McConnell I mechanism promotes ferromagnetic interactions between π-stacked Ni(II)-thiazyl complexes

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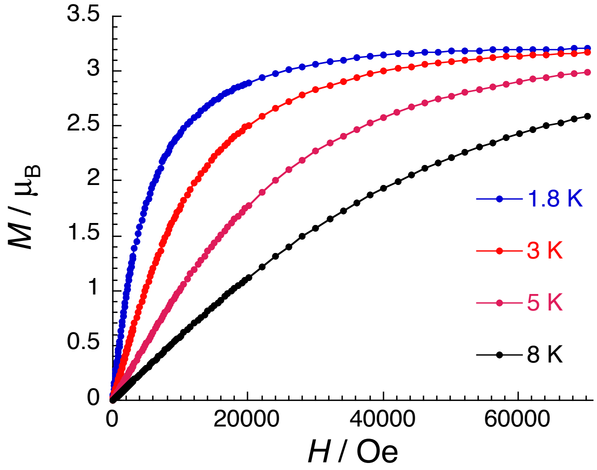

Fig. S1 *M vs. H* plot of **1** below 8 K.

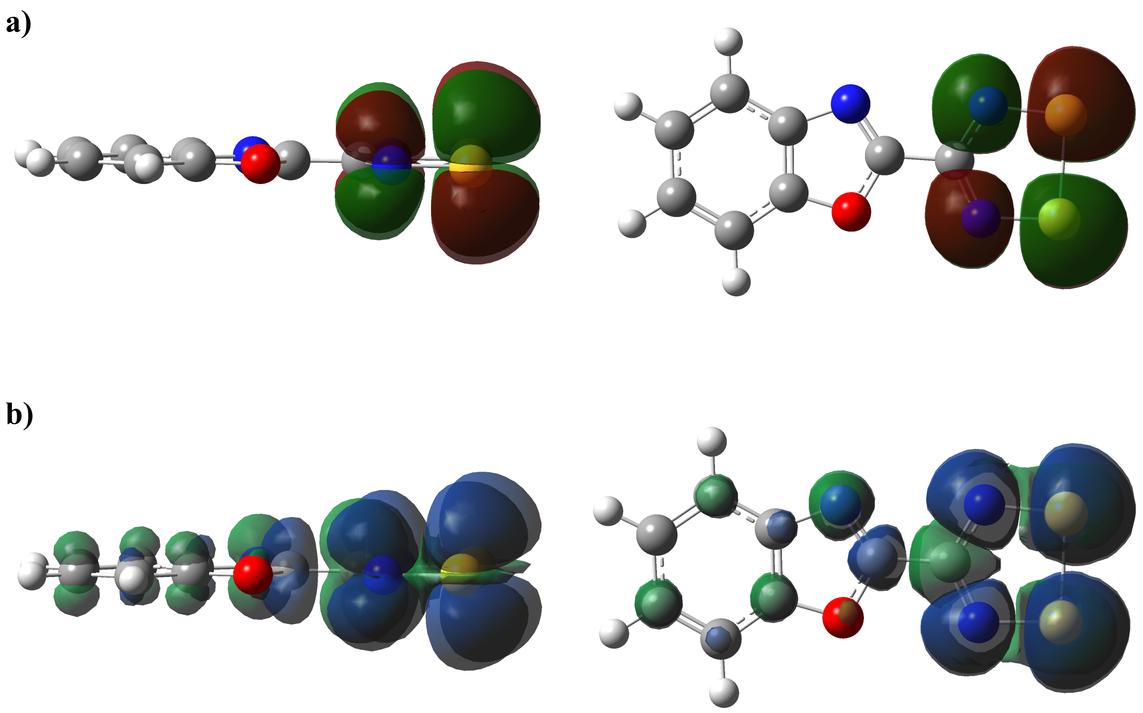

Fig. S2 (a) Two perspectives of the singly occupied molecular orbital (SOMO) of the boaDTDA ligand and (b) two perspectives of the spin density distribution of the boaDTDA ligand as calculated using uB3LYP/6-31G(d,p).[1]

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 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, Phoenix, AZ, USA. Sublimations were carried out on a multi-stage programmable temperature tube furnace. Starting material Ni(hfac)$_2$(THF)$_2$ was prepared from Ni(hfac)$_2$(H$_2$O)$_2$ according to a published procedure[2] (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato). In order to ensure the complete absence of H$_2$O, the disappearance of an OH stretch at ~3410 cm^{-1} in the IR spectrum (KBr) was confirmed. The boaDTDA radical was also prepared according to literature procedure.[3]

Ni(hfac)$_2$(boaDTDA)

Anhydrous CH_2Cl_2 (40 mL) was added to a solid mixture of Ni(hfac)$_2$(THF)$_2$ (0.2514 g, 0.4074 mmol) and boaDTDA (0.0810 g, 0.3606 mmol) under argon. The dark green solution was stirred for 1.5 hr. The solvent was removed under reduced pressure to afford a light purple brown solid. Sublimation of the dark solid at 120 °C at 10^{-2} Torr yielded black-green needles suitable for X-ray crystallography; yield (0.1735 g, 69%). IR (KBr): 3289(vw), 3144(vw), 3092(vw), 1655(ms), 1644(s), 1606(mw), 1594(mw), 1556(m), 1528(m), 1488(ms, br), 1443(m), 1352(m), 1320(w), 1257(s), 1219(s), 1181(s), 1148(s), 1108(m), 1097(m), 1015(w), 996(w), 949(w), 927(w), 882(mw), 862(mw), 812(m), 796(ms), 781(mw), 762(m), 752(m), 732(mw), 674(s), 630(w), 613(mw), 587(m), 549(mw), 529(mw), 503(w), 431(w) cm^{-1}. Anal. Calcd. for $NiC_{18}H_6N_3O_5S_2F_{12}$: C, 31.10; H, 0.87; N, 6.05%. Found: C, 31.19; H, 0.88; N, 5.82%.

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 14.6 mg introduced in a sealed polyethylene bag (3 × 0.5 × 0.02 cm) under the argon atmosphere. The magnetic data were corrected for the sample holder, and diamagnetic contributions.

Crystallographic Measurements

A single green needle of **1**, ($NiC_{18}H_6O_5F_{12}N_3S_2$) was mounted on a glass fiber. Data were collected at low temperature (150 K) on a Bruker APEX2 area detector diffractometer using an APEX II CCD detector, with a Mo Kα radiation ($\lambda = 0.71073$ Å) source. The unit cell parameters were calculated and refined from the full data set. The unit cell refinement and data reduction were carried out using SAINT.[4] The absorption correction was applied using SADABS.[5] The crystal data and refinement parameters for $NiC_{18}H_6O_5F_{12}N_3S_2$ are listed in Table S1. The reflection data and systematic absences were consistent with an orthorhombic space group: *Fdd2*.

The SHELX-TL V6.1[6] program package was used to solve (using Direct Methods) and refine the structure using successive difference Fouriers. 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 (0.475 e/Å^3) was associated with one of the fluorine atoms. Full-matrix least squares refinement on F^2 gave $R_1 = 4.50\%$ for 2σ data and $wR_2 = 8.66\%$

for all data (*GOOF* = 1.032). The crystallographic data has been submitted to the Cambridge Structural Database (http://www.ccdc.cam.ac.uk), and the accession number is 949614. Submission to the IUCr checkCIF program resulted in no A-Alert or B-Alerts.

Table S1. Crystal data and structure refinement for 1.

Empirical formula	C18 H6 F12 N3 Ni O5 S2	
Formula weight	695.09	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*F d d* 2	
Unit cell dimensions	$a = 33.536(7)$ Å	$\alpha = 90°$
	$b = 37.345(8)$ Å	$\beta = 90°$
	$c = 7.4812(16)$ Å	$\gamma = 90°$
Volume	9369(3) $Å^3$	
Z	16	
Density (calculated)	1.971 Mg/m^3	
Absorption coefficient	1.141 mm^{-1}	
F(000)	5488	
Crystal size	0.38 x 0.08 x 0.07 mm^3	
Theta range for data collection	2.66 to 25.03°	
Index ranges	$-28 \le h \le 39$, $-43 \le k \le 44$, $-8 \le l \le 8$	
Reflections collected	23937	
Independent reflections	4001 [*R*(int) = 0.0978]	
Completeness to theta = 25.03°	99.8%	
Absorption correction	Analytical	
Max. and min. transmission	0.9295 and 0.6690	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4001 / 1 / 371	
Goodness-of-fit on F^2	1.032	
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0450$, $wR_2 = 0.0788$	
R indices (all data)	$R_1 = 0.0620$, $wR_2 = 0.0866$	
Absolute structure parameter	0.034(19)	
Largest diff. peak and hole	0.475 and -0.352 e.$Å^{-3}$	

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