Supporting Information for

Ferromagnetic Ordering of –[Sm(III)-Radical]$_n$– Coordination Polymers

Elisabeth M. Fatila,[a] Adam C. Maahs,[a] Michelle B. Mills,[a] Mathieu Rouzières,[b,c] Dmitriy V. Soldatov,[a] Rodolphe Clérac,[b,c] and Kathryn E. Preuss*[a]*

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

[b] CNRS, CRPP, UPR 8641, F-33600 Pessac, France.

[c] Univ. Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France.

Experimental Section

General. Preparation of [Sm(hfac)$_3$(boaDTDA)]$_n$ (**1**; hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato-; boaDTDA = 4-(benzoxazol-2′-yl)-1,2,3,5-dithiadiazolyl) was performed under argon atmosphere using standard Schlenk line and glovebox techniques. Dried and degassed solvents were obtained from an LC solvent purification system using dry packed columns containing 3 Å molecular sieves. All other reagents were purchased from Aldrich, Alfa Aesar, Strem, and Acros Organics, and used as received. IR spectra were collected using a Nicolet 510-FTIR spectrometer at ambient temperature. Elemental analyses were performed by MHW laboratories in Phoenix, AZ, USA. Sublimations were carried out on a multi-stage programmable tube furnace. Starting material Sm(hfac)$_3$(DME) and boaDTDA radical were prepared according to literature procedures[1,2] (DME = 1,2-dimethoxyethane).

[Sm(hfac)$_3$(boaDTDA)]$_n$ (1). Anhydrous dichloromethane (15 mL) was added to a solid mixture of Sm(hfac)$_3$(DME) (0.3029 g, 0.3515 mmol) and boaDTDA (0.0750 g, 0.337 mmol) under argon. The dark brown solution was stirred for 1 hour. The solvent was removed under reduced pressure to afford a dark purple solid. Sublimation of the dark solid at 120 °C at 10^{-2} Torr yielded green needles; yield 0.0753 g (22%). Anal. Calcd. for $SmC_{23}H_7O_7F_{18}N_3S_2$: C, 27.80; H, 0.71; N, 4.23%. Found: C, 28.00; H, 0.92; N, 4.31%. IR (KBr): 1647 (vs), 1612 (w), 1561 (mw), 1535 (m), 1490 (ms,sh), 1449 (m), 1435 (w), 1339 (w), 1321 (w), 1256 (vs), 1231 (ms, sh), 1217 (m, sh), 1207 (s), 1143 (vs), 1096 (m), 998 (vw), 945 (vw), 920 (vw), 887 (vw), 847 (w), 804 (m), 784 (w), 762 (mw), 752 (mw), 741 (w), 660 (m), 617 (vw), 587 (m), 546 (vw), 529 (vw), 499 (vw), 468 (vw), 436 (vw) cm^{-1}.

Magnetic Measurements. Magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL, which works between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. For alternating-current (ac) susceptibility measurements, an oscillating ac field of 3 Oe with a frequency between 1 and 1500 Hz was employed. Measurements were performed on 18.3 mg of a polycrystalline sample of **1** sealed in a polypropylene bag (3 × 0.5 × 0.02 cm; 22.4 mg) under argon atmosphere. Prior to the experiments, the field-dependent magnetization was measured at 100 K in order to detect the presence of any bulk ferromagnetic impurities. The sample appeared to be free of any significant ferromagnetic impurities. The magnetic data were corrected for the sample holder and the diamagnetic contribution.

Crystallographic Measurements. Two crystals of $[Sm(hfac)_3(boaDTDA)]_n$ (**1**) were studied. The green prisms of the complex grown by sublimation in vacuum were mounted on MiTeGen cryoloops, protected with type NVH immersion oil and studied in the flow of nitrogen of required temperature generated by Cryojet XL device (Oxford Instruments). The first crystal with dimensions 0.25 × 0.10 × 0.08 mm was studied at 150 K. The data were collected to the maximum resolution of 0.58 Å (average redundancy > 8). The second crystal, studied subsequently, was 0.70 × 0.20 × 0.20 mm in size. This crystal was selected after screening several samples and no attempt was made to reduce its size in order to avoid cracking. For this second crystal, the data were collected at 100, 200, 250 and 300 K to the maximal resolution of 0.60, 0.64, 0.66 and 0.74 Å, respectively, and average redundancy of 13 or higher.

All measurements were conducted on a SuperNova Agilent single-crystal diffractometer equipped with a microfocus MoK_α (λ = 0.71073 Å) radiation source and Atlas CCD detector. Diffraction intensity data were collected using ω-scan. The unit cell parameters were refined using the entire data sets. The data were processed using CrysAlisPro software.[3] Absorption corrections were applied using the multiscan method. The structure was solved (direct methods) and refined (full-matrix least-squares on F^2) using SHELXS and SHELXL-97.[4] Geometric calculations were carried out using the WinGX[5] and Olex[6] software packages.

Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were introduced at calculated positions as riding on their corresponding carbon atoms and refined isotropically. Many CF_3 groups of the hfac ligands were disordered suggesting partially restricted rotation. The disorder was modeled by two complementary orientations with mild restraints on the C-F distances and stricter restraints on the F thermal ellipsoids. Most residual peaks are located near Sm as a result of inadequate absorption correction of a large crystal. A strong residual peak at 100 K as listed under "Alert level A" of the CheckCIF report is at 2.3 Å from the Sm site.

The CIF files along with structure factor tables have been deposited with the Cambridge Crystallographic Data Centre (the deposition numbers are listed in Table S1) and a copy of these data are 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.

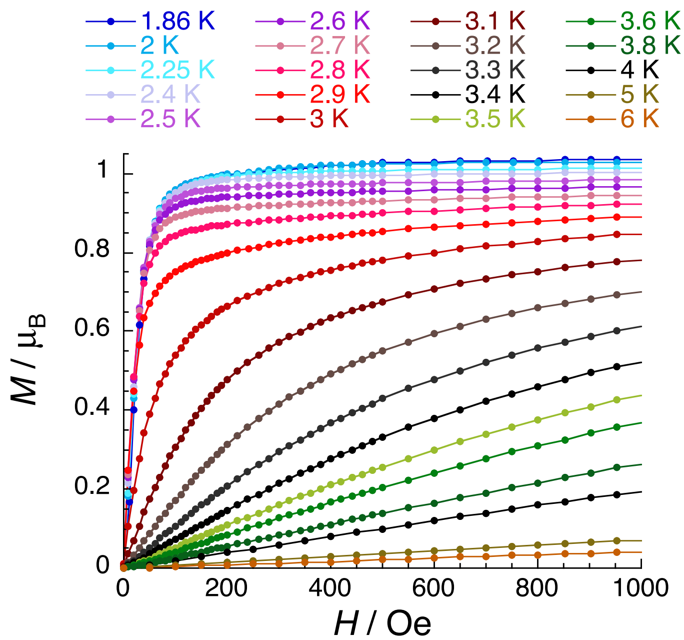

Figure S1. Low field (< 1000 Oe) *M* vs. *H* data for **1** after cooling the sample in zero-dc field from 10 K to the indicated temperature with field scanning rates between 20 and 100 Oe min^{-1}.

Table S1. Crystallographic Details for $[Ln(hfac)_3(boaDTDA)]_n$ (Ln = Sm & La).

Complex		**1**					**2**[7]
Formula		$SmC_{23}H_7F_{18}N_3O_7S_2$					$LaC_{23}H_7F_{18}N_3O_7S_2$
Formula weight		993.79					982.35
Wavelength (Å)		0.71073					0.71073
Crystal System		orthorhombic					orthorhombic
Space Group		*Pbca*					*Pbca*
T (K)		100(2)	150(2)	200(2)	250(2)	300(2)	150(2)
Unit cell dimensions (Å)	*a*	19.8011(2)	19.85308(16)	19.9769(2)	20.0503(2)	20.1162(2)	20.0045(2)
	b	14.62079(12)	14.68673(10)	14.81100(16)	14.9396(2)	15.14532(19)	14.6473(2)
	c	21.27781(15)	21.32145(13)	21.41308(19)	21.4630(2)	21.5437(2)	21.3848(3)
Volume (Å^3)		6160.09(9)	6216.84(8)	6335.66(11)	6429.10(12)	6563.64(12)	6266.03(13)
Z		8	8	8	8	8	8
Density calc. (g/cm^3)		2.143	2.124	2.084	2.053	2.011	2.083
Absorption coefficient (mm^{-1})		2.201	2.181	2.140	2.109	2.065	1.653
F(000)		3824	3824	3824	3824	3824	3784
θ range for data collection (°)		2.58 to 36.32	1.97 to 37.78	2.64 to 33.73	2.62 to 32.58	2.61 to 28.70	3.34 to 30.51
Index ranges		$-32 \leq h \leq 33$ $-24 \leq k \leq 24$ $-35 \leq l \leq 35$	$-34 \leq h \leq 34$ $-25 \leq k \leq 24$ $-36 \leq l \leq 36$	$-31 \leq h \leq 31$ $-23 \leq k \leq 23$ $-33 \leq l \leq 33$	$-30 \leq h \leq 30$ $-22 \leq k \leq 22$ $-32 \leq l \leq 32$	$-27 \leq h \leq 27$ $-20 \leq k \leq 20$ $-29 \leq l \leq 29$	$-28 \leq h \leq 28$ $-20 \leq k \leq 20$ $-30 \leq l \leq 30$
Refl. coll.		200643	145067	175977	172554	135461	145052
Ind. refl.		14915 [*R*(int) = 0.0621]	16678 [*R*(int) = 0.0405]	12652 [*R*(int) = 0.0713]	11709 [*R*(int) = 0.0627]	8465 [*R*(int) = 0.0603]	9558 [*R*(int) = 0.0307]
Completeness to θ max (%)		100	100	99.9	99.9	99.9	99.9
Absorption correction		Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission		0.667 and 0.308	0.670 and 0.311	0.674 and 0.316	0.678 and 0.320	0.683 and 0.326	0.790 and 0.595
Refinement method		Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters		14915 / 69 / 516	16678 / 87 / 543	12652 / 87 / 543	11709 / 87 / 543	8465 / 87 / 543	9558 / 234 / 514
Goof on F^2		1.179	1.088	1.108	1.100	1.092	1.043
Final *R* indices [$I > 2\sigma(I)$]		$R1 = 0.0426$ $wR2 = 0.0873$	$R1 = 0.0268$ $wR2 = 0.0556$	$R1 = 0.0369$ $wR2 = 0.0973$	$R1 = 0.0412$ $wR2 = 0.0993$	$R1 = 0.0417$ $wR2 = 0.1061$	$R1 = 0.0205$ $wR2 = 0.0510$
R indices (all data)		$R1 = 0.0722$ $wR2 = 0.1025$	$R1 = 0.0471$ $wR2 = 0.0625$	$R1 = 0.0596$ $wR2 = 0.1106$	$R1 = 0.0739$ $wR2 = 0.1173$	$R1 = 0.0697$ $wR2 = 0.1240$	$R1 = 0.0241$ $wR2 = 0.0536$
Largest diff. peak & hole (e.Å^3)		5.4 & -1.9	2.3 & -1.0	2.5 & -1.4	3.0 & -1.0	1.6 & -0.8	0.7 & -0.5
CCDC deposition number		#1413999	#1414003	#1414000	#1414001	#1414002	#936895

Table S2. Selected Contacts in the Structures for $[Ln(hfac)_3(boaDTDA)]_n$ (Ln = Sm & La).

Complex	1					2[7]
Formula	$[Sm(hfac)_3(boaDTDA)]_n$					$[La(hfac)_3(boaDTDA)]_n$
T (K)	100	150	200	250	300	150
Bond distances (Å)[a]						
Ln – N1	2.742	2.744	2.748	2.739	2.730	2.831
Ln – N4	2.961	3.006	3.071	3.176	3.335	2.935
Ln – N14	2.630	2.629	2.632	2.621	2.612	2.749
Ln – O7	3.371	3.395	3.438	3.496	3.583	3.207
Nearest neighbor intermolecular contact distances (Å)[b]						
S2...C10[c]	3.747	3.752	3.782	3.822	3.889	3.804
S2…C11	3.649	3.669	3.699	3.723	3.759	3.719
F21…C10	3.558	3.571	3.594	3.600	3.599	3.689
F21…C11	3.327	3.351	3.386	3.419	3.462	3.356
F21…C12	3.633	3.691	3.767	3.824	3.897	3.638
Angle between DTDA least-squares planes of nearest ligands in the chain (°)[d]						
	32.08	31.80	31.48	31.39	31.40	32.07

[a] Standard deviations within 0.001 – 0.004 Å.
[b] Standard deviations within 0.001 – 0.008 Å.
[c] In the free ligand, the calculated beta spin density at the C10 atom is significant. There is large alpha spin density at S2, thus short S2…C10 contacts may indicate an efficient McConnell I mechanism for FM coupling between chains.
[d] Standard deviations within 0.02 – 0.07 Å.

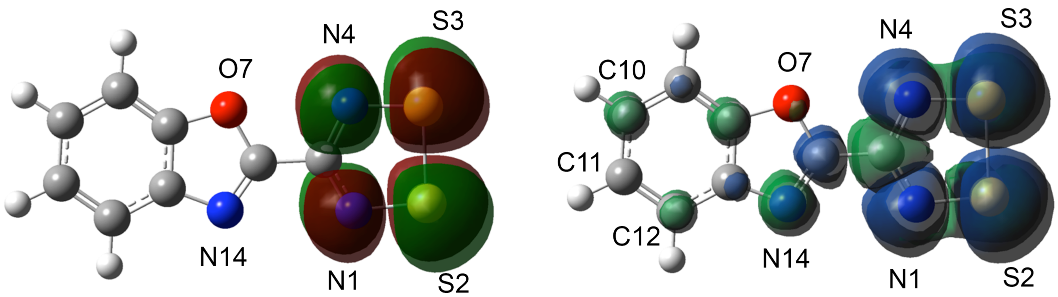

Figure S2. (a) Singly occupied molecular orbital (SOMO) of the boaDTDA ligand and (b) spin density distribution of the boaDTDA ligand (blue = alpha; green = beta) using uB3LYP/6-31G(d,p).[8]

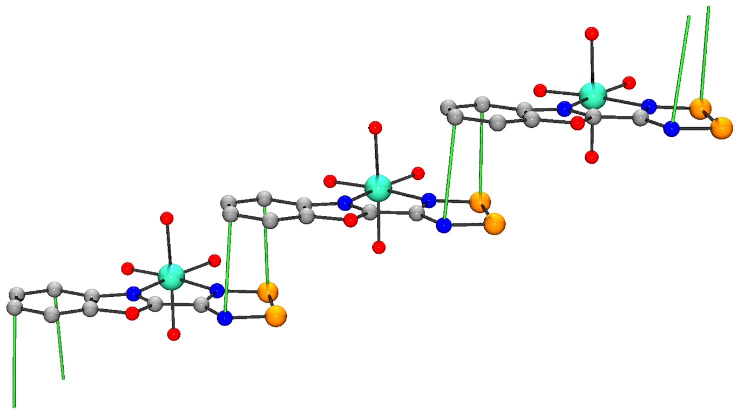

Figure S3. Excerpt from the crystal structure of the related Ni(hfac)$_2$(boaDTDA) complex[9] illustrating intermolecular contacts responsible for McConnell I ferromagnetic interactions.

Beyond the sulphur-carbon contacts described in the manuscript, contacts between chains in **1** involving the F atoms of hfac ligands and atoms of neighbouring boaDTDA ligands are also present. Sm(III) is weakly paramagnetic (0.09 cm^3 K mol^{-1}), thus the spin density is extremely small at the metal ion, and should be even smaller at the F atoms. Although unlikely to contribute significantly to the magnetic properties of **1**, the short contacts involving F atoms are also documented in Table S2 and shown in Figure S4.

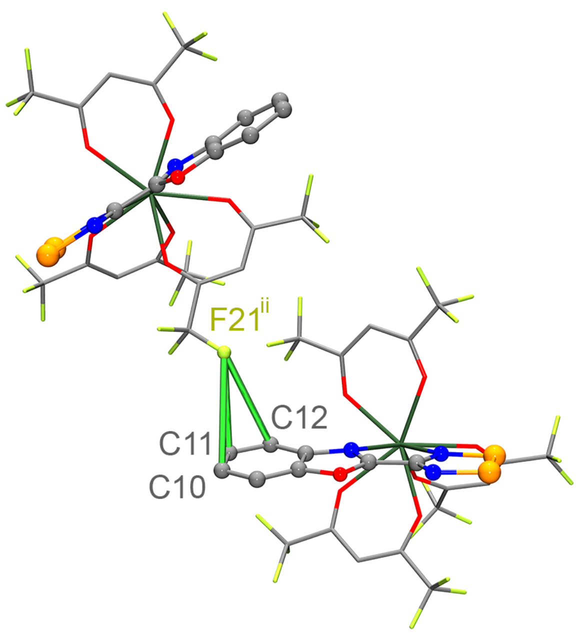

Figure S4. Excerpt from the crystal structure of **1** viewed down [010] illustrating an example of the close contacts between F atoms and boaDTDA C atoms of neighbouring chains; symmetry codes: (ii) $x - 1/2$, y, $3/2 - z$.

References for the Supporting Information

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