Exploring through-bond and through-space magnetic communication in 1,3,2-dithiazolyl radical complexes

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ESI-1 Experimental Procedures

Standard literature procedures were used for the preparation of the methylbenzodithiazolyl radical (MBDTA)¹ and bis(hexafluoroacetylacetonate)zinc(II) dihydrate,² Zn(hfac)₂·2H₂O. The complexes M(hfac)₂·2H₂O (M= Mn and Co) were purchased from sigma and used as received. Solvents were dried via an Innovative Technology Solvent Purification System and all reactions were performed under a nitrogen atmosphere using standard Schlenk and glovebox (MBraun Labmaster) techniques.

IR spectra were obtained using a Bruker Alpha FT-IR spectrometer equipped with a Platinum single reflection diamond ATR module. Elemental analysis was determined with a PerkinElmer 2400 Series II Elemental Analyzer. EPR spectra were obtained using a Bruker EMXplus X-Band EPR spectrometer equipped with a variable temperature control unit and high precision microwave frequency counter. Melting points were determined using a Stanford Research Systems MPA120 EZ-Melt Automated Melting Point Apparatus.

Preparation of M(hfac)₂·2THF (M= Mn, Co, Zn)

Under a nitrogen atmosphere, warm THF was added dropwise to $M(hfac)_2 \cdot 2H_2O$ to obtain a saturated solution. The solution was allowed to slowly cool to room temperature and was then placed in an ice bath for 20 minutes to form crystals of the THF solvate. The solvent was removed *in vacuo*. The crystals collected showed the absence of the hydrate vibration expected for $M(hfac)_2 \cdot xH_2O$ at approximately 3500 cm⁻¹.

Synthesis of Co(hfac)₂(MBDTA)₂(1)

Co(hfac)₂·2THF (0.162 mmol, 0.100 g) and MBDTA (1.95 eq, 0.316 mmol, 0.053 g) were dissolved in dry CH₂Cl₂ (15 mL) under a nitrogen atmosphere. The solution was stirred for 30 minutes and remained dark red in colour throughout. The solvent was evaporated *in vacuo* to afford a dark brown residue which was purified by sublimation (10^{-1} torr, 86 °C) onto a cold-finger under static vacuum to give dark black/red crystals suitable for X-ray diffraction (0.023 g, 18%). Elemental analysis found (Calc. for C₂₄H₁₄F₁₂CoN₂O₄S₄): C= 35.67% (35.61); H= 1.83% (1.74); N= 3.39% (3.46); mp 232 - 238 °C; EPR (DCM, 298 K): g= 2.006, a_N= 11.20 G. Phase purity was also confirmed by PXRD (Figure S2) and the IR spectrum presented in Figure S6.

Synthesis of Zn(hfac)₂(MBDTA)₂ (2)

Zn(hfac)₂·2THF (0.120 mmol, 0.075 g) and MBDTA (1.95 eq, 0.234 mmol, 0.039 g) were dissolved in dry CH₂Cl₂ (10 mL) under a nitrogen atmosphere. The solution was stirred for 30 minutes and remained dark red in colour throughout. The solvent was evaporated *in vacuo* to afford a dark purple residue which was purified by vacuum sublimation (10⁻¹ torr, 51 °C) onto a cold-finger under static vacuum to give black/purple crystals suitable for X-ray diffraction (0.012 g, 34%). Elemental analysis found (Calc. for C₂₄H₁₄F₁₂ZnN₂O₄S₄): C= 35.37% (35.33); H= 1.58% (1.73); N= 3.31% (3.43); mp 213 - 220 °C; EPR (DCM, 298 K): g= 2.006, a_N= 10.36 G. Phase purity was also confirmed by PXRD (Figure S2) and the IR spectrum presented in Figure S6.

Synthesis of Mn(hfac)₂(MBDTA)₂ (3)

Mn(hfac)₂·2THF (0.163 mmol, 0.100 g) and MBDTA (1.95 eq, 0.318 mmol, 0.053 g) were dissolved in dry CH₂Cl₂ (15 mL) under a nitrogen atmosphere. The solution was stirred for 30 minutes and remained dark red in colour throughout. The solvent was evaporated *in vacuo* to afford a dark black/green residue which was purified by vacuum sublimation (10^{-1} torr, 68 °C) onto a cold-finger under static vacuum to give dark black/green crystals suitable for X-ray diffraction (0.071 g, 54%). Elemental analysis found (Calc. for C₂₄H₁₄F₁₂MnN₂O₄S₄): C= 36.19% (35.78); H= 1.95% (1.75); N= 3.71% (3.48); mp 225 - 228 °C; EPR (DCM, 298 K): g= 2.006, a_N= 11.19 G. Phase purity was also confirmed by PXRD (Figure S2) and the IR spectrum presented in Figure S6.

ESI-2 PXRD Studies

Powder XRD measurements were recorded on a Bruker D8 Discover diffractometer using Cu–K α_1 radiation ($\lambda = 1.54187$ Å) at room temperature with a beam diameter of 0.5 mm and a Vantec-500 area detector using DIFFRAC.SUITE.³ Data were background corrected using DASH.⁴ Figure S1 shows initial formation of complex **3** from the reaction in solution and retention of its structure post-sublimation. These experimental PXRD patterns are compared with the simulated PXRD pattern based on the atomic coordinates determined from the crystal structure at 170(2) K, coupled with a Pawley refinement of the room temperature unit cell parameters to account for thermal expansion of the crystal lattice. Two low intensity impurity features were evident in the experimental data (marked with dotted lines in Figure S1) which could not be assigned to **3**, however there were insufficient peaks to be able to unambiguously assign this impurity. However we note that MBDTA is volatile under the sublimation conditions employed and exhibits its most intense reflection near 10°. Figure S2 compares the PXRD patterns for tetragonal **3** in relation to triclinic **1** and **2**.



Figure S1: Room temperature PXRD profiles for Mn(hfac)₂(MBDTA)₂ after removal of solvent (presublimation) and post-sublimation. The simulation is based on the refined trigonal cell based on the room temperature powder data (a = b = 29.722, c = 10.602 Å) and the coordinates derived from the single crystal data at 170(2) K.



Figure S2: Comparison of PXRD profiles for M(hfac)₂(MBDTA)₂ complexes (M= Mn, Co and Zn), highlighting the similarity in PXRD profiles for **1** and **2** in relation to **3**.

ESI-3 EPR Studies

EPR spectra were recorded on a Bruker EMXplus EPR spectrometer at room temperature in DCM. Figure S3 shows the evolution of the EPR spectrum during titration of Mn(hfac)₂·2THF with MBDTA in CH₂Cl₂. The initial Mn(hfac)₂·2THF complex reveals a sextet pattern consistent with high spin Mn(II) (⁵⁵Mn, 100% natural abundance, I = 5/2). Addition of MBDTA did not appear to lead to any marked changes in the EPR spectrum, merely an increase in the intensity of the MBDTA resonance and some subtle changes in hyperfine coupling and linewidth which can be attributed to exchange coupling⁵ and dipolar broadening.⁶ Indeed EPR studies on **1**, **2** and **3** all reveal similar spectra (Figure S4).



Figure S3. EPR studies of the titration of Mn(hfac)₂·2THF with MBDTA in CH₂Cl₂.



Figure S4: Experimental EPR spectra of MBDTA (g = 2.006, $a_N = 11.19$ G), Mn(hfac)₂(MBDTA)₂ (g = 2.006, $a_N = 11.19$ G), Co(hfac)₂(MBDTA)₂ (g = 2.006, $a_N = 11.20$ G) and Zn(hfac)₂(MBDTA)₂ (2.006, $a_N = 10.36$ G).

ESI-4 Single Crystal X-Ray Diffraction

For **1** and **3** crystals were mounted on a cryoloop with paratone oil and data were collected using ϕ and ω scans at 170(2) K on a Bruker D8 Venture four circle diffractometer equipped with a Photon CCD area detector using a high intensity copper IμS Cu-Kα source. For 2 data were collected on a Bruker APEX-II Xray diffractometer equipped with an Incoatec Mo IuS source. The temperature was controlled with an Oxford Cryosystems Cryostat (700 Series Cryostream for 1 and 3 and a 700 Series Cryostream Plus for 2). Data were integrated with SAINT⁷ within the APEX-II software and an absorption correction was applied using SADABS.⁸ Structures were solved using intrinsic phasing and refined against F^2 within the SHELXTL suite.⁹ A summary of the crystallographic data is shown in Table S1. Structures are available from the Cambridge Crystallographic Data Centre (CSD deposition numbers: 1913687, 1914612 and 1913688). For complex 1, one of the CF₃ groups was disordered and modelled over two sites using anisotropic U_{ii} for the F atoms and appropriate 1,2- and 1,3- DFIX constraints. Complex 2 also exhibited disorder in one of the CF₃ groups which was modelled over three sites using a common U_{iso} for the F atoms and appropriate 1,2- and 1,3- DFIX constraints for the C-F and F···F distances. The structure of **3** was particularly prone to merohedral twinning with structure refinement typically stalling around $R_1 \simeq 0.18$ for several data sets collected. The application of the twin law (0 1 0 1 0 0 0 0 -1) corresponding to a switching of the crystallographic a and b axes plus inversion along c improved the refinement. Typically the BASF parameter revealed a near perfect merohedral twin (BASF ~ 0.5). In addition to the twinning problems, the whole of the crystallographically unique hfac⁻ anion was severely disordered over two positions corresponding to rotation about the N-Mn-N vector. The geometry of the hfac⁻ anion was restrained with common C-O, C-C and C-F bond lengths as well as F···F distances (DFIX). There was evidence for additional rotational disorder of the CF₃ groups but, given the already problematic nature of the structure, additional Uii restraints were employed to suppress splitting of F atom positions and provided satisfactory final residuals ($R_1 = 0.07$) and residual electron density (Table S1).

The different packing of **3** in relation to **1** and **2** is associated with the difference in the orientation of the MBDTA ring in relation to the four CF_3 groups in the equatorial plane (Figure S5). This leads to very different intermolecular contacts between MBDTA radicals (Figure S6).

Compound	1	2	3
CSD deposition number	1913687	1914612	1913688
Empirical formula	$C_{24}H_{14}C0F_{12}N_2O_4S_4$	C24H14ZnF12N2O4S4	C24H14MnF12N2O4S4
Formula weight	809.54	815.98	805.55
Temperature	170(2) K	150(2) K	170(2) K
Crystal size	0.18 x 0.14 x 0.07 mm	0.19 x 0.14 x 0.06 mm	0.16 x 0.12 x 0.03 mm
Wavelength	1.54178 Å	0.71073 Å	1.54178 Å
Crystal system	Triclinic	Triclinic	Trigonal
Space group	P-1	P-1	R-3
Unit cell dimensions	a = 8.4591(4) Å	a = 8.4587(4) Å	a = 28.857(2) Å
	b = 8.6474(4) Å	b = 8.5811(5) Å	b = 28.857(2) Å
	c = 10.5245(5) Å	c = 10.6424(5) Å	c = 10.4312(7) Å
	$\alpha = 100.022(4)^{\circ}$	$\alpha = 99.800(3)^{\circ}$	α = 90°
	β = 98.821(3)°	β = 97.782(2)°	β = 90°
	γ = 92.677(3)°	γ = 91.947(2)°	γ = 120°
Volume	747.01(6) ų	752.91(7) Å ³	7522.7(12) ų
Z	1	1	9
Density (calculated)	1.800 Mg/m ³	1.800 Mg/m ³	1.600 Mg/m ³
Absorption coefficient	8.164 mm ⁻¹	1.203 mm⁻¹	6.483 mm⁻¹
Max. and min. transmission	0.7526 and 0.5423	0.7457 and 0.6992	0.7526 and 0.4781
F(000)	403	406	3609
Theta range for data collection	4.32 to 65.24°	1.962 to 27.500°	3.063 to 65.106°.
	$-9 \le h \le 9$	-10 ≤ <i>h</i> ≤ 10	$-31 \le h \le 33$
Index ranges	$-10 \le k \le 10$	$-11 \leq k \leq 11$	-33 ≤ <i>k</i> ≤ 33
	-12 ≤ / ≤ 12	-13 ≤ / ≤ 13	-12 ≤ <i>l</i> ≤ 12
Reflections collected	11514	19983	24732
Independent reflections	2545 [R(int) = 0.0787]	3441 [R(int) = 0.0331]	2854 [R(int) = 0.0787]
Data completeness	99.5 %	99.8 %	100 %
Data/restraints/parameters	2545 /54/226	3441/22/230	2854/234/ 270
Goodness-of-fit on <i>F</i> ²	1.064	1.131	1.066
Einal P indicos $[1 > 2\sigma(1)]$	$R_1 = 0.0581$	$R_1 = 0.0451$	$R_1 = 0.0690$
	$wR_2 = 0.1127$	$wR_2 = 0.1005$	$wR_2 = 0.1732$
Ripdices (all data)	$R_1 = 0.0805$	$R_1 = 0.0505$	$R_1 = 0.0918$
in indices (all data)	$wR_2 = 0.1245$	$wR_2 = 0.1033$	$wR_2 = 0.1935$
Largest diff. peak and hole	+0.880	0.803	0.466
<u>e</u> ⁻ /Å ³	-0.491	-0.644	-0.398

Table S1Crystal data for compounds 1 – 3



Figure S5. Orientation of the MBDTA ring plane in relation to the $M(hfac)_2$ plane for 1 - 3.





Figure S6. Intermolecular contacts between MBDTA radicals in **1** – **3**.

ESI-5 IR Studies

IR spectra were obtained using a Bruker Alpha FT-IR spectrometer equipped with a Platinum single reflection diamond ATR module. IR spectra of complexes 1 - 3 are compared with MBDTA and the starting material M(hfac)₂·2THF in Figure S7 and reveal near identical FT-IR fingerprints.



Figure S7. IR spectra of MBDTA and $M(hfac)_2 \cdot 2THF$ starting materials as well as $M(hfac)_2(MBDTA)_2$ (M= Mn, Co, Zn) complexes 1 - 3.

ESI-6 DFT Studies

DFT studies were undertaken to probe the strength of the intermolecular exchange couplings based on the different packing motifs for the $M(hfac)_2(MBDTA)_2$ complexes (triclinic P-1 for **1** and **2** and trigonal R-3 for **3**). Unrestricted DFT calculations of the broken symmetry singlet and the triplet were computed using the 6-31G(TM)(d,p) basis set and either the M06-2X or B3LYP functional within Jaguar¹⁰ using convergence criteria of 5×10^{-6} Hartrees for the total energy and 5×10^{-7} for the RMS in the density matrix change. The M06-2X functional has been shown to be particularly well-suited for main group elements¹¹ whereas the B3LYP functional has been successfully used to quantify exchange couplings in other thiazyl radicals.¹² The strength of the magnetic exchange interaction between the two spins was computed using the method of Yamaguchi¹³ where the exchange coupling is determined from the energies (E) and expectation values (<S²>) of the triplet and broken symmetry singlet states:

$$J = \frac{-(E_T - E_{BSS})}{\langle S^2 \rangle_T - \langle S^2 \rangle_{BSS}}.....eqn. S1$$

For complex **2** (containing Zn^{2+}) one of the two MBDTA radicals on each complex was replaced by an NH₃ group *in silico* while otherwise retaining the same crystallographic contacts between MBDTA radicals highlighted in Figure S6. For complex **3** a similar approach was applied with the Mn ion additionally replaced by Zn. Single point calculations of the exchange coupling between the two S = $\frac{1}{2}$ Zn(hfac)₂(MBDTA)(NH₃) molecules were then undertaken in the two possible packing conformations associated with **2** and **3**.The computed exchange couplings for these two geometries ("in-plane S…S" appropriate for **1** and **2** *vs* " π … π " associated with **3**) are summarized in Table S3. The spin density distributions for the ground state (B3LYP/6-31G(TM)(d,p)) for both conformations are shown in Figure S8.

Table S3. Computed exchange couplings between $Zn(hfac)_2(MBDTA)(NH_3)$ units adopting either the "in plane S…S" contacts observed in **1** and **2** or the out-of-plane " $\pi \dots \pi$ " contacts observed in **3**. Results from M06-2X are compared to B3LYP.

Contact type	M06-2X	B3LYP
	Exchange coupling J (cm ⁻¹)	Exchange coupling J (cm ⁻¹)
in-plane S····S	+2	-1
π…π	-316	-360



Figure S8. Spin density for the antiferromagnetic ground state (B3LYP/6-31G(TM)(d,p)) associated with (left) the in-plane S···S contact and (right) the π ··· π interaction (surfaces plotted at 0.001).

ESI-7 Magnetic Measurements

DC SQUID magnetic measurements were made on a Quantum Design SQUID magnetometer. M vs T measurements were made in an applied field of 1000 Oe for 1 - 3 and M vs H measurements were made in fields up to 5 T. All samples were pre-screened by PXRD (Figure S2) for phase purity and there was no remnant magnetization observed in M vs H plots (Figure S9) which might have indicated the presence of ferromagnetic impurities. Samples of 1 - 3 (54, 63 and 66 mg respectively) were sealed in gelatin capsules and corrections made for the diamagnetism of the sample and sample holder. Temperature dependent measurements for 1 - 3 are presented in Figures S10 – S12 respectively.



Figure S9 M vs H plots for complexes 1 – 3 (top left, top right and bottom left respectively)



Figure S10

(left) Temperature dependence of $1/\chi$ for **1** in the low temperature region with the red dotted corresponding to the best fit to Curie-Weiss behavior (C = 0.707 emu·K·mol⁻¹, θ = -2.9 K); (centre) temperature dependence of χ for **1**; (right) temperature dependence of χ T for **1**.



Figure S11 (left) Temperature dependence of $1/\chi$ for **2** above 50 K (the dotted line is the best fit to Curie-Weiss behavior ($C = 0.754 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$, $\theta = -19.2$ K); (centre) temperature dependence of χ vs T for **2** using a log scale to highlight the fit to the Bleaney-Bowers expression (dotted red line, J/k = -4.7 K); (right) temperature dependence of χ T for **2**.



Figure S12 (left) Temperature dependence of $1/\chi$ for **3** (the dotted line is the best fit to Curie-Weiss behavior; $C = 5.068 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$, $\theta = -175.6 \text{ K}$); (centre) temperature dependence of χ for **3**; (right) temperature dependence of χ T for **3** (dotted red line, two-parameter PHI fit of the data using J/k = -17.6(4) K and zJ' = -6.35(8) K).

ESI-8: References

- 1 G. Wolmershäuser, M. Schnauber and T. Wilhelm, *Chem. Commun.*, 1984, 573 574; G.D. McManus, J.M. Rawson, N. Feeder, F. Palacio and P. Oliete, *J. Mater. Chem.*, 2000, **10**, 2001 2003.
- 2 J. Olivier, S. Golhen, R. Świetlik, O. Cador, F. Pointillart and L. Ouahab, *European Journal of Inorganic Chemistry*, 2009, **2009**, 3282-3290.
- 3 DIFFRAC.SUITE, Bruker AXS, Madison, WI, USA.
- 4 W. I. F. David, K. Shankland, J. van de Streek, E. Pidcock, W. D. S. Motherwell and J. C. Cole, *J. Appl. Cryst.*, 2006, **39**, 910 915.
- 5 B. L. Bales and M. Peric, *J. Phys. Chem. B.*, 1997, **101**, 8707 8716.
- 6 C.P. Poole and H.A. Farach, *Bull. Magn. Reson.*, 1979, **1**, 162 194.
- 7 SAINT, Bruker AXS, Madison, WI, USA.
- 8 SADABS 2016/2, Bruker AXS, Madison, WI, USA.
- 9 G.M. Sheldrick, *Acta. Crystallogr. C.*, 2015, **71**, 3 8.
- 10 Jaguar, version 9.8, Schrodinger, Inc., New York, NY, 2017; A. D. Bochevarov, E. Harder, T. F. Hughes, J. R. Greenwood, D. A. Braden, D. M. Philipp, D. Rinaldo, M. D. Halls, J. Zhang, R. A. Friesner, *Int. J. Quantum Chem.*, 2013, **113**, 2110 2142.
- 11 Y. Zhao and D. G. Truhlar, *Theo. Chem. Accts.*, 2008, **120**, 215 241.
- 12 (a) J.M. Rawson, J. Luzon and F. Palacio, *Coord. Chem. Rev.*, 2005, **249**, 2631 2641; (b) M. Deumal, J.M. Rawson, A. E. Goeta, J.A. K. Howard, R. C. B. Copley, M. A. Robb and J. J. Novoa, *Chem. Eur. J.*, 2010, **16**, 2741 2750.
- 13 H. Nagao, M. Nishino, Y. Shigeta, T. Soda, Y. Kitagawa, T. Onishi, Y. Yoshioka and K. Yamaguchi, *Coord. Chem. Rev.*, 2000, **198**, 265 295.