinium(III), and especially heavy lanthanide ions, such as terbium(III) and dysprosium(III),[15] have large anisotropies, which arise from strong spin–orbit coupling, and have become good candidates for the construction of SMMs and SCMs.[12,16–18] Another crucial factor affecting magnetic relaxation is the magnetic-exchange coupling that moderates the magnetic relaxation of the single ions.[19] However, the promotion of magnetic-exchange interactions in lanthanide systems is a difficult task. To overcome this obstacle, a rational approach is to choose a radical ligand that is directly coordinated to a lanthanide ion to produce stronger magnetic coupling.[20] Up to now, few SMMs and SCMs containing radicals and lanthanide ions have been reported.[14,21] Herein, we report two new radical–lanthanide complexes bearing the same nitronyl nitroxide ligand, namely the mononuclear tri-spin complex [Tb(hfac)$_3$(NITPhSCH$_3$)$_2$] (**1**) and the one-dimensional chain complex [Tb(hfac)$_3$(NITPhSCH$_3$)]$_n$ {**2**; NITPhSCH$_3$ = 2-[4-(methylthio)phenyl]-4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide}. Magnetic studies showed that both complexes exhibit slow magnetic relaxation at low temperature, which suggests SMM and SCM behavior for complexes **1** and **2**, respectively. To the best of our knowledge this is the first time an SMM and SCM have been prepared by using the same radical ligand.

Results and Discussion

Synthesis

The two radical–lanthanide compounds were synthesized in heptane/dichloromethane according to previously re-

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ported procedures.[22] By varying the relative proportions of [Tb(hfac)$_3$] and the NITPhSCH$_3$ radical ligand, we successfully isolated two different complexes: One is a blue mononuclear Tb^{III} complex with two radical ligands, the other is a green one-dimensional Tb^{III} chain bridged by two NO groups of the radical ligand. For complex **2**, we could not obtain crystals suitable for X-ray analysis; however, preliminary X-ray analysis,[23] elemental analysis, and infrared spectroscopy confirmed that complex **2** is a one-dimensional chain bridged by the nitroxide groups of NITPhSCH$_3$ radical ligands.

Crystal Structure of Complex 1

The X-ray analysis showed that complex **1** crystallizes in the monoclinic space group $P2_1/n$. Figure 1 shows the molecular structure of complex **1** in which the nitronyl nitroxide radicals act as monodentate ligands towards Tb^{III} through the oxygen atom of the N–O group to form a tri-spin complex.[24] The Tb^{III} ion is octacoordinated by six oxygen atoms from three bidentate hfac ligands and two oxygen atoms from two NITPhSCH$_3$ ligands. The bond lengths between the Tb^{III} ion and the oxygen atoms of the hfac ligands are in the range 2.3173(19)–2.4003(19) Å, whereas the Tb–O bond lengths of the two nitroxide groups are 2.3340(18) and 2.3245(19) Å, which are comparable to those of the reported [Ln(hfac)$_3$] with nitronyl nitroxides.[25] The uncoordinated N–O distances (1.280, 1.275 Å) are shorter than the coordinated N–O distances (1.303, 1.308 Å). The dihedral angles formed by the phenyl ring and the nitroxide groups of the radical ligand are 32.6 and 37.4° for the two NITPhSCH$_3$ ligands. Figure 2 shows the packing diagram for complex **1**. The shortest Tb···Tb distance is 10.623 Å, whereas the shortest distance between the uncoordinated NO groups is 2.826 Å, which indicates that weak magnetic coupling may exist between the NITPhSCH$_3$ radicals.

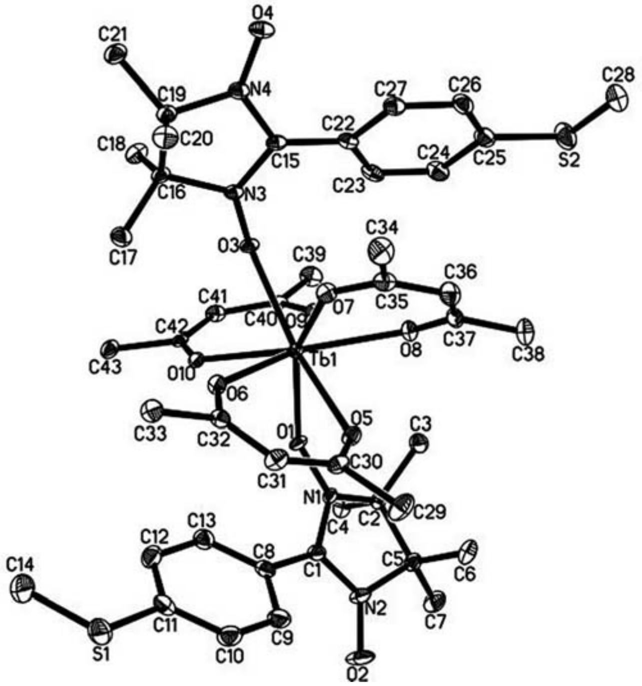

Figure 1. Molecular structure of **1**. Fluorine and hydrogen atoms are not shown for the sake of clarity.

Magnetic Properties of Complexes 1 and 2

The temperature dependence of the magnetic susceptibilities of complexes **1** and **2** was measured in the 2–300 K range under an applied magnetic field of 2000 G and the magnetic behavior is shown in Figures 3 and 4. At room temperature the value of $\chi_M T$ for **1** is 12.87 cm^3 K mol^{-1}, in agreement with the expected value (12.57 cm^3 K mol^{-1}) for an uncoupled Tb^{III} ion ($^7F_6$, g = 3/2) and two organic radicals (S = 1/2), whereas the value of $\chi_M T$ for **2** is 12.08 cm^3 K mol^{-1}, which again is close to the expected value (12.20 cm^3 K mol^{-1}) for an uncoupled Tb^{III} ion and one organic radical. For complex **1**, upon cooling, the $\chi_M T$ value gradually decreases to reach a value of

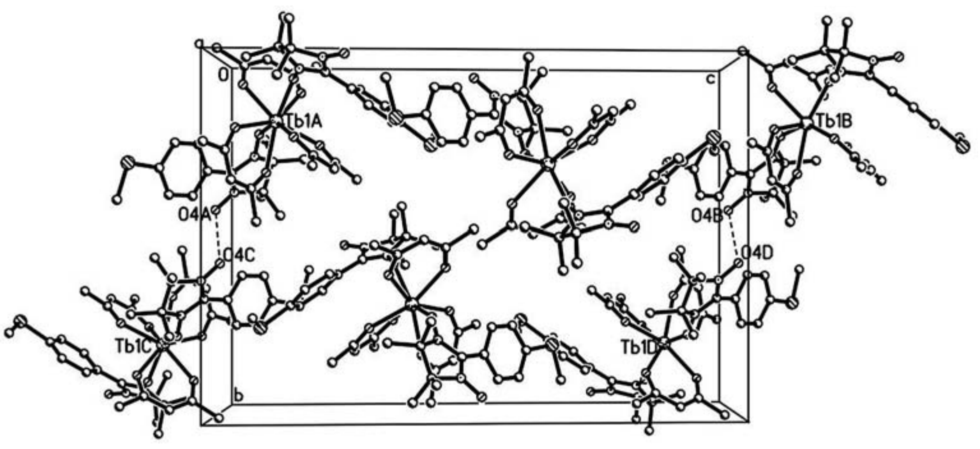

Figure 2. Packing diagram of **1**.

12.11 $cm^3\,K\,mol^{-1}$ at 35 K, which can mainly be attributed to the depopulation of the Tb^{III} Stark sublevels. Below 35 K, the value of $\chi_M T$ rapidly increases to a maximum value of 12.68 $cm^3\,K\,mol^{-1}$ at 7.0 K, which suggests the presence of ferromagnetic interactions between the Tb^{III} ions and the coordinated NO group of the organic radicals, which may be due to the effect of spin polarization of the unpaired electron of the radical ligand on the empty orbitals of Tb^{III}. Then $\chi_M T$ decreases on cooling, which can be attributed to intermolecular magnetic coupling. For complex **2**, the value of $\chi_M T$ gradually increases on cooling, then increases sharply to a peak value of 20.6 $cm^3\,K\,mol^{-1}$ at 6.0 K and then decreases on further cooling. As is well known, both nearest-neighbor (NN) metal–radical magnetic coupling and next-nearest-neighbor (NNN) metal–metal or radical–radical magnetic interactions may be simultaneously present in the lanthanide–radical chain, with these last two being antiferromagnetic in nature.[26] The overall behavior indicates that ferromagnetic coupling dominates in **2**.

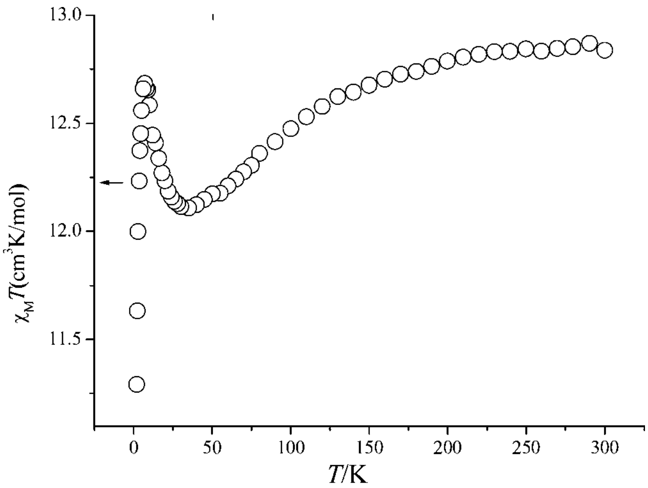

Figure 3. Plots of $\chi_M T$ vs. T for **1**.

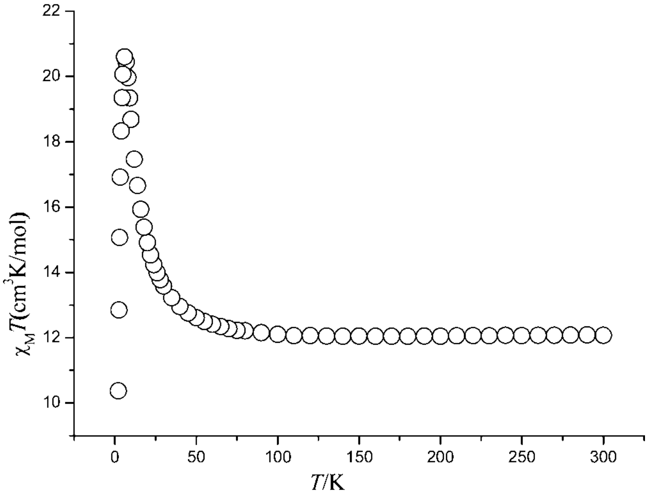

Figure 4. Plots of $\chi_M T$ vs. T for **2**.

To examine the spin dynamics of complexes **1** and **2**, alternating current (ac) measurements were carried out in the 2–15 K range under zero dc field with an ac field of 3 Oe with oscillating frequencies. For **1**, the data obtained show that below 4.0 K both the in-phase (χ') and out-of-phase (χ'') ac susceptibilities are frequency-dependent (Figure 5), which indicates the presence of slow magnetic relaxation at low temperature, indicative of an SMM. However, there are no maxima visible down to 2.0 K, which may be because the tunneling process shortens the magnetic relaxation time at zero dc field. For **2**, the data obtained (Figure 6) reveal that both the in-phase (χ') and out-of-phase (χ'') ac susceptibilities are strongly frequency-dependent below 6.0 K. Complex **2** clearly shows a χ'' signal at higher temperatures than **1** and exhibits maxima values. The shift in the peak temperature (T_p) of the in-phase signal (χ') is determined from $\phi = (\Delta T_p/T_p)/\Delta(\log f) = 0.19$, which excludes the possibility of a spin-glass ($0.01 < \phi < 0.08$).[27] The peak temperatures of χ'' can be fitted by the Arrhenius law, $\tau = \tau_0 \exp(\Delta/k_B T)$, in which T is the temperature of the maximum χ'' at different frequencies and $\tau = 1/2\pi\nu$, which permits estimation of the magnetization relaxation parameters; the pre-exponential factor $\tau_0 = 2 \times 10^{-9}$ s and the energy barrier for the relaxation of the magnetization Δ/k_B = 29.96 K with R = 0.99923 (Figure 7). The observed τ_0 value is perfectly consistent with the super-paramagnetic-like character of the relaxation dynamics.[14b] The Δ value obtained is comparable to those of reported lanthanide–radi-

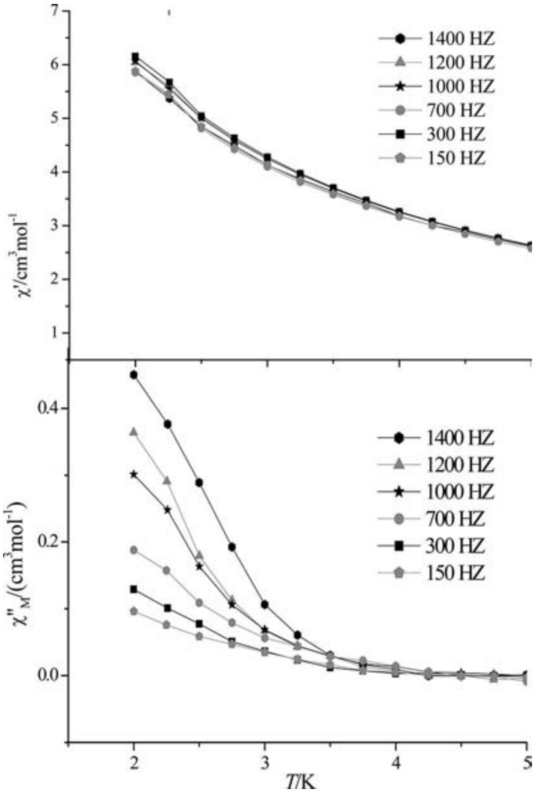

Figure 5. Temperature dependence of the in-phase (top) and out-of-phase (bottom) ac magnetic susceptibilities for complex **1** under zero static field.

cal chains showing SCM behavior.[14] A plot of $\ln(\chi_M T)$ against T^{-1} decreases almost linearly between 35 and 14 K with an energy gap $\Delta\xi/k_B$ of 5.4 K, which confirms the 1D nature of **2** (Figure 8). The low-temperature deviation (below 14 K) from the linear regime is in agreement with the geometrical limitation of the correlation length due to the presence of defects.[28] The dynamic of the magnetization relaxation of **2** suggests classic SCM behavior.

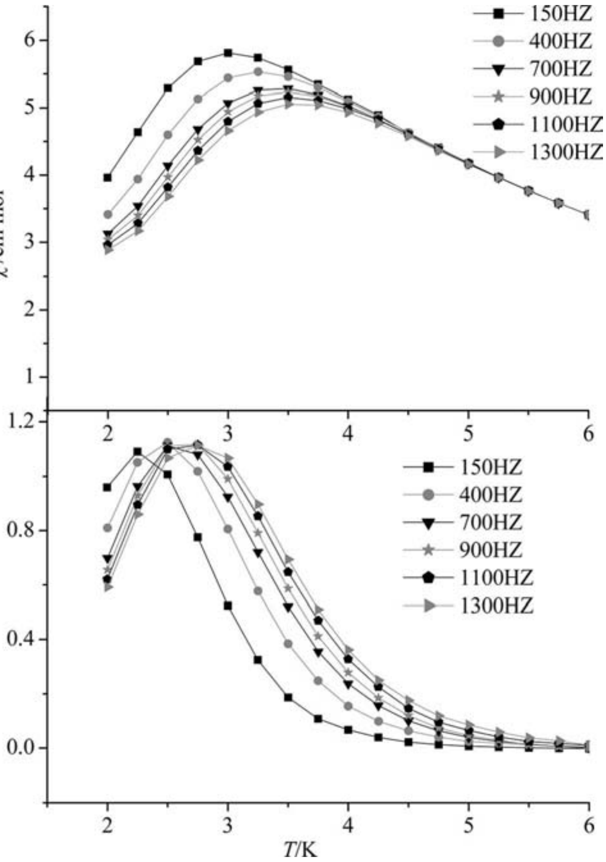

Figure 6. Temperature dependence of the in-phase (top) and out-of-phase (bottom) ac magnetic susceptibilities for complex **2** under zero static field.

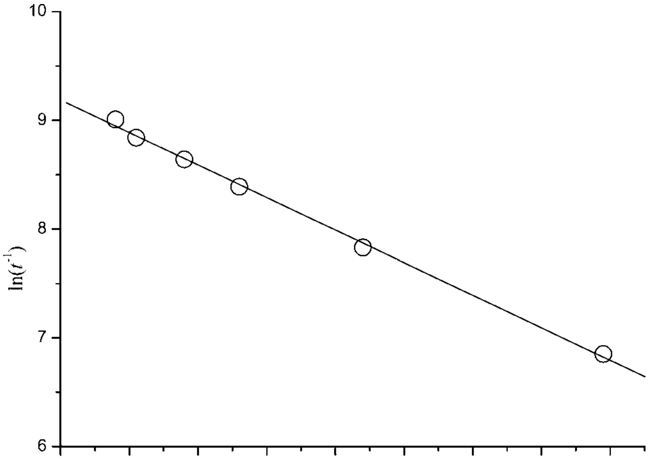

Figure 7. Plot of $\ln(\tau^{-1})$ vs. (T^{-1}) fitting the Arrhenius law for complex **2**.

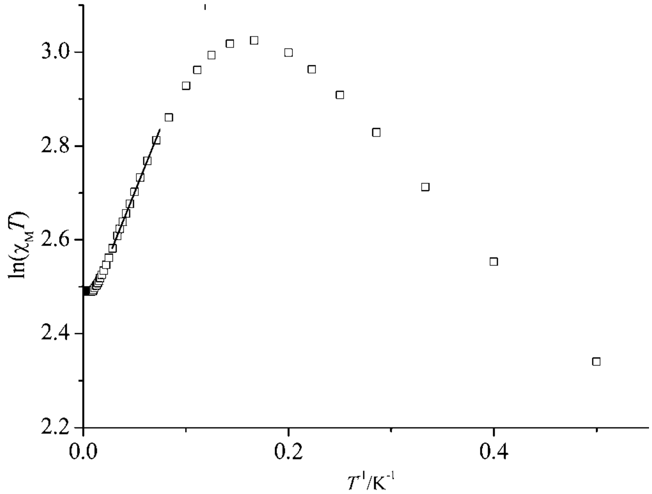

Figure 8. Plot of $\ln(\chi_M T)$ vs. T^{-1} for complex **2**. The solid line represents the fit to the expression $\chi T/C = \exp(\Delta\xi/k_B T)$.

Conclusions

We have prepared a monometallic tri-spin complex and a one-dimensional chain complex based on the same rare-earth ion and nitronyl nitroxide radical ligand. The monometallic tri-spin complex $[Tb(hfac)_3(NITPhSCH_3)_2]$ (**1**) shows SMM-like behavior, which makes it a good building block for 1D assembly. By changing the relative proportions of the reactants, we obtained the one-dimensional chain complex $[Tb(hfac)_3(NITPhSCH_3)]_n$ (**2**), which behaves as an SCM with a higher blocking temperature than that of **1**. It is the first example of the use of radical–metal SMM units in the construction of an SCM system.

Experimental Section

Materials and Physical Measurements: All of the reagents used in the syntheses were of analytical grade. Hexafluoroacetylacetone and 4-(methylthio)benzaldehyde were purchased from Aldrich Chemical Company, and the $NITPhSCH_3$ radical ligand was synthesized according to literature methods.[29] Elemental analyses (C, H, N) were carried out with a Perkin–Elmer 240 elemental analyzer. Infrared spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} with a Bruker Tensor 27 IR spectrometer. Magnetic measurements were performed with an MPMS XL-7 SQUID magnetometer. Diamagnetic corrections were made by using Pascal's constants for all the constituent atoms.

Preparation of $[Tb(hfac)_3(NITPhSCH_3)_2]$ (1): A solution of $[Tb(hfac)_3]\cdot 2H_2O$ (41 mg, 0.05 mmol) in dry *n*-heptane (20 mL) was heated at reflux for 2 h. After that, the solution was cooled to about 60 °C, and a solution of $NITPhSCH_3$ (28 mg, 0.1 mmol) in CH_2Cl_2 (3.0 mL) was added. The resulting mixture was stirred for 10 min and then cooled to room temperature. The filtrate was allowed to stand at room temperature for 1 d to give blue elongated crystals suitable for X-ray analysis. Yield: 65%. $C_{43}H_{41}F_{18}N_4O_{10}S_2Tb$

(1338.84): calcd. C 38.57, H 3.09, N 4.18; found C 38.56, H 3.10, N 4.17. IR (KBr): $\tilde{\nu}$ = 1654 (s), 1509 (m), 1352 (m), 1256 (s), 1201 (s), 1141 (s), 796 (m), 661 (m) cm^{-1}.

Preparation of [Tb(hfac)$_3$(NITPhSCH$_3$)]$_n$ (2): A solution of [Tb(hfac)$_3$]·2H$_2$O (41 mg, 0.05 mmol) in dry *n*-heptane (20 mL) was heated at reflux for 3 h. After that, the solution was cooled to ca. 80 °C, and a solution of NITPhSCH$_3$ (14 mg, 0.05 mmol) in CH$_2$Cl$_2$ (3.0 mL) was added. The resulting mixture was stirred for 30 min and then cooled to room temperature. The filtrate was allowed to stand at room temperature for several days. Green crystals were produced, but these were unsuitable for X-ray analysis. Yield: 60%. $C_{29}H_{22}F_{18}N_2O_8STb$ (1059.45): calcd. C 32.84, H 2.09, N 2.64; found C 32.80, H 2.12, N 2.68. IR (KBr): $\tilde{\nu}$ = 1652 (s), 1530 (m), 1355 (m), 1255 (s), 1203 (s), 1147 (s), 835 (m), 632 (m) cm^{-1}.

X-ray Crystallography: Diffraction-intensity data for complex **1** were collected with a Rigaku Saturn CCD diffractometer at 113 K by employing graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXS-97[30] and SHELXL-97[31] programs, respectively. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined isotropically by using a riding model. Disordered fluorine atoms were observed in the hfac ligands. The crystallographic data for complex **1** are listed in Table 1, and selected bond lengths and angles are listed in Table 2. CCDC-784529 (for **1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data for complex **1**.

Empirical formula	$C_{43}H_{41}F_{18}N_4O_{10}S_2Tb$
Formula mass	1338.84
T [K]	113(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	12.821(3)
b [Å]	16.783(3)
c [Å]	24.736(5)
β [°]	94.58(3)
V [Å^3]	5305.5(18)
Z	4
$D_{\text{calcd.}}$ [g cm^{-3}]	1.676
θ range [°]	1.65–25.02
Reflections collected/unique, R_{int}	35227/9321, 0.0280
GOF on F^2	1.046
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0270, wR_2 = 0.0675
R indices (all data)	R_1 = 0.0303, wR_2 = 0.0697
Largest diff. peak and hole [e Å^{-3}]	1.446 and –0.705

Table 2. Selected bond lengths [Å] and angles [°] for complex **1**.

Tb(1)–O(6)	2.3173(19)	Tb(1)–O(5)	2.3938(19)
Tb(1)–O(3)	2.3245(19)	Tb(1)–O(7)	2.4003(19)
Tb(1)–O(1)	2.3340(18)	O(1)–N(1)	1.303(3)
Tb(1)–O(8)	2.339(2)	O(2)–N(2)	1.280(3)
Tb(1)–O(10)	2.3691(19)	O(3)–N(3)	1.308(3)
Tb(1)–O(9)	2.3727(18)	O(4)–N(4)	1.275(3)
O(6)–Tb(1)–O(3)	91.47(7)	O(1)–Tb(1)–O(9)	76.28(7)
O(6)–Tb(1)–O(1)	99.64(7)	O(8)–Tb(1)–O(9)	75.88(7)
O(3)–Tb(1)–O(1)	137.50(6)	O(10)–Tb(1)–O(9)	73.96(7)
O(6)–Tb(1)–O(8)	136.18(7)	O(6)–Tb(1)–O(5)	73.68(7)
O(3)–Tb(1)–O(8)	104.05(7)	O(3)–Tb(1)–O(5)	148.01(7)
O(1)–Tb(1)–O(8)	95.84(7)	O(1)–Tb(1)–O(5)	73.91(7)
O(6)–Tb(1)–O(10)	74.44(7)	O(8)–Tb(1)–O(5)	71.75(7)
O(3)–Tb(1)–O(10)	72.65(6)	O(10)–Tb(1)–O(5)	127.11(7)
O(1)–Tb(1)–O(10)	71.22(6)	O(9)–Tb(1)–O(5)	132.81(7)
O(8)–Tb(1)–O(10)	149.23(7)	O(6)–Tb(1)–O(7)	72.98(7)
O(6)–Tb(1)–O(9)	147.70(7)	O(3)–Tb(1)–O(7)	73.32(6)
O(3)–Tb(1)–O(9)	72.85(7)	O(1)–Tb(1)–O(7)	149.13(6)
O(9)–Tb(1)–O(7)	125.77(7)	O(8)–Tb(1)–O(7)	72.83(7)
O(5)–Tb(1)–O(7)	75.26(7)	O(10)–Tb(1)–O(7)	131.51(7)

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