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Electronic Supplementary Information

Ferromagnetic exchange in a twisted, oxime-bridged [Mn^{III}_2] dimer

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Table S1 Crystal data for complex **1**

	[Mn_2].4MeOH (1)
Formula[a]	$C_{50}H_{54}N_4O_{14}Mn_2$
M_W	1044.85
Crystal System	Orthorhombic
Space group	Pbca
a/Å	8.4931(17)
b/Å	22.495(5)
c/Å	24.783(5)
α/°	90
β/°	90
γ/°	90
V/Å^3	4734.9(16)
Z	4
T/K	150(2)
λ^b/Å	0.7107
D_c/g cm^{-3}	1.466
μ(Mo-Ka)/ mm^{-1}	0.607
Meas./indep.(R_{int}) refl.	14243 / 4330(0.0264)
wR2 (all data)	0.0984
$R1^{d,e}$	0.0384
Goodness of fit on F^2	1.133

[a] Includes guest molecules.[b] Mo-Kα radiation, graphite monochromator. [c] $wR2= [\Sigma w(|F_o^2|- |F_c^2|)^2/ \Sigma w|F_o^2|^2]^{1/2}$. [d]For observed data. [e] $R1= \Sigma||F_o|- |F_c||/ \Sigma|F_o|$.

FT-IR and Raman Measurements on [Mn^{III}_2(Napth-sao)$_2$(MeOH)$_2$].4MeOH (1)

FT-IR and Raman experimental information

Infra-red spectra were recorded on a Perkin Elmer FT-IR *Spectrum One* spectrometer equipped with a Universal ATR Sampling accessory. Raman measurements were recorded at room temperature using a Kaiser Optical Systems Raman spectrometer (*RamanRxn2^{TM} 1000 Analyzer*) equipped with a 993 nm laser diode excitation source and an InGaAs array detector. A laser power of ~200 mW (at the sample) with an exposure time of 10 × 8 seconds was used and spectra were collected from 250 to 4000 cm^{-1} (at a resolution of 5 cm^{-1}). Raman spectra of the coloured complex **1** was collected from a solid dispersion (approximately 1.5% by weight of complex) in dry KBr which was pressed into a disk using a hydraulic press and a 13 mm die set. This was done to minimise sample burning due to excessive absorption of excitation light. All data were normalised to the peak of maximum intensity and baseline corrected using standard methods.

FT-IR and Raman characterisation

Raman spectra were obtained from a polycrystalline sample of LH_2 and a 1.5% in KBr solid matrix of complex **1**, while FT-IR spectra were obtained from polycrystalline samples of **1** and LH_2. The Raman spectra provide information in the 250 to 700 cm^{-1} spectral region that is not accessible by our FT-IR measurements. For the LH_2 precursor, the Raman spectrum shows two peaks at 425 and 530 cm^{-1} with smaller associated bands at 448 and 518 cm^{-1} respectively. These we tentatively ascribe to out-of-plane ring deformation vibrations.[1] In the complex, only a single band at 507 cm^{-1} is observed, and this may arise because of the increased rigidity of the complex (Fig. S3).

The intense IR peaks observed at 743 cm^{-1} (LH_2) and 753 cm^{-1} (**1**) respectively are attributed to aromatic ν(C-H) out-of-plane deformation vibrations, readily observed for 1, 2-disubtituted naphthalene moieties. The equivalent Raman bands are known to be weak in nature and this is confirmed in our Raman measurement where we do not observe any significant bands here (Fig. S4). Likewise the IR (*weak*) and Raman (*strong and sharp*) bands in the 1587-1614 cm^{-1} and 1368-1379 cm^{-1} regions respectively (Figures S5 and S6) are due to multiple aromatic ν(C=C) stretching vibrations.[1] The bands centred at 1633 cm^{-1} may be tentatively attributed to the ν(C=N) oxime stretching mode, as observed elsewhere.[2] Attempts at assigning the ν(N-O) stretching modes in LH_2 and **1** are severely hampered by the significant spectral overlap in the 900-1150 cm^{-1} region of both the IR and Raman spectra (Figures S1 and S2). Previous reports on ligating aromatic oximes have documented ν(N-O) stretching IR bands in the ~1050-1250 cm^{-1} spectral range and so should be considered here.[3] However we cannot rule out the presence of multiple C-H out-of-plane deformation vibrational bands.[1] This uncertainty is further compounded by the multiple N-O bonding environments observed in **1**.

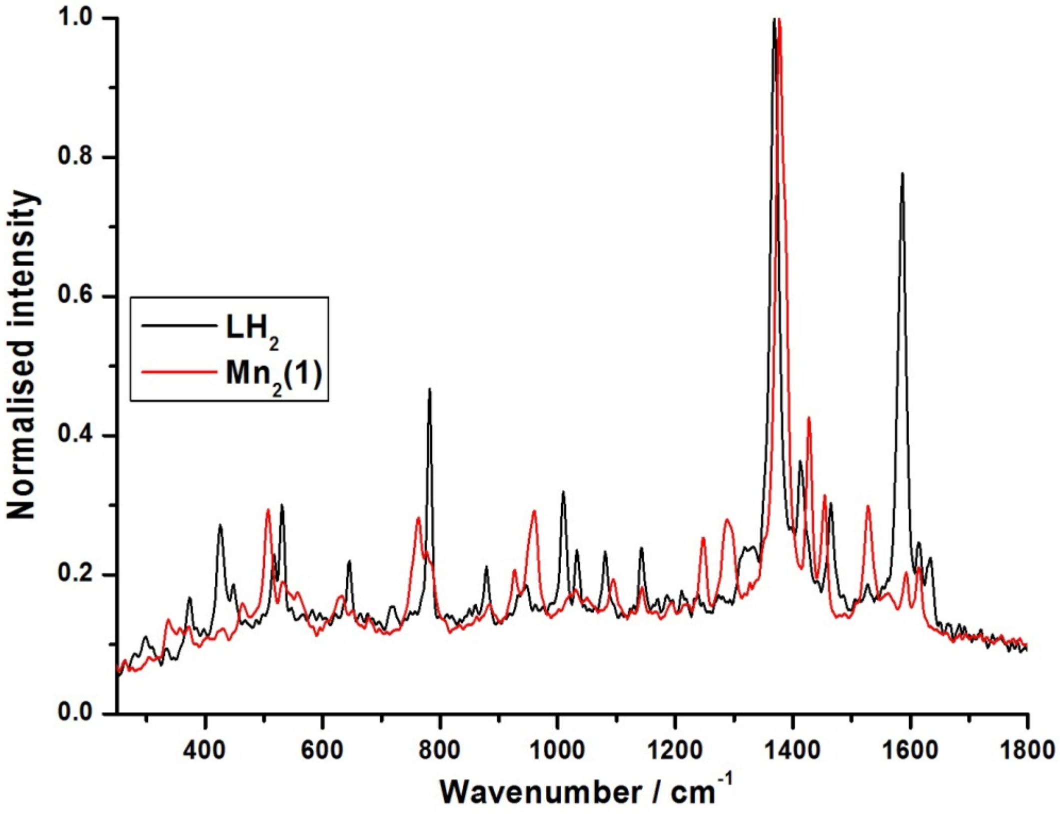

Fig. S1 Overlay of Raman spectra obtained from LH$_2$ (black line) and **1** (red).

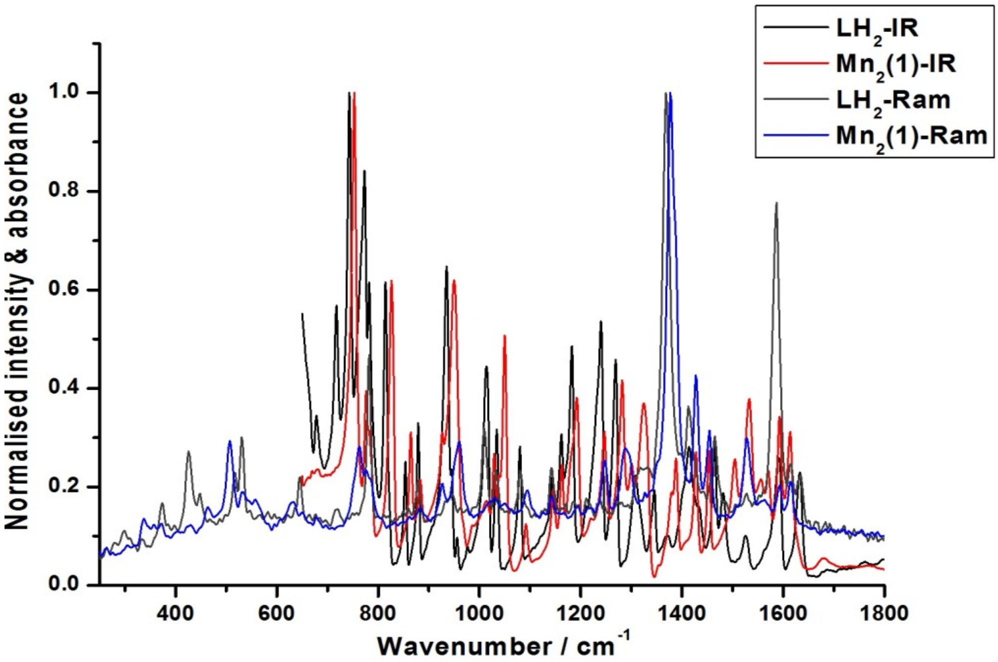

Fig. S2 Overlay of FT-IR and Raman spectra obtained from LH$_2$ (black and grey lines respectively) and **1** (red and blue lines respectively).

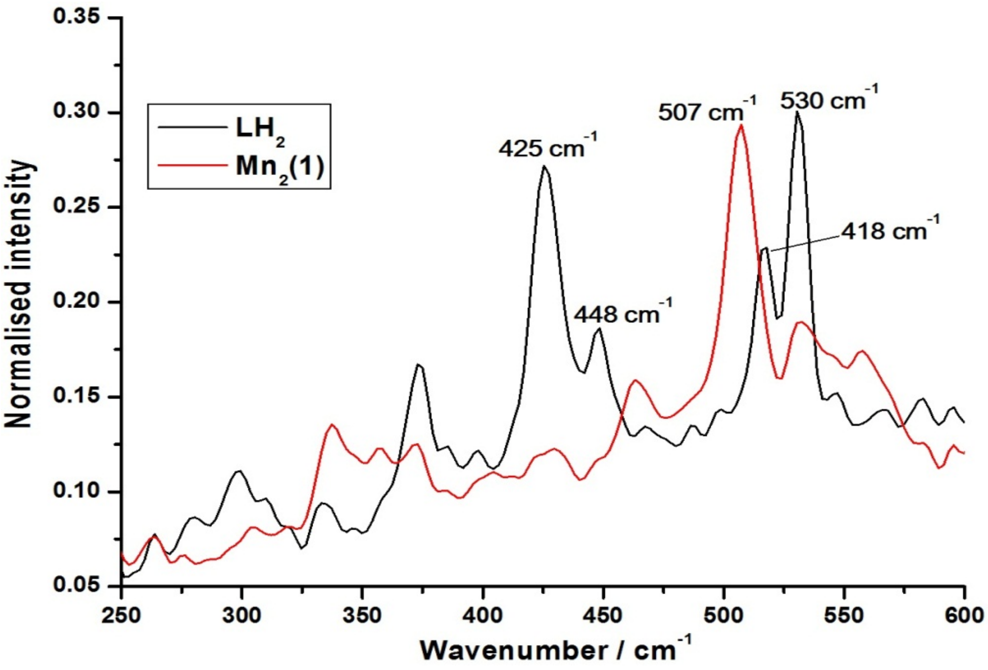

Fig. S3 Raman spectra (black and red lines) in the 250-600 cm^{-1} region obtained from crystalline sample of **LH$_2$** and **1**. All data were normalised and baseline corrected using standard methods.

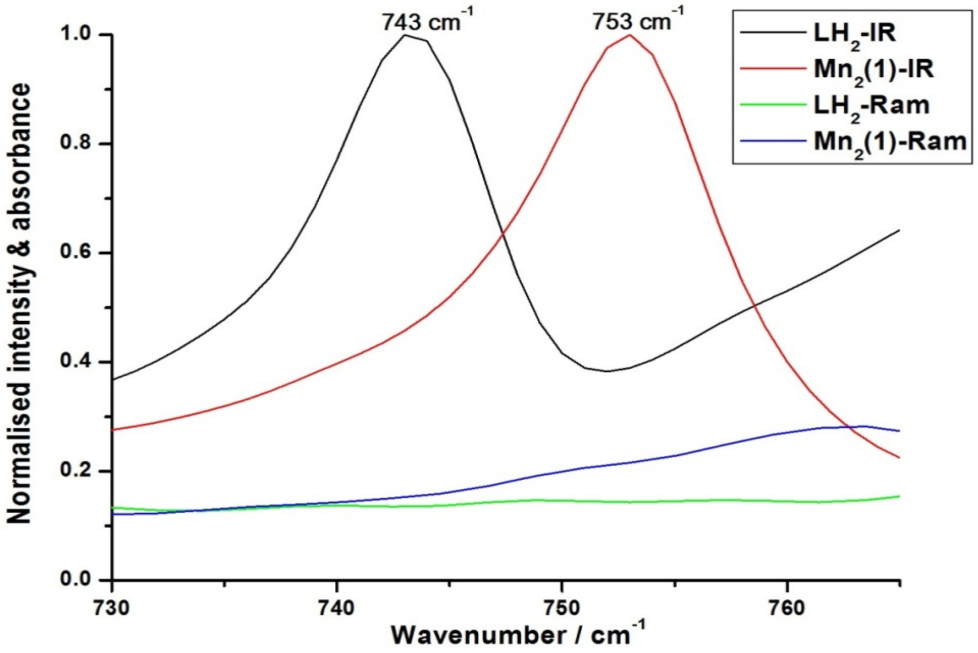

Fig. S4 Infra-Red (black and red lines) and Raman spectra (green and blue lines) obtained from crystalline sample of **LH$_2$** and **1**. Data were normalised and baseline corrected using standard methods.

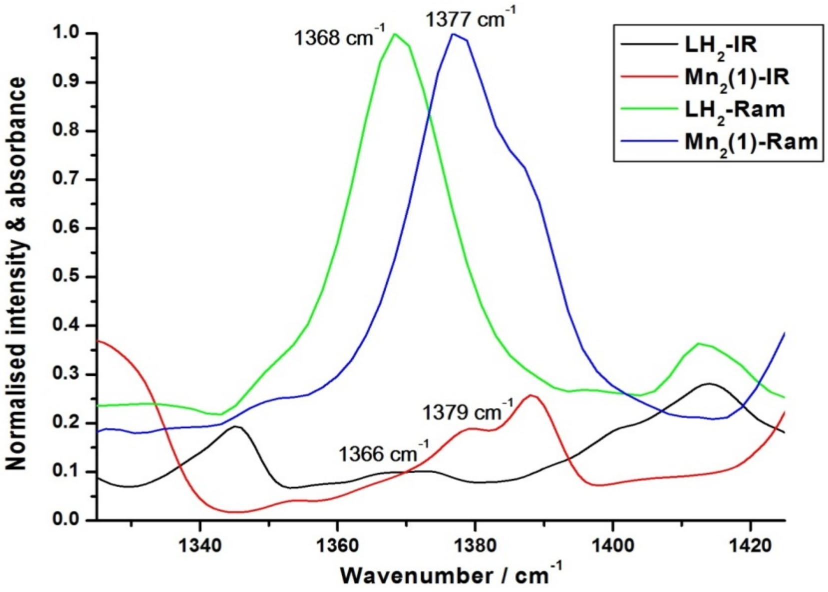

Fig. S5 Infra-Red (black and red lines) and Raman spectra (green and blue lines) obtained from crystalline sample of **LH$_2$** and **1** as viewed in the 1300-1420 cm^{-1} spectral range.

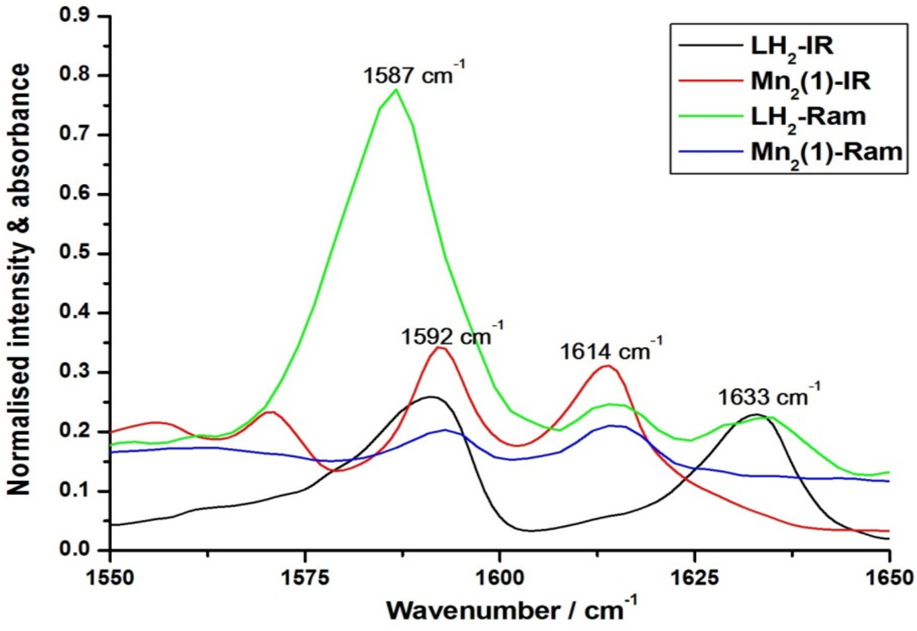

Fig. S6 Infra-Red (black and red lines) and Raman spectra (green and blue lines) obtained from crystalline sample of **LH$_2$** and **1**.

References

1. G. Socrates. *Infra-Red and Raman Characteristic Group Frequencies.* (2004) Wiley VCH Publishing.

2. F. Birkelbach, M. Winter, U. Flörke, H.-J. Haupt, C. Butzlaff, M. Lengen, E. Bill, A. X. Trautwein, K. Wieghardt and P. Chaudhuri. *Inorg. Chem.,* 1994, **33**, 3990-4001.

3. (a) C. Papatriantafyllopoulou, G. Aromi, A. J. Tasiopoulos, V. Nastopolos, C. P. Raptopoulou, S. J. Teat, A. Escuer and S. P. Perlepes. *Eur. J. Inorg. Chem.,* 2007, 2761-2774. (b) T. Weyhermüller, R. Wagner, S. Khandra and P. Chaudhuri. *Dalton Trans.,* 2005, 2539-2546. (c) P. Chaudhuri, M. Winter, U. Flörke and H.-J. Haupt. *Inorg. Chim. Acta.,* 1995, **232**, 125-130.