

Supporting Information:

A Mixed Valence Manganese Triangle in a Trigonal Lattice: Structure and Magnetism.

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Experimental

Elemental analyses were performed by Stephen Boyer at the Microanalysis Service, London Metropolitan University. Infra-red spectra ($400\text{--}4000\text{ cm}^{-1}$) were recorded from KBr pellets using a Bruker Tensor 27 FTIR spectrophotometer. MALDI-TOF mass spectra were obtained using a Bruker Ultraflex MALDI TOF mass spectrometer. MALDI-TOF-MS samples were prepared by dissolution of the compounds in CH_2Cl_2 (10 μL) and then mixing this solution with a solution of the matrix DCTB (Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile) in MeCN (20 μL). A sample of the resulting solution (5 μL) was deposited onto a plate, the solvent was removed in air, and the sample transferred to the mass spectrometer for analysis. Powder X-ray diffraction patterns data were collected using a Philips XPERT θ -2 θ diffractometer with Cu-K α radiation. The simulated powder pattern was generated by the software package POWDERCELL, taking the single crystal structural data for the compound as a model. Direct current (DC) and alternating current (AC) magnetic data were recorded on a Quantum design MPMS XL SQUID magnetometer. All chemicals and solvents were used as received. All preparations and manipulations were performed under aerobic conditions. $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ was prepared as previously reported^{S1}.

X-Ray Crystallography. Diffraction data were collected at 150(2) K on a Bruker AXS SMART APEX CCD equipped with an Oxford Cryosystems open flow cryostat (graphite monochromated Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$); ω scans). Absorption corrections were applied by a semi-empirical approach (SADABS). The crystal structure of (**2**) was solved by direct methods using SHELXS-97^{S2}. All non hydrogen-atoms were located using subsequent difference Fourier methods^{S2} and refined with anisotropic displacement

parameters. Hydrogen atoms were placed and refined using a geometric riding model except for the hydrogen attached to the oxygen atom of the coordinated MeOH molecule which could not be located, but was included in the formula sum. Two disordered methanol molecules could not be modelled in terms of discrete atomic sites: they were modelled using the SQUEEZE function within PLATON, which also produced a set of solvent-free diffraction intensities for the final cycles of refinement.^{S3}

Additional discussion related to Magnetic measurements.

A least squares fit using an equation described by Christou et al.^{S4} (see below) was used to obtain values for J1 and J2 yielding two possible parameter sets.

$$\chi^2 T = \frac{Ng^2\mu_B^2}{6k} \frac{1}{2} \times \left[\frac{1365\exp(28\alpha + 20\beta) + 858\exp(15\alpha + 20\beta) + 858\exp(23\alpha + 12\beta)}{14\exp(28\alpha + 20\beta) + 12\exp(15\alpha + 20\beta) + 12\exp(23\alpha + 12\beta)} + \frac{495\exp(4\alpha + 20\beta) + 495\exp(12\alpha + 12\beta) + 495\exp(18\alpha + 6\beta)}{10\exp(4\alpha + 20\beta) + 10\exp(12\alpha + 12\beta) + 10\exp(18\alpha + 6\beta)} + \frac{252\exp(20\beta - 5\alpha) + 252\exp(3\alpha + 12\beta) + 252\exp(9\alpha + 6\beta)}{8\exp(20\beta - 5\alpha) + 8\exp(3\alpha + 12\beta) + 8\exp(9\alpha + 6\beta)} + \frac{252\exp(13\alpha + 2\beta) + 105\exp(20\beta - 12\alpha) + 105\exp(12\beta - 4\alpha)}{8\exp(13\alpha + 2\beta) + 6\exp(20\beta - 12\alpha) + 6\exp(12\beta - 4\alpha)} + \frac{105\exp(2\alpha + 6\beta) + 105\exp(6\alpha + 2\beta) + 105\exp(8\alpha)}{6\exp(2\alpha + 6\beta) + 6\exp(6\alpha + 2\beta) + 6\exp(8\alpha)} + \frac{30\exp(20\beta - 17\alpha) + 30\exp(12\beta - 9\alpha) + 30\exp(6\beta - 3\alpha)}{4\exp(20\beta - 17\alpha) + 4\exp(12\beta - 9\alpha) + 4\exp(6\beta - 3\alpha)} + \frac{30\exp(\alpha + 2\beta) + 3\exp(12\beta - 12\alpha) + 3\exp(6\beta - 6\alpha)}{4\exp(\alpha + 2\beta) + 2\exp(12\beta - 12\alpha) + 2\exp(6\beta - 6\alpha)} \right] \quad (S1)$$

with $\alpha = J_2 / kT$ and $\beta = J_1 / kT$.

A least squares fit of J1 and J2 to the experimental data optimised to two points in parameter space depending on initial guesses for J1 and J2. The slightly better fit is obtained for $J_1 = -3.86 \pm 0.03 \text{ cm}^{-1}$ and $J_2 = -5.61 \pm 0.03 \text{ cm}^{-1}$ ($\chi^2/\text{d.o.f.} = 7 \times 10^{-3}$), while the

fit for $J_1 = -7.71 \pm 0.11 \text{ cm}^{-1}$ and $J_2 = -5.12 \pm 0.05 \text{ cm}^{-1}$ ($\chi^2/\text{d.o.f.} = 2 \times 10^{-2}$) is only slightly worse (**Error! Reference source not found.2**, main text).

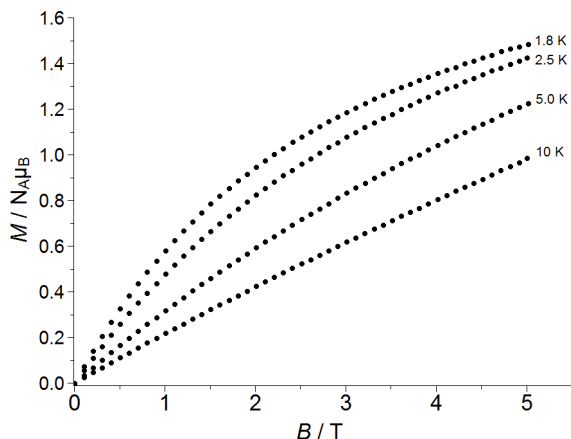


Figure S1. Magnetisation as a function of temperature recorded on a powder sample of **1** at different temperatures as indicated in the Figure.

- (S1) R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141–143; R. Sessoli, H. L. Tsai, A. R. Schake, S. Y. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1993, **115**, 1804–1816.
- (S2) G.M. Sheldrick, *Acta Crystallogr., Sect. A* 2008, **64**, 112.
- (S3) a) P. v der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A*, 1990, **46**, 194; b) A.L. Spek, *Acta Crystallogr., Sect. D*, 2009, **65**, 148-155.
- (S4) J.B. Vincent, H.R. Chang, K. Folting, J.C. Huffman, G. Christou, D.N. Hendrickson, *J. Am. Chem. Soc.* 1987, **109**, 5703–5711.