Ferromagnetic Superexchange in a 1D –[La^{III}-Radical]– Coordination Polymer

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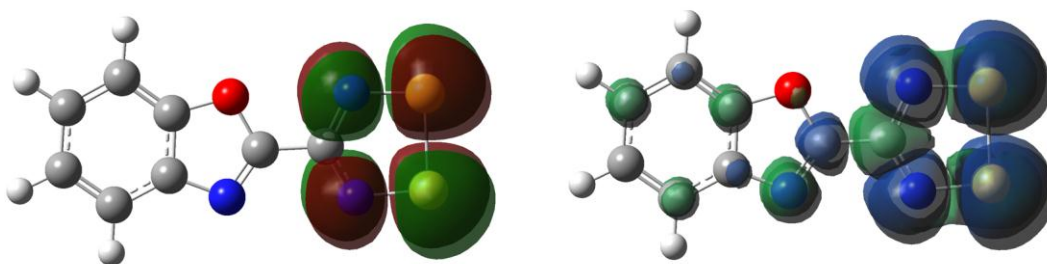[d] FreeLance Crystallography, 185 Chelsea Avenue, London, ON, N6J 3J5, Canada.

Fig. S1 (a) Singly occupied molecular orbital (SOMO) of the boaDTDA ligand and (b) spin density distribution of the boaDTDA ligand as calculated using uB3LYP/6-31G(d,p).[1]
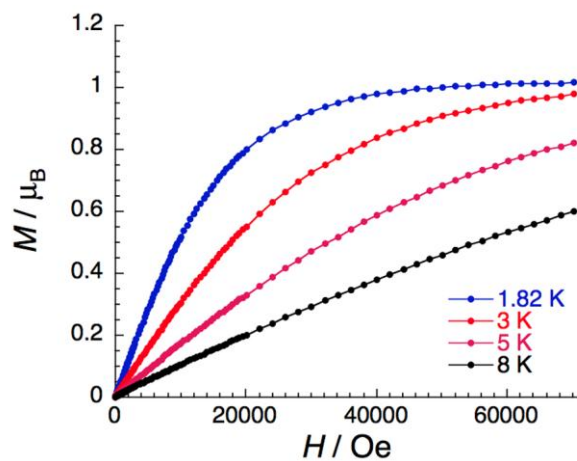

Fig. S2 *M vs. H* plot of **1** below 8 K.

Experimental Section

General Considerations

Preparation of all metal complexes was 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 Aldrich, Alfa Aesar, Acros Organics and MP Biomedicals and used as received. IR spectra were collected using a Nicolet 510-FTIR spectrometer at ambient temperature. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ, USA. Sublimations were carried out on a multi-stage programmable temperature tube furnace. La(hfac)$_3$(DME) was prepared according to literature procedure (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato-; DME = 1,2-dimethoxyethane).[2]

La(hfac)$_3$(boaDTDA)

Anhydrous CH$_2$Cl$_2$ (20 mL) was added to a solid mixture of La(hfac)$_3$(DME) (0.2300 g, 0.2705 mmol) and boaDTDA (0.0591g, 0.266 mmol) under argon. The green solution was stirred for 40 min. The solvent was removed under reduced pressure to afford a dark red-purple solid. Sublimation of the dark solid at 120 °C at 10^{-2} Torr yielded green needles; yield 0.0550 g (21%). IR (KBr): 3130(vw), 1648(vs), 1608(w), 1556(mw), 1530(m), 1492(ms,sh), 1450(m), 1422(w), 1341(w), 1320(w), 1255(vs), 1206(s), 1145(vs), 1095(m), 1008(vw), 993(vw), 946(vw), 886(vw), 840(mw), 800(m), 783(w), 762(mw), 751(mw), 742(mw), 660(m), 613(vw), 584(m), 542(vw), 527(vw), 498(vw), 460(vw), 433(vw) cm^{-1}. Anal. Calcd. for LaC$_{23}$H$_7$O$_7$F$_{18}$N$_3$S$_2$: C, 28.12; H, 0.72; N, 4.28%. Found: C, 27.96; H, 0.89; N, 4.21%.

Magnetic Measurements

The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL functioning between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. Measurements were performed on a polycrystalline sample of 12.2 mg introduced in a sealed polyethylene bag (3 × 0.5 × 0.02 cm) under the argon atmosphere of a dry box. The magnetic data were corrected for the sample holder, a small ferromagnetic impurity and diamagnetic contributions.

Crystallographic Measurements

A single green prism of **1**, (LaC$_{23}$H$_7$O$_7$F$_{18}$N$_3$S$_2$) was mounted on a glass fiber. Data were collected at low temperature (150 K) on a SuperNova Agilent diffractometer equipped with a microfocus

Mo Kα radiation (λ = 0.71073 Å) source and Atlas CCD detector. Diffraction intensity data were collected using ω-scan to the resolution of 0.7 Å. The unit cell parameters were calculated and refined from the full data set. The unit cell refinement and data reduction were carried out using CrysAlisPro software.[3] The absorption correction was applied using the multiscan method.[4] The crystal data and refinement parameters for $LaC_{23}H_7O_7F_{18}N_3S_2$ are listed in Table S1. The reflection data and systematic absences were consistent with an orthorhombic space group: *Pbca*.

The SHELXTL/PC V6.14 for Windows NT[5] suite of programs was used to solve the structure by direct methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located. The complex consisted of $La(hfac)_3$ moieties linked together into linear chains by the boaDTDA ligand. The $La(hfac)_3(boaDTDA)$ complex was well ordered except for one $-CF_3$ moiety. This $-CF_3$ was modeled anisotropically in a 0.65/0.35 ratio; the C-F bond lengths were allowed to refine but restrained to be identical. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms.

The largest residue electron density peak (0.65 e/Å^3) was associated with one of the hfac rings. Full-matrix least squares refinement on F^2 gave R_1 = 2.05% for 2σ data and wR_2 = 5.36% for all data (GOOF = 1.043). The crystallographic data has been submitted to the Cambridge Structural Database (http://www.ccdc.cam.ac.uk), and the accession number is 936895.

Submission to the IUCr checkCIF program resulted in one A-Alert and three B-Alerts associated with the disordered -CF$_3$. These alerts are due to the intention to maintain an anisotropic model resulting in some prolate shaped ellipsoids.

Table S1. Crystal data and structure refinement for 1.

Empirical formula	La C23 H7 O7 F18 N3 S2
Formula weight	982.35
Temperature	150(1) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P b c a
Unit cell dimensions	a = 20.0045(2) Å
	b = 14.6473(2) Å
	c = 21.3848(3) Å
Volume	6266.03(13) Å^3
Z	8
Density (calculated)	2.083 Mg/m^3
Absorption coefficient	1.653 mm^{-1}
F(000)	3784
Crystal size	0.35 × 0.25 × 0.15 mm^3
Theta range for data collection	3.34 to 30.51°.
Index ranges	-28 ≤ h ≤ 28, -20 ≤ k ≤ 20, -30 ≤ l ≤ 30
Reflections collected	145052
Independent reflections	9558 [R(int) = 0.0307]
Completeness to theta = 30.51°	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7896 and 0.5954
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9558 /234 /514
Goodness-of-fit on F^2	1.043
Final R indices [$I > 2\ \sigma(I)$]	R1 = 0.0205, wR2 = 0.0510
R indices (all data)	R1 = 0.0241, wR2 = 0.0536
Largest diff. peak and hole	0.654 and -0.511 e.Å^{-3}

References for the Supporting Information

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