Supplementary Data

Synthesis and Magnetic Properties of a 4-(2'-Pyrimidyl)-1,2,3,5-Dithiadiazolyl

Dimanganese Complex

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General. All reactions were performed under argon atmosphere with strict exclusion of air and water, using standard Schlenk line and glove box techniques. Solvents were rigorously dried and distilled under argon prior to use; toluene was dried over sodium metal, THF over sodium and benzophenol, and acetonitrile over P_2O_5. All reagents were purchased from Aldrich and used as received unless otherwise stated. Modified procedures were employed to synthesize 2-cyanopyrimidine based on the literature[1]. The diethyl ether adduct of lithium bis(trimethylsilyl)amide (LiN(TMS)$_2$·Et$_2$O) was prepared following literature procedure[2]. Manganese bis(hexafluoroacetylacetonate) dihydrate (Mn(hfac)$_2$·2H$_2$O) was prepared following literature procedure[3] and prior to use was dehydrated by re-crystallization in warm THF to yield Mn(hfac)$_2$·2THF; absence of hydrate peak at 3413 cm^{-1} in IR (KBr)[4]. NMR spectra were recorded on a Brüker Avance-400 spectrometer at 293 K. IR spectra were collected using a Nicolet 510-FTIR spectrometer at ambient temperature. EPR spectra were obtained using a Brüker EMX X-band EPR spectrometer. Mass spectra were obtained with a Varian CP3800

spectrometer and determined at an ionized voltage of 70 eV. Cyclic voltammetric measurements were performed using a three-electrode glass cell, thermostated at 25 ºC, and sealed under dry argon atmosphere. Platinum working, reference, and counter electrodes were employed. All electrodes were carefully cleaned with toluene and ethanol, and then dried prior to use. All electrochemical measurements were referenced *in situ* against the ferrocene/ferrocenium couple, as recommended by the IUPAC, and [n-Bu$_4$][NPF$_6$] was used as supporting electrolyte. The electrochemical instrument used was an Autolab PGSTAT30.

Synthetic Procedures

Preparation of 2-cyanopyrimidine : A mixture of 2-chloropyrimidine (5.75 g, 50.2 mmol), KCN (3.58 g, 55.0 mmol) and 1,4-diazabicyclo[2,2,2] octane (DABCO, 1.07 g, 9.54 mmol) was ground to a fine powder and placed in a 100 mL 3-neck RBF. A solution containing 5 mL of DMSO and 10 drops of H$_2$O was added dropwise to the prepared mixture at 1 drop per minute with a addition funnel and the resulting slurry was stirred for 48 h at room temperature under argon. This was then extracted with 90% diethyl ether and 10% hexane (5 × 50 mL), washed with 100 mL water and dried over MgSO$_4$. The solvent was removed *in vacuo* and the crude product was purified by sublimation with a cold finger (10^{-2} Torr, Variac at 40%) to give white crystalline 2-cyanopyrimidine (4.22 g, 80%), mp 42 $^{\circ}$C. ν_{max}(KBr)/cm^{-1}: 1993(w), 1633(w), 1565(s), 1399(s), 1269(m), 1182(w), 1088(s), 1071(w), 991(s), 819(s), 789(s), 642(m), 558(s), 549(s). δ_H (CDCl$_3$, 400 MHz), ppm: 8.84 (d, 2H, J$_{HH}$ = 5.2 Hz), 7.55 (t, 1H, J$_{HH}$ = 4.8 Hz). δ_C (CDCl$_3$, 100.6 MHz) ppm: 158.02(s), 145.09(s), 123.64(s), 115.52(s).

Preparation of 2-(2'-pyrimidyl)-*N*,*N*,*N*′-tris(trimethylsilyl)amidine : A solution of 2-cyanopyrimidine (1.79 g, 18.0 mmol) in 10 mL toluene was slowly added to a cold (0 ºC) solution of LiN(TMS)$_2$·Et$_2$O (4.24 g, 18.0 mmol) in 30 mL of toluene while stirring. The mixture was stirred for 5 h at 0 ºC. Chlorotrimethylsilane (Me$_3$SiCl, 2.22 mL, 18.0 mmol) was added dropwise. The reaction mixture was refluxed overnight then cooled to RT and filtered to afford a greenish yellow solution and pale yellow solid at the frit. The toluene was removed *in vacuo* from the filtrate and the oily crude product was obtained. This was distilled (75 ºC, 10^{-2} Torr) yielding pure N,N,N'-tris(trimethysiyl)pyrimidin-2-carboxamidine as a greenish yellow oil (3.29 g, 57%). ν_{max}(KBr)/cm^{-1}: 3395(s), 3145(s), 3045(s), 2803(s), 1999(w), 1749(w), 1707(s), 1633(w), 1568(s), 1573(w), 1403(s), 1260(w), 1083(m), 841(w), 814(s), 668(w), 637(m), 476(w). δ_H (CDCl$_3$, 400 MHz), ppm: 8.89 (d, 2H, J_{HH} = 4.8 Hz), 7.47 (t, 1H, J_{HH} = 4.8 Hz), 0.15 (m, 27H).

Preparation of [4-(2'-pyrimidyl)-1,2,3,5-DTDA] chloride: A solution of sulfur monochloride (5.0 mL, 62 mmol) in 50 mL acetonitrile was added dropwise to a solution of N,N,N'-tris(trimethylsilyl) pyrimidine-2-carboxamidine (3.38 g, 10.0 mmol) in 50 mL acetonitrile. The reaction mixture was refluxed overnight and hot filtered to recover the crude product as a yellow powder which was then washed with hot acetonitrile (3 × 30 mL). Yield: 2.08 g, 85%. mp 180 ºC (decomp). ν_{max}(KBr)/cm^{-1}: 3049(w), 1699(w), 1614(w), 1564(s), 1441(m), 1380(s), 1295(w), 1206(m), 1101(m), 995(m), 946(w), 891(s), 841(s), 714(w), 695(s), 630(s), 549(m). δ_H (DMSO-d6, 400 MHz), ppm: 9.02 (d, 2H, J_{HH} = 4.8

Hz), 7.72 (d, 1H, J_{HH} = 4.6 Hz).

Preparation of 4-(2'-pyrimidyl)-1,2,3,5-dithiadiazolyl (1): A slurry of 4-(2'-pyrimidyl)-1,2,3,5-dithiadiazolium chloride (1.00 g, 4.60 mmol) in 15 mL cold dry acetonitrile was degassed with argon for 10 min. Triphenylantimony (0.81g, 2.30 mmol) was added generating a dark purple solution. The solution was stirred for 30 min, then cooled in the fridge for 2 h. The crude solid product was recovered by cold filtration, washed with cold acetonitrile, dried *in vacuo* and purified by sublimation at 90 ^{o}C (10^{-2} Torr) using a gradient-temperature tube furnace, to give dark purple crystals (0.73 g, 73%). Crystals suitable for X- ray crystallography were grown by re-sublimation at 100 ºC under static vacuum (10^{-3} Torr), mp 110 ºC (decomp). ν_{max}(KBr)/cm^{-1}: 3124(w), 3068(w), 3021(w), 2972(w), 1702(w), 1561(s), 1437(s), 1371(s), 1296(w), 1256(m), 1200(m), 1189(m), 1104(w), 993(m), 922(s), 836(m), 817(s), 803(s), 775(s), 729(w), 707(s), 683(w), 646(s), 632(s), 508(s), 460(w), 417(w). *m/z* (EI, 70eV) 183 (M^{+}, 99%), 105 (M^{+}–C$_5$H$_4$N, 25%), 78 (C$_4$N$_2$H$_2^{+}$,60%), 64 (S$_2^{+}$, 23%), 46 (SN^{+}, 24%). Anal. Calc. for C$_5$H$_3$N$_4$S$_2$: C, 32.79; H, 1.65; N, 30.61. Found: C, 32.87; H, 1.47; N, 30.89%.

Preparation of [4-(2'-pyrimidyl)-1,2,3,5-DTDA]Mn$_2$(hfac)$_4$ (2): A mixture of Mn(hfac)$_2$·2THF (1.76 g, 2.84 mmol) and 4-(2'-pyrimidyl)-1,2,3,5-dithiadiazolyl radical **1** (0.261 g, 1.42 mmol) were dissolved in 10 mL of dry THF. The solution was stirred for 1 h at RT under Ar. The solvent was removed *in vacuo* to afford complex **2** as a dark purple powder (1.68 g, 53%). The crude product was purified by dynamic vacuum sublimation in a gradient temperature furnace at 120 ^{o}C (10^{-2} Torr) yielding dark green crystals. The

single crystal suitable for X-ray crystallography was grown by static vacuum sublimation at 120 $^{\circ}$C (10^{-2} Torr). ν_{max}(KBr)/cm^{-1}: 1640(s), 1585(w), 1563(m), 1529(m), 1487(m), 1390(s), 1259(s), 1207(s), 1148(s), 1098(w), 855(w), 819(m), 796(s), 743(m), 669(s), 648(m), 586(s), 528(m). Anal. Calc. for $C_{25}H_7F_{24}Mn_2N_4O_8S_2$: C, 26.78; H, 0.63; N, 5.00. Found : C, 26.62; H, 0.50; N, 5.24%.

Crystallography

Ligand 1: Crystals of $[C_5N_4S_2H_3]$ arrived from the University of Guelph pre-mounted and coated with epoxy. The large, dark red, block was mounted on a goniometer head. Data were collected at low temperature (-173 °C) on a Nonius Kappa-CCD area detector diffractometer with COLLECT (Nonius B.V., 1997-2002). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN (Otwinowski & Minor, 1997). The absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK). The reflection data and systematic absences were consistent with a monoclinic space group: P2(1)/c.

The SHELXTL/PC V6.14 for Windows NT (Sheldrick, G.M., 2001) suite of programs was used to solve the structure by direct methods. The molecule showed a simple disorder. The two halves of the molecule were disordered across the central C-C bond. This was modeled as a 50/50 mixture of the two rings. The three chemically different bond distances in the six-membered ring were each restrained to be identical to their matching bonds. These values were allowed to refine, giving the following bond

distances; the C_{apical}-N (1.337 Å) bond, the N-C (1.325 Å) bond and the C-C (1.400 Å) bond. 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 (0.292 e/Å^3) was associated with one of the sulfur atoms. Full-matrix least squares refinement on F^2 gave $R_1 = 4.11$ for 2σ data and $wR_2 = 8.98$ for all data (GOOF = 1.234).

Complex 2: Crystals of $[\{Mn(C_5HF_6O_2)_2\}_2(\mu-C_5H_3N_4S_2)]$ arrived from the University of Guelph pre-mounted and coated with epoxy. The olive-coloured shoebox was mounted on a goniometer head. Data were collected at low temperature (-173 °C) on a Nonius Kappa-CCD area detector diffractometer with COLLECT (Nonius B.V., 1997-2002). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN (Otwinowski & Minor, 1997). The absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK). The reflection data and systematic absences were consistent with a triclinic space group: P(-1).

The SHELXTL/PC V6.14 for Windows NT (Sheldrick, G.M., 2001) suite of programs was used to solve the structure by direct methods. There were two half molecules in the asymmetric unit. Both were well ordered. There was disorder across the ligand that bridged the Mn atoms, since it was located on a center of symmetry. The atoms of the ligand were refined isotropically, at half-occupancy, and the displacement parameters of "matching" atoms were restrained to have identical values. All of the

remaining 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 (0.766 e/Å^3) was associated with one of the fluorine atoms. Full-matrix least squares refinement on F^2 gave $R_1 = 5.84$ for 2σ data and $wR_2 = 12.32$ for all data (GOOF $= 0.875$).

Magnetometry of 2: Magnetic susceptibilities were measured on a Quantum Design MPMS-XL7 DC-SQUID magnetometer using an applied field of 1000 Oe. Molecular diamagnetic corrections were achieved using Pascal's constants. The microcrystalline sample was loaded into the sample space of a Delrin sample holder and mounted directly to the sample rod. The measured magnetic susceptibility of the empty Delrin sample holder was subtracted out as the background.

The modeling of the measured χT versus T data is described in the main text. For comparison, we also modeled the data using MAGMUN, a Windows-based software package written by Dr. Zhiquiang Xu in collaboration with Prof. L. K. Thompson and Dr. O. Waldmann. For this we used a linear three-spin system ($\mathbf{H} = -J(2\mathbf{S}_{Mn}\mathbf{S}_{DTDA}) + g\beta SH + \chi_{TIP}$.) The best fitting parameters were found to be $g = 2.0447$, $J = -32.8$ cm^{-1}, θ (Weiss constant) $= +0.79$ K and $\chi_{TIP} = 0.001$ cm^{-1}. These parameters compare well to those obtained using the ChiT Pro 1.0 software, with the exception of the somewhat smaller antiferromagnetic exchange coupling between the Mn atoms and the ligand. This is to be expected since we did not account for the possibility of exchange coupling between the two Mn atoms (i.e., we used a linear model) in the MAGMUN simulation. A small

antiferromagnetic exchange interaction between the two Mn atoms would necessitate a larger antiferromagnetic exchange interaction between the DTDA and each Mn atom in order to obtain a fit to the measured data. We found exactly this with the ChiT Pro 1.0 fit.
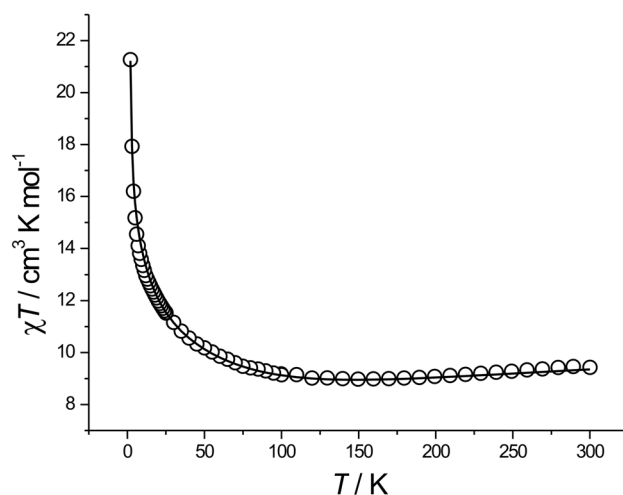

Figure 1. Measured χT versus T data (o) and the best fit found using MAGMUN as described above (—).

References

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