# Supporting Information

## Supramolecular Aggregates of Single-Molecule Magnets: Exchange-biased Quantum Tunneling of Magnetization in a Rectangular [$Mn_3$]$_4$ Tetramer

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### X-ray Crystallography

X-ray intensity data were collected at 100K on a Bruker DUO diffractometer using MoK$_\alpha$ radiation ($\lambda$ = 0.71073 Å) and an APEXII CCD area detector. Suitable crystals of **3**.x$CH_3OH$.y$CH_3CN$, **4**.x$C_4H_{10}O$.y$CH_2Cl_2$, **5**.x$CH_2Cl_2$ and **6**.x$CH_2Cl_2$ were attached to glass fibers using silicone grease and transferred to a goniostat where they were cooled to 100 K for data collection. Raw data frames were read by the program SAINT and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections, their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects, and numerical absorption corrections were applied based on indexed and measured faces. The structures were solved and refined in SHELXTL6.1, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms.

For **3**.x$CH_3OH$.y$CH_3CN$, the asymmetric unit consists of a half $Mn_6$ cluster, one and a half methanol and one acetonitrile solvent molecules. The solvent molecules were disordered and could not be modeled properly; thus the program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. Atom O12 is protonated; its H atoms were obtained from a different Fourier map and refined freely. The phenyl ring C9-C14 (C9'-C14') was disordered and refined in two parts whose site occupation factors were dependently refined. In the final cycle of refinement, 9225 reflections (of which 6757 are observed with $I > 2\sigma(I)$) were used to refine 423 parameters and the resulting $R_1$, $wR_2$ and S (goodness of fit) were 4.60%, 12.76% and 1.080, respectively.

For **4**. x$C_4H_{10}O$. y$CH_2Cl_2$, the asymmetric unit consists of a $Mn_6$ cluster cation, two perchlorate anions, two ether and four dichloromethane solvent molecules. Both anions were disordered. In the first case it was resolved in two parts while in the second case the minor and major parts shared atom O23. The solvent molecules were disordered and could not be modeled properly; thus the program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. In the final cycle of refinement, 10839 reflections (of which 7710 are observed with $I > 2\sigma(I)$) were used to refine 1014 parameters and the resulting $R_1$, $wR_2$ and S (goodness of fit) were 7.32%, 20.28% and 1.112, respectively.

For **5**.x$CH_2Cl_2$, the asymmetric unit consists of two $Mn_{12}$ cluster cations, eight perchlorate anions, and 52 dichloromethane solvent molecules. Three perchlorate anions were disordered along one of the Cl-O bonds, thus the three O atoms were refined in two parts whose site occupation factors were dependently refined. Those are on Cl2, Cl6 and Cl7. The Cl8 perchlorate anion was completely refined in two parts. In this case there was a ¼ dichloromethane associated with each disordered part of the Cl8 anion. Additionally, most of the 52 dichloromethane solvent molecules were significantly disordered and could not be modeled properly; thus program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. In the final cycle of refinement, 81724 reflections (of which 18367 are observed with $I > 2\sigma(I)$) were used to refine 2905 parameters and the resulting $R_1$, $wR_2$ and S (goodness of fit) were 7.40%, 16.17% and 0.624, respectively.

For **6**.x$CH_2Cl_2$, the asymmetric unit consists of a half $Mn_{12}$ cluster cation, two perchlorate anions and ten dichloromethane solvent molecules. The solvent molecules were disordered and could not be modeled properly, thus program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. The methyl groups on C102 and C122 were disordered and each set was refined in two parts whose site occupation factors fixed at values of 0.6 and 0.4. They were also constrained to maintain equivalent geometries using SADI and EADP in the final refinement model. In the final cycle of refinement, 31525 reflections (of which 15982 are observed with $I > 2\sigma(I)$) were used to refine 1275 parameters and the resulting $R_1$, $wR_2$ and S (goodness of fit) were 5.05%, 11.25% and 0.840, respectively.

## BOND DISTANCES AND ANGLES

**Table S1**. Selected distances (Å) and angles (°) for $[Mn_6O_2(O_2CCH_3)_8(MeOH)_2(pdpd)_2]$ (**3**)

| | | | |
|---|---|---|---|
| Mn1-Mn2 | 3.1082(6) | Mn3-O1 | 2.0500(18) |
| Mn1-Mn3 | 3.3940(2) | Mn3-O12 | 2.162(2) |
| Mn2-Mn3 | 3.3730(3) | Mn3-O11 | 2.163(2) |
| Mn1-O1 | 1.8262(18) | Mn3-O9 | 2.176(2) |
| Mn1-O6 | 1.950(2) | Mn3-O7 | 2.195(2) |
| Mn1-N2 | 2.021(2) | Mn3-O5 | 2.199(2) |
| Mn1-N1 | 2.052(2) | | |
| Mn1-O4 | 2.1910(19) | Mn2-O1-Mn1 | 116.76(10) |
| Mn1-O3 | 2.2134(19) | Mn2-O1-Mn3 | 121.02(9) |
| Mn2-O1 | 1.8238(18) | Mn1-O1-Mn3 | 122.20(9) |
| Mn2-O8 | 1.9464(19) | | |
| Mn2-N3 | 2.040(2) | | |
| Mn2-N4 | 2.042(2) | | |
| Mn2-O10 | 2.163(2) | | |
| Mn2-O2 | 2.3115(19) | | |

**Table S2**. Selected distances (Å) and angles ($^{o}$) for [Mn$_6$O$_2$(O$_2$CMe)$_8$(py)$_2$(dppd)$_2$] (ClO$_4$)$_2$ **(4)**

| | | | |
|---|---|---|---|
| Mn1-Mn2 | 3.1610(15) | Mn4-O12 | 1.877(5) |
| Mn1-Mn3 | 3.2913(19) | Mn4-O15 | 1.922(5) |
| Mn2-Mn3 | 3.2922(15) | Mn4-N7 | 2.016(6) |
| Mn4-Mn5 | 3.1641(21) | Mn4-N6 | 2.019(6) |
| Mn4-Mn6 | 3.2817(16) | Mn4-O17 | 2.167(6) |
| Mn5-Mn6 | 3.2864(18) | Mn4-O14 | 2.200(5) |
| Mn1-O1 | 1.889(5) | Mn5-O12 | 1.894(5) |
| Mn1-O6 | 1.919(5) | Mn5-O21 | 1.913(5) |
| Mn1-N2 | 2.015(6) | Mn5-N8 | 2.009(6) |
| Mn1-N1 | 2.031(6) | Mn5-N9 | 2.044(6) |
| Mn1-O3 | 2.154(5) | Mn5-O19 | 2.150(5) |
| Mn1-O4 | 2.185(5) | Mn5-O13 | 2.180(5) |
| Mn2-O1 | 1.890(5) | Mn6-O12 | 1.852(4) |
| Mn2-O8 | 1.924(5) | Mn6-O18 | 1.915(6) |
| Mn2-N4 | 2.001(6) | Mn6-O20 | 1.942(6) |
| Mn2-N3 | 2.023(6) | Mn6-N10 | 2.092(6) |
| Mn2-O10 | 2.161(6) | Mn6-O22 | 2.181(5) |
| Mn2-O2 | 2.221(5) | Mn6-O16 | 2.215(5) |
| Mn3-O1 | 1.853(5) | | |
| Mn3-O11 | 1.930(5) | | |
| Mn3-O5 | 1.942(5) | | |
| Mn3-N5 | 2.091(6) | | |
| Mn3-O7 | 2.182(6) | | |
| Mn3-O9 | 2.194(5) | | |
| Mn3-O1-Mn1 | 123.2(2) | Mn6-O12-Mn4 | 123.3(3) |
| Mn3-O1-Mn2 | 123.2(3) | Mn6-O12-Mn5 | 122.6(3) |
| Mn1-O1-Mn2 | 113.6(2) | Mn4-O12-Mn5 | 114.1(2) |

**Table S3**. Selected interatomic distances (Å) and angles ($^{o}$) for both cations in the asymmetric unit of [Mn$_{12}$O$_4$(O$_2$CMe)$_{12}$(dppd)$_6$](ClO$_4$)$_4$ **(5)**

| | | | | | |
|---|---|---|---|---|---|
| Mn1-Mn3 | 3.184(2) | Mn4-N17 | 1.985(7) | Mn9-O6 | 2.199(6) |
| Mn1-Mn2 | 3.212(2) | Mn4-N18 | 2.010(6) | Mn9-O28 | 2.213(6) |
| Mn2-Mn3 | 3.201(2) | Mn4-O12 | 2.179(6) | Mn10-O40 | 1.867(5) |
| Mn4-Mn6 | 3.173(2) | Mn4-O23 | 2.235(6) | Mn10-O35 | 1.899(6) |
| Mn4-Mn5 | 3.189(2) | Mn5-O38 | 1.887(5) | Mn10-N7 | 2.011(7) |
| Mn5-Mn6 | 3.216(2) | Mn5-O24 | 1.919(6) | Mn10-N8 | 2.038(6) |
| Mn7-Mn8 | 3.180(2) | Mn5-N15 | 2.004(7) | Mn10-O3 | 2.197(6) |
| Mn7-Mn9 | 3.206(2) | Mn5-N16 | 2.063(7) | Mn10-O31 | 2.259(6) |
| Mn8-Mn9 | 3.205(2) | Mn5-O9 | 2.174(5) | Mn11-O40 | 1.838(5) |
| Mn10-Mn11 | 3.185(2) | Mn5-O21 | 2.249(6) | Mn11-O32 | 1.928(6) |
| Mn10-Mn12 | 3.197(2) | Mn6-O38 | 1.860(5) | Mn11-N3 | 2.006(8) |

| | |
|---|---|
| Mn11-Mn12 | 3.218(2) |
| Mn1-O37 | 1.894(5) |
| Mn1-O13 | 1.924(6) |
| Mn1-N19 | 1.984(7) |
| Mn1-N20 | 2.026(7) |
| Mn1-O1 | 2.156(5) |
| Mn1-O15 | 2.214(6) |
| Mn2-O37 | 1.848(5) |
| Mn2-O17 | 1.936(5) |
| Mn2-N2 | 2.037(7) |
| Mn2-N1 | 2.038(6) |
| Mn2-O11 | 2.163(6) |
| Mn2-O14 | 2.225(6) |
| Mn3-O37 | 1.875(5) |
| Mn3-O16 | 1.906(6) |
| Mn3-N22 | 2.011(7) |
| Mn3-N21 | 2.014(7) |
| Mn3-O10 | 2.178(5) |
| Mn3-O18 | 2.204(6) |
| Mn4-O38 | 1.862(5) |
| Mn4-O19 | 1.936(6) |
| Mn13-O78 | 1.879(5) |
| Mn13-O76 | 1.961(5) |
| Mn13-N28 | 2.006(6) |
| Mn13-N27 | 2.009(6) |
| Mn13-O42 | 2.161(6) |
| Mn13-O56 | 2.182(6) |
| Mn14-O78 | 1.867(5) |
| Mn14-O53 | 1.938(5) |
| Mn14-N44 | 1.988(7) |
| Mn14-N43 | 2.034(7) |
| Mn14-O41 | 2.178(5) |
| Mn14-O75 | 2.225(6) |
| Mn15-O78 | 1.864(5) |
| Mn15-O55 | 1.925(6) |
| Mn15-N31 | 2.023(6) |
| Mn15-N32 | 2.025(7) |
| Mn15-O43 | 2.181(5) |
| Mn15-O54 | 2.194(6) |
| Mn16-O77 | 1.869(6) |
| Mn16-O57 | 1.921(6) |
| Mn16-N25 | 1.993(7) |
| Mn16-N26 | 2.018(7) |
| Mn16-O45 | 2.170(6) |
| Mn16-O59 | 2.229(6) |
| Mn17-O77 | 1.888(5) |
| Mn6-O22 | 1.941(5) |
| Mn6-N23 | 2.008(7) |
| Mn6-N24 | 2.029(7) |
| Mn6-O20 | 2.165(6) |
| Mn6-O8 | 2.195(5) |
| Mn7-O39 | 1.879(5) |
| Mn7-O27 | 1.936(6) |
| Mn7-N14 | 2.005(8) |
| Mn7-N13 | 2.017(7) |
| Mn7-O5 | 2.171(6) |
| Mn7-O25 | 2.198(7) |
| Mn8-O39 | 1.865(5) |
| Mn8-O26 | 1.942(6) |
| Mn8-N11 | 1.990(8) |
| Mn8-N12 | 2.037(7) |
| Mn8-O7 | 2.151(5) |
| Mn8-O29 | 2.191(6) |
| Mn9-O39 | 1.860(6) |
| Mn9-O30 | 1.915(6) |
| Mn9-N9 | 2.015(7) |
| Mn9-N10 | 2.041(7) |
| Mn18-O61 | 2.226(6) |
| Mn19-O80 | 1.853(5) |
| Mn19-O63 | 1.957(5) |
| Mn19-N42 | 2.015(8) |
| Mn19-N41 | 2.021(7) |
| Mn19-O51 | 2.167(6) |
| Mn19-O65 | 2.235(7) |
| Mn20-O80 | 1.880(5) |
| Mn20-O66 | 1.937(7) |
| Mn20-N40 | 2.013(7) |
| Mn20-N39 | 2.015(8) |
| Mn20-O50 | 2.164(5) |
| Mn20-O67 | 2.208(6) |
| Mn21-O80 | 1.866(5) |
| Mn21-O68 | 1.926(5) |
| Mn21-N46 | 2.014(7) |
| Mn21-N45 | 2.021(7) |
| Mn21-O52 | 2.181(5) |
| Mn21-O64 | 2.207(5) |
| Mn22-O79 | 1.872(4) |
| Mn22-O71 | 1.903(6) |
| Mn22-N37 | 2.015(7) |
| Mn22-N38 | 2.040(7) |
| Mn22-O48 | 2.202(5) |
| Mn22-O70 | 2.252(6) |
| Mn11-N4 | 2.025(7) |
| Mn11-O4 | 2.162(5) |
| Mn11-O33 | 2.258(6) |
| Mn12-O40 | 1.891(5) |
| Mn12-O34 | 1.918(5) |
| Mn12-N6 | 1.957(8) |
| Mn12-N5 | 2.000(7) |
| Mn12-O2 | 2.176(7) |
| Mn12-O36 | 2.185(6) |
| Mn13-Mn15 | 3.189(2) |
| Mn13-Mn14 | 3.205(2) |
| Mn14-Mn15 | 3.200(2) |
| Mn16-Mn18 | 3.194(2) |
| Mn16-Mn17 | 3.204(2) |
| Mn17-Mn18 | 3.205(2) |
| Mn19-Mn20 | 3.187(2) |
| Mn19-Mn21 | 3.201(2) |
| Mn20-Mn21 | 3.191(2) |
| Mn22-Mn24 | 3.1946(17) |
| Mn22-Mn23 | 3.2109(17) |
| Mn23-Mn24 | 3.2116(19) |
| Mn24-O49 | 2.162(5) |
| Mn24-O74 | |
| 2.272(5) | |

| | | | |
|---|---|---|---|
| Mn17-O62 | 1.910(7) | Mn23-O79 | 1.875(5) |
| Mn17-N29 | 1.993(7) | Mn23-O73 | 1.931(5) |
| Mn17-N30 | 2.057(7) | Mn23-N47 | 2.000(6) |
| Mn17-O46 | 2.162(5) | Mn23-N48 | 2.005(7) |
| Mn17-O58 | 2.198(5) | Mn23-O47 | 2.161(6) |
| Mn18-O77 | 1.873(5) | Mn23-O72 | 2.181(6) |
| Mn18-O60 | 1.939(6) | Mn24-O79 | 1.878(5) |
| Mn18-N34 | 2.017(7) | Mn24-O69 | 1.914(6) |
| Mn18-N33 | 2.019(6) | Mn24-N35 | 2.008(6) |
| Mn18-O44 | 2.197(6) | Mn24-N36 | 2.040(7) |

| | | | |
|---|---|---|---|
| Mn2-O37-Mn1 | 118.3(2) | Mn14-O78-Mn13 | 117.6(3) |
| Mn3-O37-Mn1 | 115.3(3) | Mn15-O78-Mn13 | 116.8(3) |
| Mn2-O37-Mn3 | 118.6(3) | Mn15-O78-Mn14 | 118.1(3) |
| Mn4-O38-Mn5 | 116.5(3) | Mn16-O77-Mn17 | 117.1(3) |
| Mn6-O38-Mn4 | 116.9(3) | Mn16-O77-Mn18 | 117.3(3) |
| Mn6-O38-Mn5 | 118.2(3) | Mn18-O77-Mn17 | 116.9(3) |
| Mn8-O39-Mn7 | 116.3(3) | Mn19-O80-Mn20 | 117.2(3) |
| Mn9-O39-Mn7 | 118.0(3) | Mn19-O80-Mn21 | 118.8(3) |
| Mn9-O39-Mn8 | 118.7(3) | Mn21-O80-Mn20 | 116.8(3) |
| Mn11-O40-Mn10 | 118.5(3) | Mn22-O79-Mn23 | 117.9(3) |
| Mn10-O40-Mn12 | 116.6(3) | Mn22-O79-Mn24 | 116.8(3) |
| Mn11-O40-Mn12 | 119.3(3) | Mn23-O79-Mn24 | 117.7(2) |

**Table S4**. Selected interatomic distances (Å) and angles ($^0$) for the cation in the asymmetric unit of $[Mn_{12}O_4(O_2C^tBu)_{12}(dppd)_6](ClO_4)_4$ **(6)**

| | | | |
|---|---|---|---|
| Mn1-Mn2 | 3.1982(6) | Mn4-O2 | 1.872(2) |
| Mn1-Mn3 | 3.1970(6) | Mn4-O15 | 1.927(2) |
| Mn2-Mn3 | 3.2024(7) | Mn4-N8 | 2.018(2) |
| Mn4-Mn5 | 3.1990(6) | Mn4-N7 | 2.019(2) |
| Mn4-Mn6 | 3.1971(7) | Mn4-O17 | 2.186(2) |
| Mn5-Mn6 | 3.2055(6) | Mn4-O7 | 2.2071(19) |
| Mn1-O1 | 1.8716(19) | Mn5-O2 | 1.8706(19) |
| Mn1-O9 | 1.919(2) | Mn5-O19 | 1.933(2) |
| Mn1-N2 | 2.011(2) | Mn5-N10 | 2.008(2) |
| Mn1-N1 | 2.019(2) | Mn5-N9 | 2.026(2) |
| Mn1-O4 | 2.1705(19) | Mn5-O8 | 2.1741(19) |
| Mn1-O11 | 2.204(2) | Mn5-O16 | 2.184(2) |
| Mn2-O1 | 1.8809(19) | Mn6-O2 | 1.8758(19) |
| Mn2-O14 | 1.938(2) | Mn6-O18 | 1.9255(19) |
| Mn2-N4 | 2.011(2) | Mn6-N12 | 2.015(2) |
| Mn2-N3 | 2.020(2) | Mn6-N11 | 2.032(2) |
| Mn2-O5 | 2.1969(19) | Mn6-O6 | 2.1743(19) |
| Mn2-O10 | 2.211(2) | Mn6-O20 | 2.2203(19) |

| | | |
|---|---|---|
| Mn3-O1 | 1.8668(19) | |
| Mn3-O12 | 1.931(2) | |
| Mn3-N5 | 2.020(3) | |
| Mn3-N6 | 2.021(2) | |
| Mn3-O13 | 2.177(2) | |
| Mn3-O3 | 2.1919(19) | |

| | | | |
|---|---|---|---|
| Mn3-O1-Mn1 | 117.56(10) | Mn6-O2-Mn4 | 117.08(10) |
| Mn3-O1-Mn2 | 117.41(10) | Mn6-O2-Mn5 | 117.66(10) |
| Mn1-O1-Mn2 | 116.92(10) | Mn4-O2-Mn5 | 117.46(10) |

## Bond valence sums for Mn and selected O atoms

- The **bold** value is the one closest to the charge for which it was calculated. The oxidation state of a particular atom can be taken as the nearest integer to the value in bold.
- The O atom is not protonated if the BVS is ~1.8-2.2, mono-protonated if the BVS is ~1.0-1.4, and doubly-protonated if the BVS is ~0.2-0.4.

Complex **3**

| | **Mn(II)** | **Mn(III)** | **Mn(IV)** | **Assignment** |
|---|---|---|---|---|
| Mn1 | 3.29 | **3.07** | 3.12 | Mn(III) |
| Mn2 | 3.21 | **3.00** | 3.04 | Mn(III) |
| Mn3 | **2.25** | 2.10 | 2.14 | Mn(II) |
| | BVS | Assignment | | |
| O1 | **2.17** | $O^{2-}$ | | |
| O12 | **1.31** | OH | | |

Complex **4**

| | **Mn(II)** | **Mn(III)** | **Mn(IV)** | **Assignment** |
|---|---|---|---|---|
| Mn1 | 3.29 | **3.07** | 3.12 | Mn(III) |
| Mn2 | 3.29 | **3.07** | 3.12 | Mn(III) |
| Mn3 | 3.29 | **3.06** | 3.13 | Mn(III) |
| Mn4 | 3.26 | **3.03** | 3.09 | Mn(III) |
| Mn5 | 3.25 | **3.03** | 3.09 | Mn(III) |

|  |  |  |  |  |
|---|---|---|---|---|
| Mn6 | 3.30 | **3.06** | 3.14 | Mn(III) |
|  | BVS | Assignment |  |  |
| O1 | **2.17** | $O^{2-}$ |  |  |
| O12 | **2.19** | $O^{2-}$ |  |  |

Complex **5**

|  | Mn(II) | Mn(III) | Mn(IV) | Assignment |
|---|---|---|---|---|
| Mn1 | 3.31 | **3.10** | 3.14 | Mn(III) |
| Mn2 | 3.26 | **3.04** | 3.09 | Mn(III) |
| Mn3 | 3.30 | **3.07** | 3.13 | Mn(III) |
| Mn4 | 3.35 | **3.13** | 3.17 | Mn(III) |
| Mn5 | 3.20 | **2.99** | 3.03 | Mn(III) |
| Mn6 | 3.31 | **3.10** | 3.14 | Mn(III) |
| Mn7 | 3.30 | **3.09** | 3.13 | Mn(III) |
| Mn8 | 3.37 | **3.12** | 3.16 | Mn(III) |
| Mn9 | 3.28 | **3.07** | 3.11 | Mn(III) |
| Mn10 | 3.28 | **3.07** | 3.11 | Mn(III) |
| Mn11 | 3.35 | **3.13** | 3.18 | Mn(III) |
| Mn12 | 3.43 | **3.22** | 3.25 | Mn(III) |
| Mn13 | 3.29 | **3.08** | 3.12 | Mn(III) |
| Mn14 | 3.30 | **3.09** | 3.13 | Mn(III) |
| Mn15 | 3.30 | **3.08** | 3.13 | Mn(III) |
| Mn16 | 3.30 | **3.08** | 3.13 | Mn(III) |
| Mn17 | 3.30 | **3.08** | 3.13 | Mn(III) |
| Mn18 | 3.24 | **3.03** | 3.07 | Mn(III) |
| Mn19 | 3.27 | **3.06** | 3.10 | Mn(III) |
| Mn20 | 3.28 | **3.07** | 3.11 | Mn(III) |
| Mn21 | 3.30 | **3.08** | 3.13 | Mn(III) |
| Mn22 | 3.25 | **3.04** | 3.08 | Mn(III) |
| Mn23 | 3.32 | **3.10** | 3.16 | Mn(III) |
| Mn24 | 3.25 | **3.04** | 3.08 | Mn(III) |
|  | BVS | Assignment |  |  |
| O37 | **2.20** | $O^{2-}$ |  |  |
| O38 | **2.21** | $O^{2-}$ |  |  |
| O39 | **2.22** | $O^{2-}$ |  |  |
| O40 | **2.25** | $O^{2-}$ |  |  |
| O77 | **2.17** | $O^{2-}$ |  |  |
| O78 | **2.21** | $O^{2-}$ |  |  |
| O79 | **2.18** | $O^{2-}$ |  |  |
| O80 | **2.27** | $O^{2-}$ |  |  |

Complex **6**

|  | **Mn(II)** | **Mn(III)** | **Mn(IV)** | **Assignment** |
|---|---|---|---|---|
| Mn1 | 3.32 | **3.11** | 3.15 | Mn(III) |
| Mn2 | 3.24 | **3.03** | 3.07 | Mn(III) |
| Mn3 | 3.26 | **3.03** | 3.09 | Mn(III) |
| Mn4 | 3.28 | **3.07** | 3.11 | Mn(III) |
| Mn5 | 3.31 | **3.10** | 3.14 | Mn(III) |
| Mn6 | 3.26 | **3.05** | 3.09 | Mn(III) |

|  | BVS | Assignment |
|---|---|---|
| O1 | **2.19** | $O^{2-}$ |
| O12 | **2.19** | $O^{2-}$ |

## VAN VLECK EQUATIONS

$C = N\mu_B^2/3k$
N = Avogadro’s number
g = Lande’s factor
k = Boltzmann constant
T = Temperature
TIP = Temperature independent paramagnetism
**Van Vleck equation for complex 3:**

num = + 52.5000×exp( 8.7500 ×m+ 0.0000 ×n)
+ 15.0000 ×exp( 1.7500 ×m+ 2.0000 ×n)
+ 52.5000 ×exp( 6.7500 ×m+ 2.0000 ×n)
+ 126.0000 ×exp( 13.7500 ×m+ 2.0000 ×n)
+ 1.5000 ×exp( -5.2500 ×m+ 6.0000 ×n)
+ 15.0000 ×exp( -2.2500 ×m+ 6.0000 ×n)
+ 52.5000 ×exp( 2.7500 ×m+ 6.0000 ×n)
+ 126.0000 ×exp( 9.7500 ×m+ 6.0000 ×n)
+ 247.5000 ×exp( 18.7500 ×m+ 6.0000 ×n)
+ 1.5000 ×exp( -11.2500 ×m+ 12.0000 ×n)
+ 15.0000 ×exp( -8.2500 ×m+ 12.0000 ×n)
+ 52.5000 ×exp( -3.2500 ×m+ 12.0000 ×n)
+ 126.0000 ×exp( 3.7500 ×m+ 12.0000 ×n)
+ 247.5000 ×exp( 12.7500 ×m+ 12.0000 ×n)
+ 429.0000 ×exp( 23.7500 ×m+ 12.0000 ×n)
+ 15.0000 ×exp( -16.2500 ×m+ 20.0000 ×n)
+ 52.5000 ×exp( -11.2500 ×m+ 20.0000 ×n)
+ 126.0000 ×exp( -4.2500 ×m+ 20.0000 ×n)
+ 247.5000 ×exp( 4.7500 ×m+ 20.0000 ×n)
+ 429.0000 ×exp( 15.7500 ×m+ 20.0000 ×n)
+ 682.5000 ×exp( 28.7500 ×m+ 20.0000 ×n)

denom = + 6.0000 ×exp( 8.7500 ×m+ 0.0000 ×n)
+ 4.0000 ×exp( 1.7500 ×m+ 2.0000 ×n)
+ 6.0000 ×exp( 6.7500 ×m+ 2.0000 ×n)
+ 8.0000 ×exp( 13.7500 ×m+ 2.0000 ×n)
+ 2.0000 ×exp( -5.2500 ×m+ 6.0000 ×n)
+ 4.0000 ×exp( -2.2500 ×m+ 6.0000 ×n)
+ 6.0000 ×exp( 2.7500 ×m+ 6.0000 ×n)
+ 8.0000 ×exp( 9.7500 ×m+ 6.0000 ×n)
+ 10.0000 ×exp( 18.7500 ×m+ 6.0000 ×n)
+ 2.0000 ×exp( -11.2500 ×m+ 12.0000 ×n)
+ 4.0000 ×exp( -8.2500 ×m+ 12.0000 ×n)
+ 6.0000 ×exp( -3.2500 ×m+ 12.0000 ×n)
+ 8.0000 ×exp( 3.7500 ×m+ 12.0000 ×n)
+ 10.0000 ×exp( 12.7500 ×m+ 12.0000 ×n)
+ 12.0000 ×exp( 23.7500 ×m+ 12.0000 ×n)
+ 4.0000 ×exp( -16.2500 ×m+ 20.0000 ×n)
+ 6.0000 ×exp( -11.2500 ×m+ 20.0000 ×n)
+ 8.0000 ×exp( -4.2500 ×m+ 20.0000 ×n)
+ 10.0000 ×exp( 4.7500 ×m+ 20.0000 ×n)
+ 12.0000 ×exp( 15.7500 ×m+ 20.0000 ×n)
+ 14.0000 ×exp( 28.7500 ×m+ 20.0000 ×n)
m = J/(kT)
n = J′/(kT)
$\chi_M = 2\times(C\times g^2/T)\times num/denom + TIP$

FIT PARAMETERS

R = 0.99876397 $R^2$ = 0.99752948

| | **Coefficient** | **Std. Error** |
|---|---|---|
| J | -9.9423 | 0.4593 |
| J′ | 10.4183 | 3.8722 |
| g | 1.9600 | 0.0376 |

**Van Vleck equation for complex 4:**

num = + 30.0000×exp( 6.0000×m+ 0.0000×n)
+ 6.0000×exp( 0.0000×m+ 2.0000×n)
+ 30.0000×exp( 4.0000×m+ 2.0000×n)
+ 84.0000×exp( 10.0000×m+ 2.0000×n)
+ 0.0000×exp( -6.0000×m+ 6.0000×n)
+ 6.0000×exp( -4.0000×m+ 6.0000×n)

$+ 30.0000\times\exp( 0.0000\times m+ 6.0000\times n)$
$+ 84.0000\times\exp( 6.0000\times m+ 6.0000\times n)$
$+ 180.0000\times\exp( 14.0000\times m+ 6.0000\times n)$
$+ 6.0000\times\exp( -10.0000\times m+ 12.0000\times n)$
$+ 30.0000\times\exp( -6.0000\times m+ 12.0000\times n)$
$+ 84.0000\times\exp( 0.0000\times m+ 12.0000\times n)$
$+ 180.0000\times\exp( 8.0000\times m+ 12.0000\times n)$
$+ 330.0000\times\exp( 18.0000\times m+ 12.0000\times n)$
$+ 30.0000\times\exp( -14.0000\times m+ 20.0000\times n)$
$+ 84.0000\times\exp( -8.0000\times m+ 20.0000\times n)$
$+ 180.0000\times\exp( 0.0000\times m+ 20.0000\times n)$
$+ 330.0000\times\exp( 10.0000\times m+ 20.0000\times n)$
$+ 546.0000\times\exp( 22.0000\times m+ 20.0000\times n)$

$\mathrm{denom} = + 5.0000\times\exp( 6.0000\times m+ 0.0000\times n)$
$+ 3.0000\times\exp( 0.0000\times m+ 2.0000\times n)$
$+ 5.0000\times\exp( 4.0000\times m+ 2.0000\times n)$
$+ 7.0000\times\exp( 10.0000\times m+ 2.0000\times n)$
$+ 1.0000\times\exp( -6.0000\times m+ 6.0000\times n)$
$+ 3.0000\times\exp( -4.0000\times m+ 6.0000\times n)$
$+ 5.0000\times\exp( 0.0000\times m+ 6.0000\times n)$
$+ 7.0000\times\exp( 6.0000\times m+ 6.0000\times n)$
$+ 9.0000\times\exp( 14.0000\times m+ 6.0000\times n)$
$+ 3.0000\times\exp( -10.0000\times m+ 12.0000\times n)$
$+ 5.0000\times\exp( -6.0000\times m+ 12.0000\times n)$
$+ 7.0000\times\exp( 0.0000\times m+ 12.0000\times n)$
$+ 9.0000\times\exp( 8.0000\times m+ 12.0000\times n)$
$+ 11.0000\times\exp( 18.0000\times m+ 12.0000\times n)$
$+ 5.0000\times\exp( -14.0000\times m+ 20.0000\times n)$
$+ 7.0000\times\exp( -8.0000\times m+ 20.0000\times n)$
$+ 9.0000\times\exp( 0.0000\times m+ 20.0000\times n)$
$+ 11.0000\times\exp( 10.0000\times m+ 20.0000\times n)$
$+ 13.0000\times\exp( 22.0000\times m+ 20.0000\times n)$

$m = J/(kT)$
$n = J'/(kT)$
$\chi_M = 2\times(C\times g^2/T)\times \mathrm{num}/\mathrm{denom} + \mathrm{TIP}$

FIT PARAMETERS

$R = 0.99971104$ $R^2 = 0.99942217$

| | **Coefficient** | **Std. Error** |
|---|---|---|
| J | -4.9333 | 0.1134 |
| J′ | 28.4128 | 1.9838 |
| g | 1.9926 | 0.0120 |

## Van Vleck equation for complex 5 and 6

num = + 30.0000×exp( 6.0000×m+ 0.0000×n)
+ 6.0000×exp( 0.0000×m+ 2.0000×n)
+ 30.0000×exp( 4.0000×m+ 2.0000×n)
+ 84.0000×exp( 10.0000×m+ 2.0000×n)
+ 0.0000×exp( -6.0000×m+ 6.0000×n)
+ 6.0000×exp( -4.0000×m+ 6.0000×n)
+ 30.0000×exp( 0.0000×m+ 6.0000×n)
+ 84.0000×exp( 6.0000×m+ 6.0000×n)
+ 180.0000×exp( 14.0000×m+ 6.0000×n)
+ 6.0000×exp( -10.0000×m+ 12.0000×n)
+ 30.0000×exp( -6.0000×m+ 12.0000×n)
+ 84.0000×exp( 0.0000×m+ 12.0000×n)
+ 180.0000×exp( 8.0000×m+ 12.0000×n)
+ 330.0000×exp( 18.0000×m+ 12.0000×n)
+ 30.0000×exp( -14.0000×m+ 20.0000×n)
+ 84.0000×exp( -8.0000×m+ 20.0000×n)
+ 180.0000×exp( 0.0000×m+ 20.0000×n)
+ 330.0000×exp( 10.0000×m+ 20.0000×n)
+ 546.0000×exp( 22.0000×m+ 20.0000×n)

denom = + 5.0000×exp( 6.0000×m+ 0.0000×n)
+ 3.0000×exp( 0.0000×m+ 2.0000×n)
+ 5.0000×exp( 4.0000×m+ 2.0000×n)
+ 7.0000×exp( 10.0000×m+ 2.0000×n)
+ 1.0000×exp( -6.0000×m+ 6.0000×n)
+ 3.0000×exp( -4.0000×m+ 6.0000×n)
+ 5.0000×exp( 0.0000×m+ 6.0000×n)
+ 7.0000×exp( 6.0000×m+ 6.0000×n)
+ 9.0000×exp( 14.0000×m+ 6.0000×n)
+ 3.0000×exp( -10.0000×m+ 12.0000×n)
+ 5.0000×exp( -6.0000×m+ 12.0000×n)
+ 7.0000×exp( 0.0000×m+ 12.0000×n)
+ 9.0000×exp( 8.0000×m+ 12.0000×n)
+ 11.0000×exp( 18.0000×m+ 12.0000×n)
+ 5.0000×exp( -14.0000×m+ 20.0000×n)
+ 7.0000×exp( -8.0000×m+ 20.0000×n)
+ 9.0000×exp( 0.0000×m+ 20.0000×n)
+ 11.0000×exp( 10.0000×m+ 20.0000×n)
+ 13.0000×exp( 22.0000×m+ 20.0000×n)

m =J/(kT)
n =J′/(kT)
$\chi_M = 4\times(C\times g^2/T)\times num/denom + TIP$

## FIT PARAMETERS

**For complex 5:**

R = 0.99923491 $R^2$ = 0.99847041

| | **Coefficient** | **Std. Error** |
|---|---|---|
| J | 16.7771 | 0.6111 |
| J´ | 1.5439 | 0.7360 |
| g | 1.9140 | 0.0029 |

**For complex 6:**

R = 0.99893376 $R^2$ = 0.99786866

| | **Coefficient** | **Std. Error** |
|---|---|---|
| J | 13.4792 | 0.7579 |
| J´ | 3.7775 | 1.0064 |
| g | 1.9066 | 0.0028 |

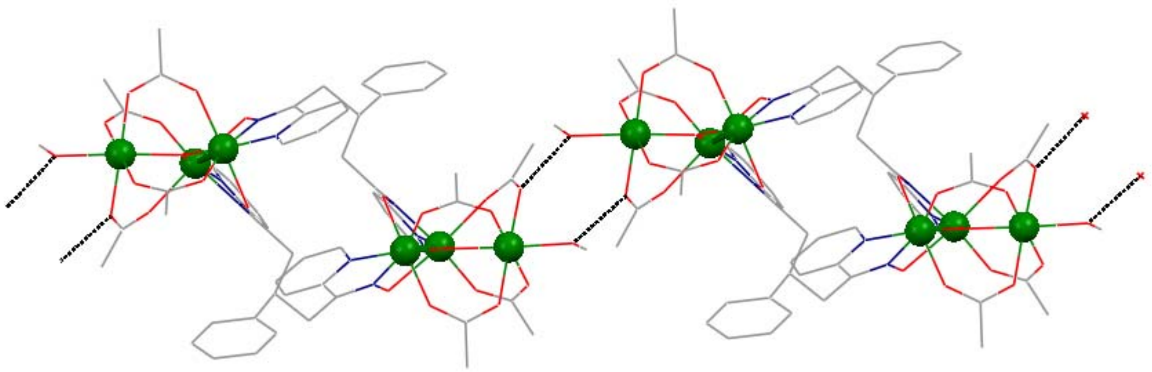


**Figure S1.** Hydrogen-bonds (dotted bonds) connecting $[Mn_3]_2$ dimers of complex **3.**

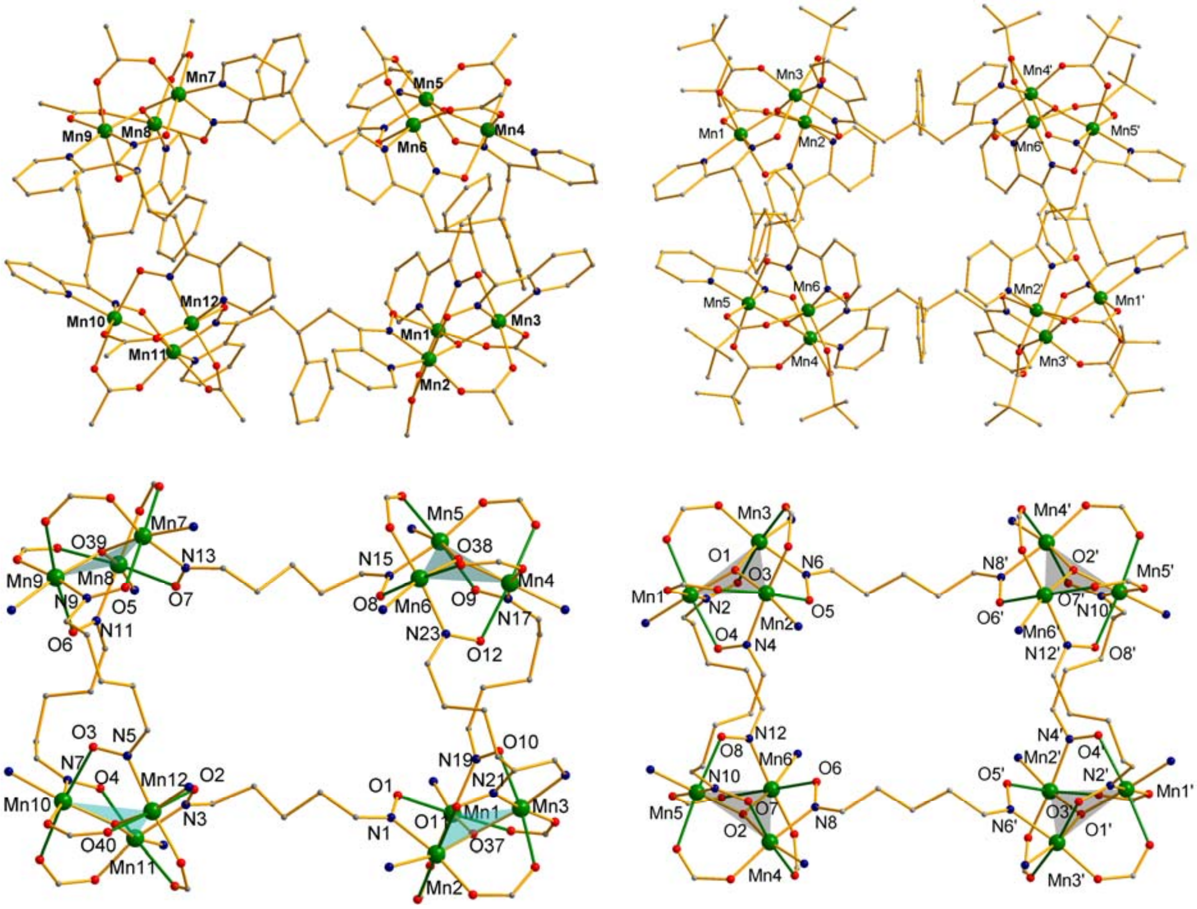


**Figure S2.** (top) Complete molecular structure of the cations of **5** (left) and **6** (right), with H atoms omitted for clarity. (bottom) The cores, emphasizing the connectivity between $Mn_3$ subunits, the $Mn_3$ planes, and the Jahn-Teller axes (green bonds). Color code: $Mn^{III}$ green; O red; N blue; C grey.

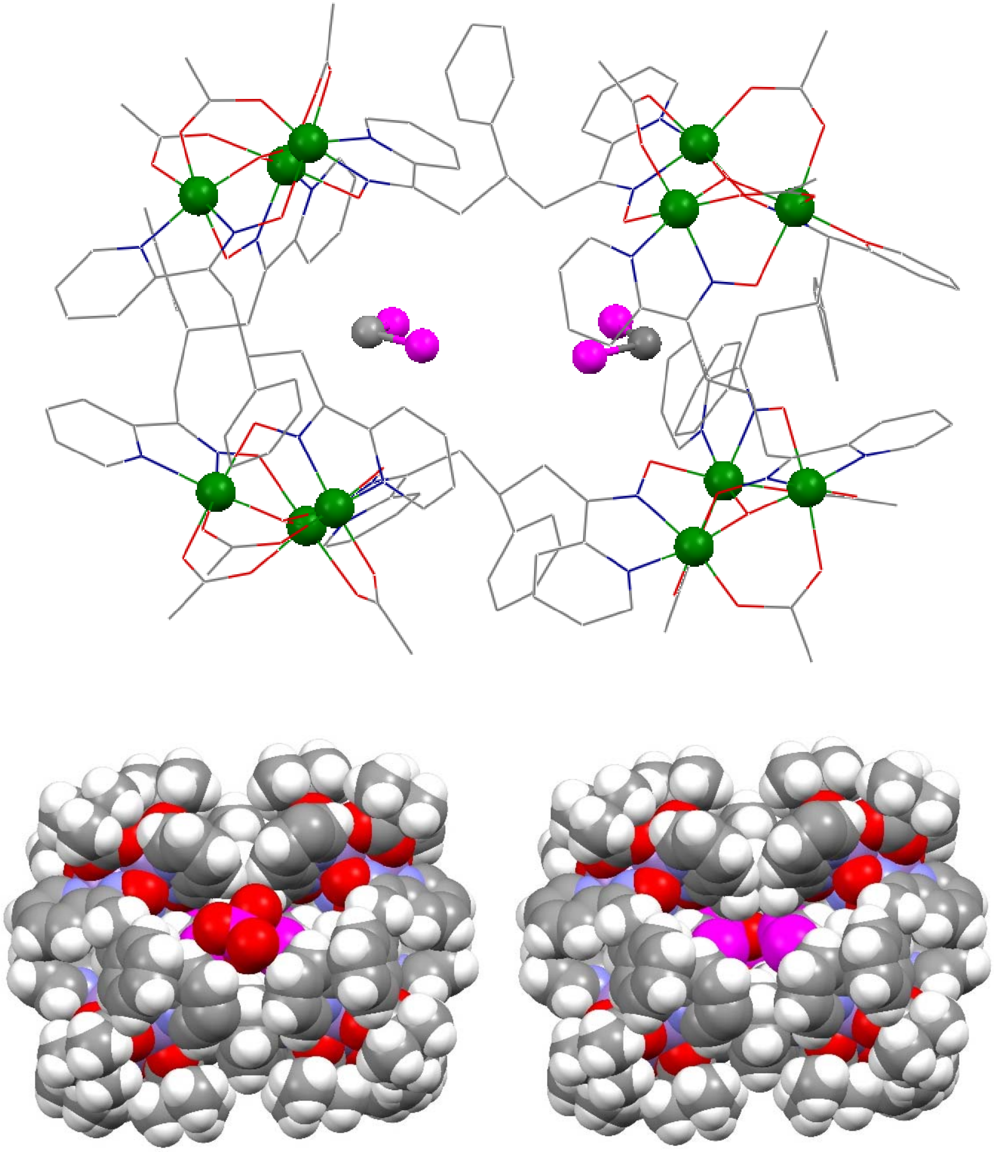


**Figure S3. (top)** Encapsulation of two $CH_2Cl_2$ molecules inside the $[Mn_3]_4$ cation of complex **5**. H atoms have been removed for clarity. **(bottom)** Space-filling representations of **6** showing the encapsulation: (left) with a $ClO_4^-$ anion (and its symmetry partner on the other side) plugging the only significant gaps at the center of the rectangle, and (right) with the $ClO_4^-$ anions removed. Color code: Cl mauve, O red, N blue, Mn purple, C gray, H white.

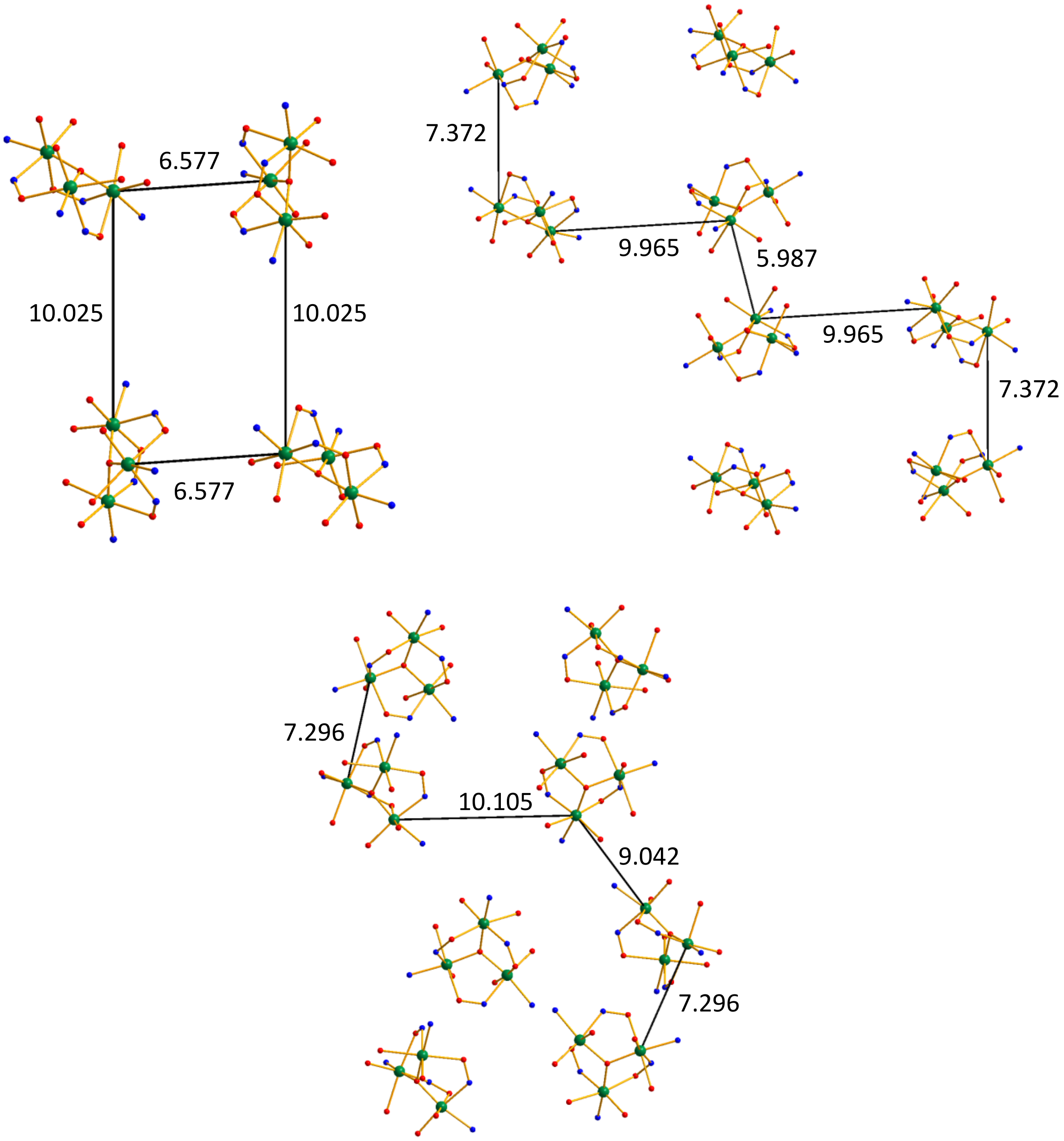


**Figure S4.** Shortest distances (Å) between $Mn_3$ units in complex **2** (top left)**,** **5** (top right) and **6** (bottom). mpko$^-$ and pdpd$^{2-}$ groups have been omitted for clarity.

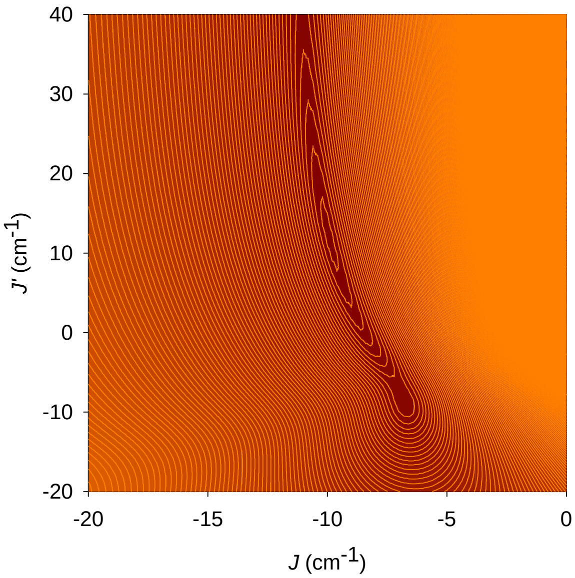


**Figure S5**. Two-dimensional contour plot of the fitting error vs. $J'$ and $J$ for complex **3**. The dark-brown region has the lowest errors.

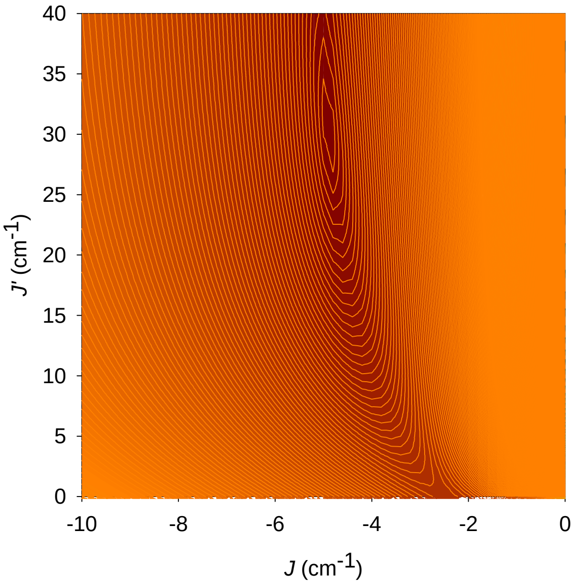


**Figure S6**. Two-dimensional contour plot of the fitting error vs. $J'$ and $J$ complex **4**. The dark-brown region has the lowest errors.

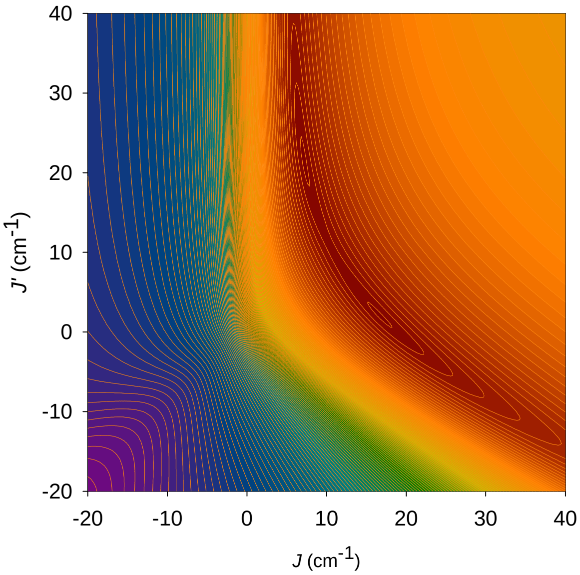


**Figure S7**. Two-dimensional contour plot of the fitting error vs. *J*′ and *J* for complex **5**. The dark-brown region has the lowest errors whereas the blue-purple region has the highest errors.

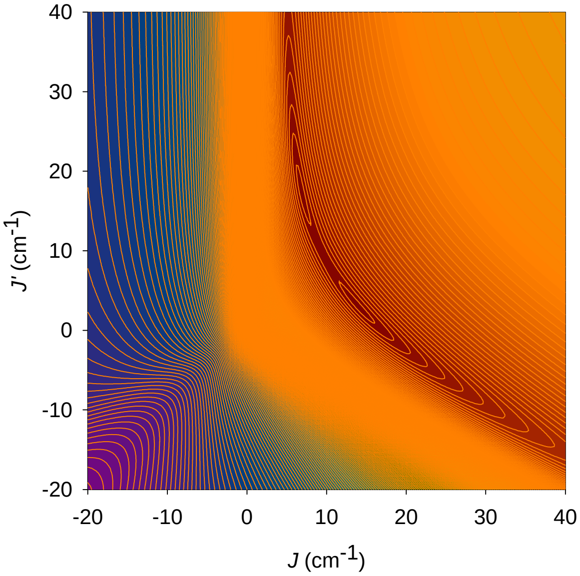
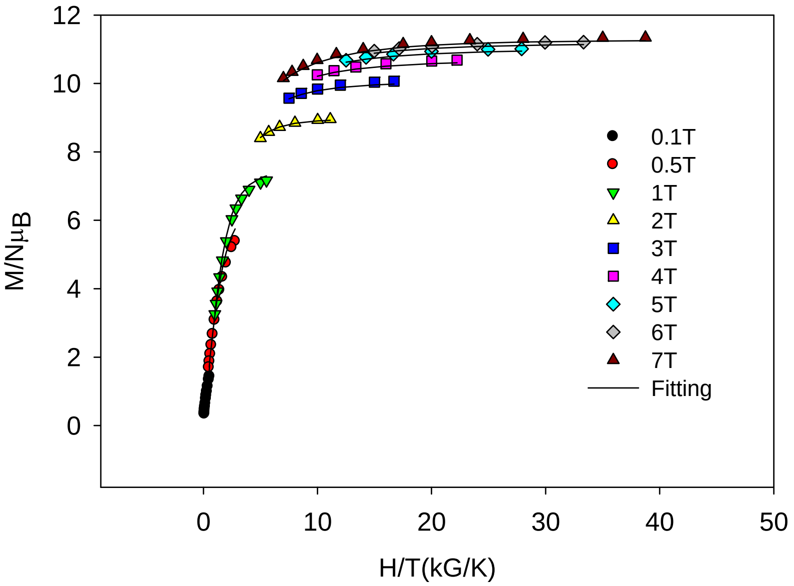


**Figure S8**. Two-dimensional contour plot of the fitting error vs. *J*′ and *J* for complex **6**. The dark-brown region has the lowest errors whereas the blue-purple region has the highest errors.



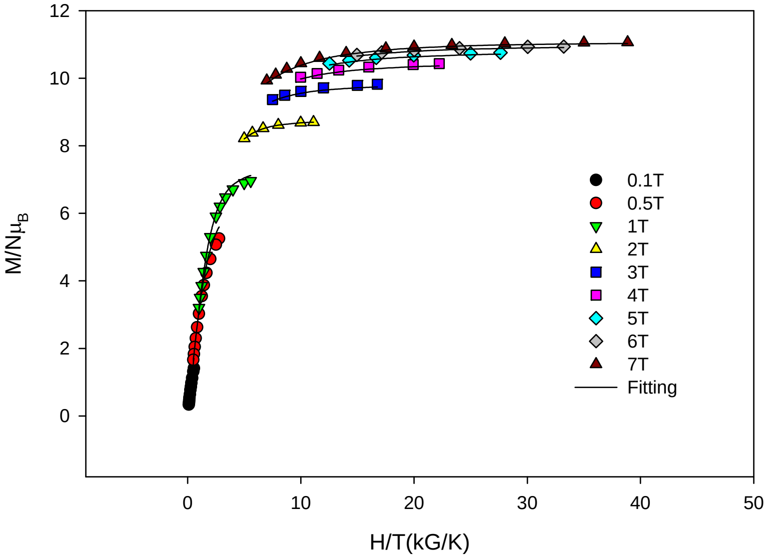


**Figure S9**. $M/N\mu_B$ (per $Mn_3$) vs. $H/T$ for complexes **5** (top) and **6** (bottom). The solid lines are the fit to the data. See the text for the fit parameters

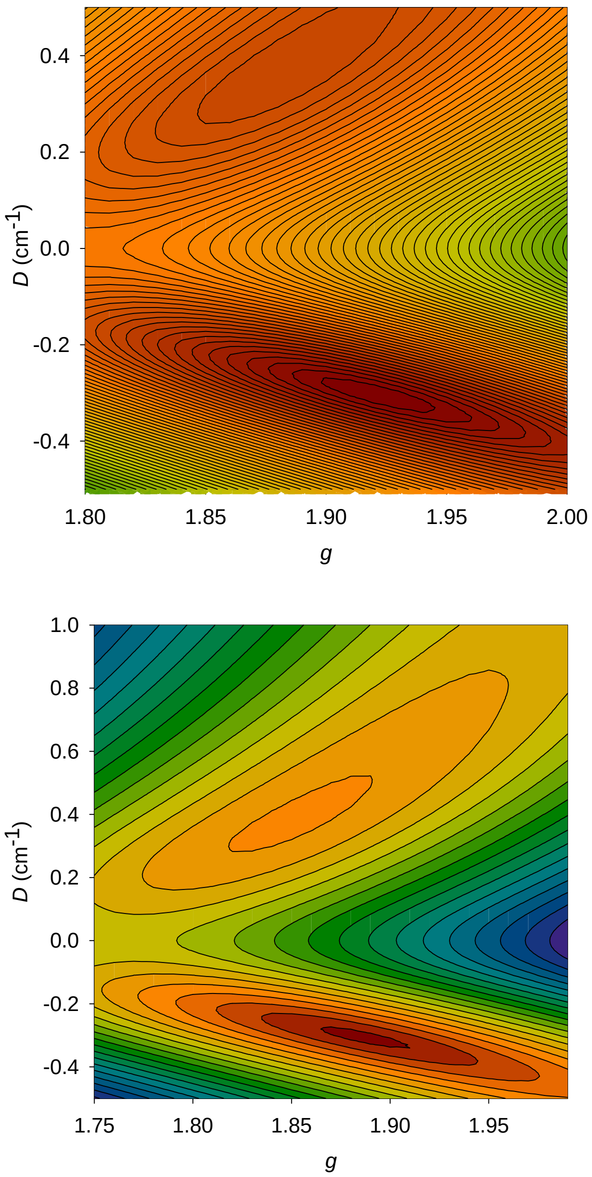


**Figure S10**. Two-dimensional contour plots of *g* vs *D* fitting error for **5** (top) and **6** (bottom). The dark-brown region has the lowest errors whereas the blue-purple region has the highest errors.

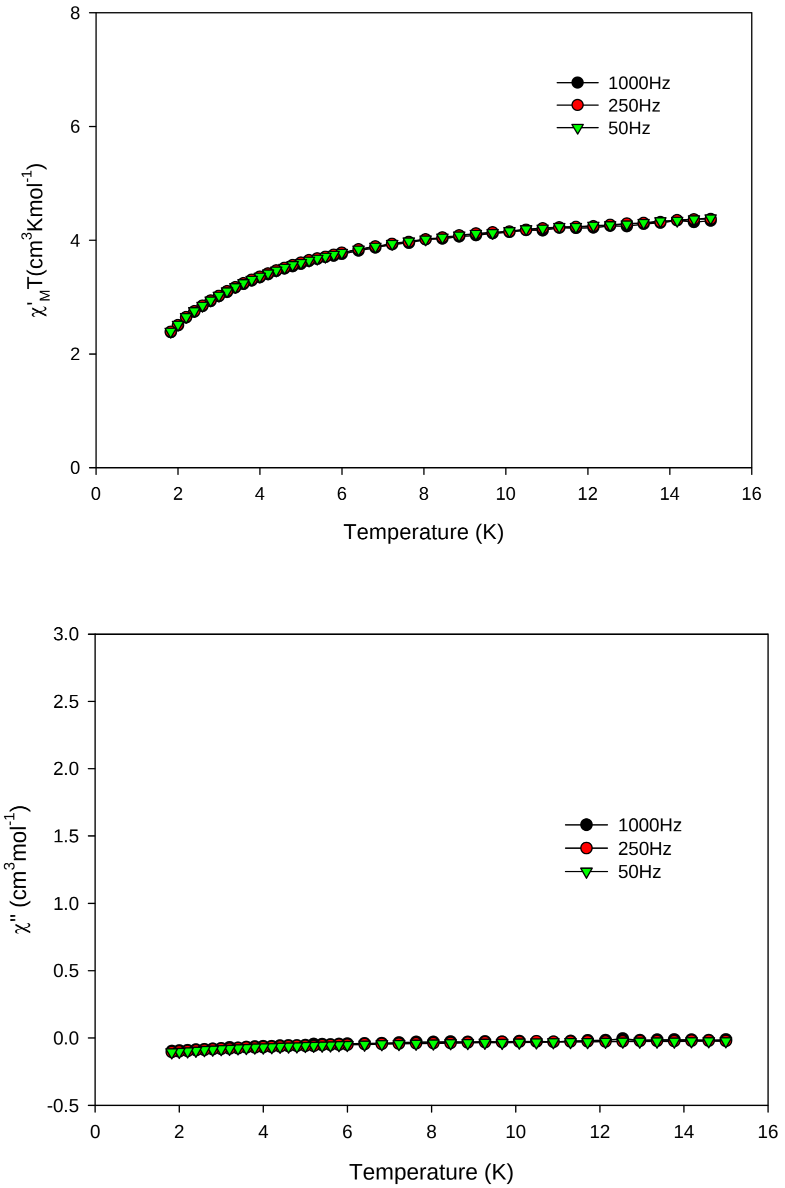


**Figure S11**. Plots of in-phase ($\chi'_{\mathrm{M}}$, as $\chi'_{\mathrm{M}}T$) and out of-phase ($\chi''$) ac susceptibility signal vs temperature for a microcrystalline sample of complex **3** in a 3.5G field oscillating at the indicated frequencies.

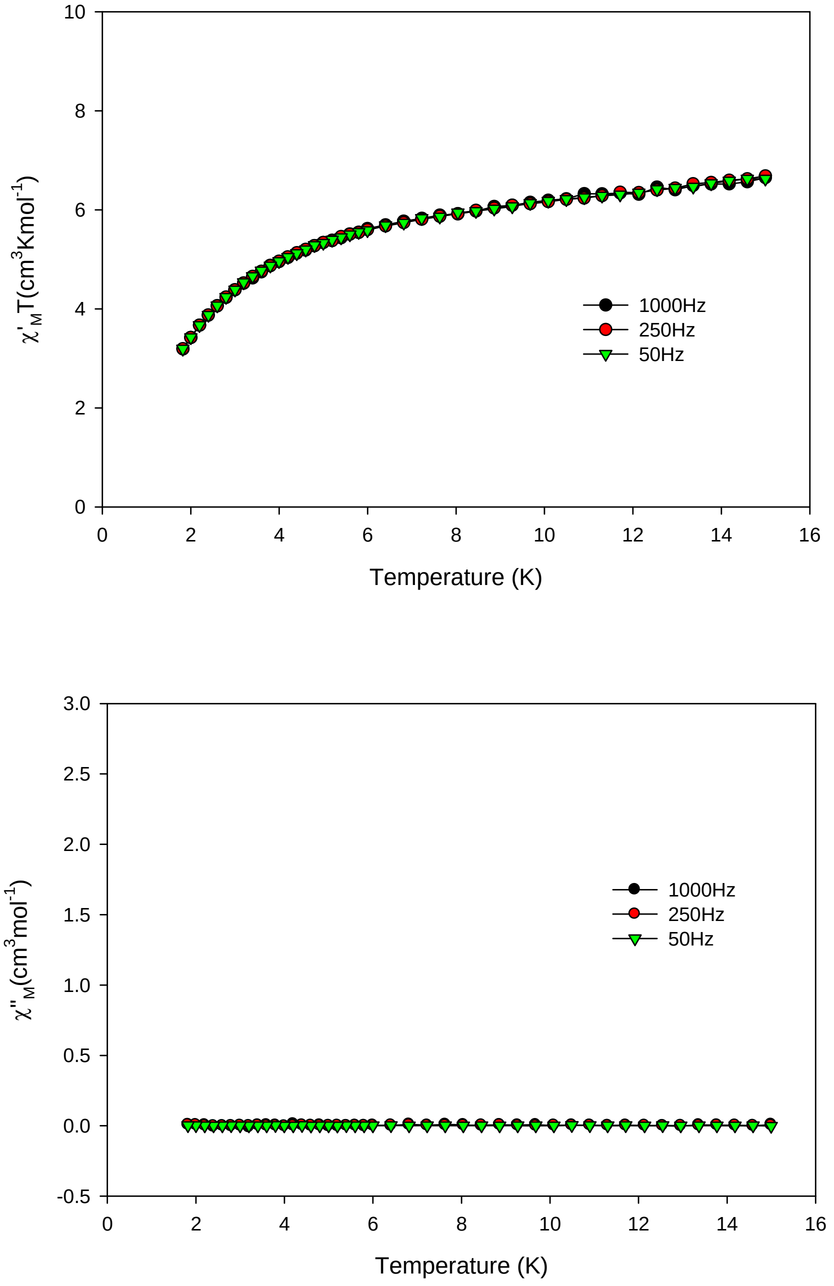


**Figure S12**. Plots of in-phase ($\chi'_{\mathrm{M}}$, as $\chi'_{\mathrm{M}}T$) and out of-phase ($\chi''$) ac susceptibility signal vs temperature for a microcrystalline sample of complex **4** in a 3.5G field oscillating at the indicated frequencies.

.

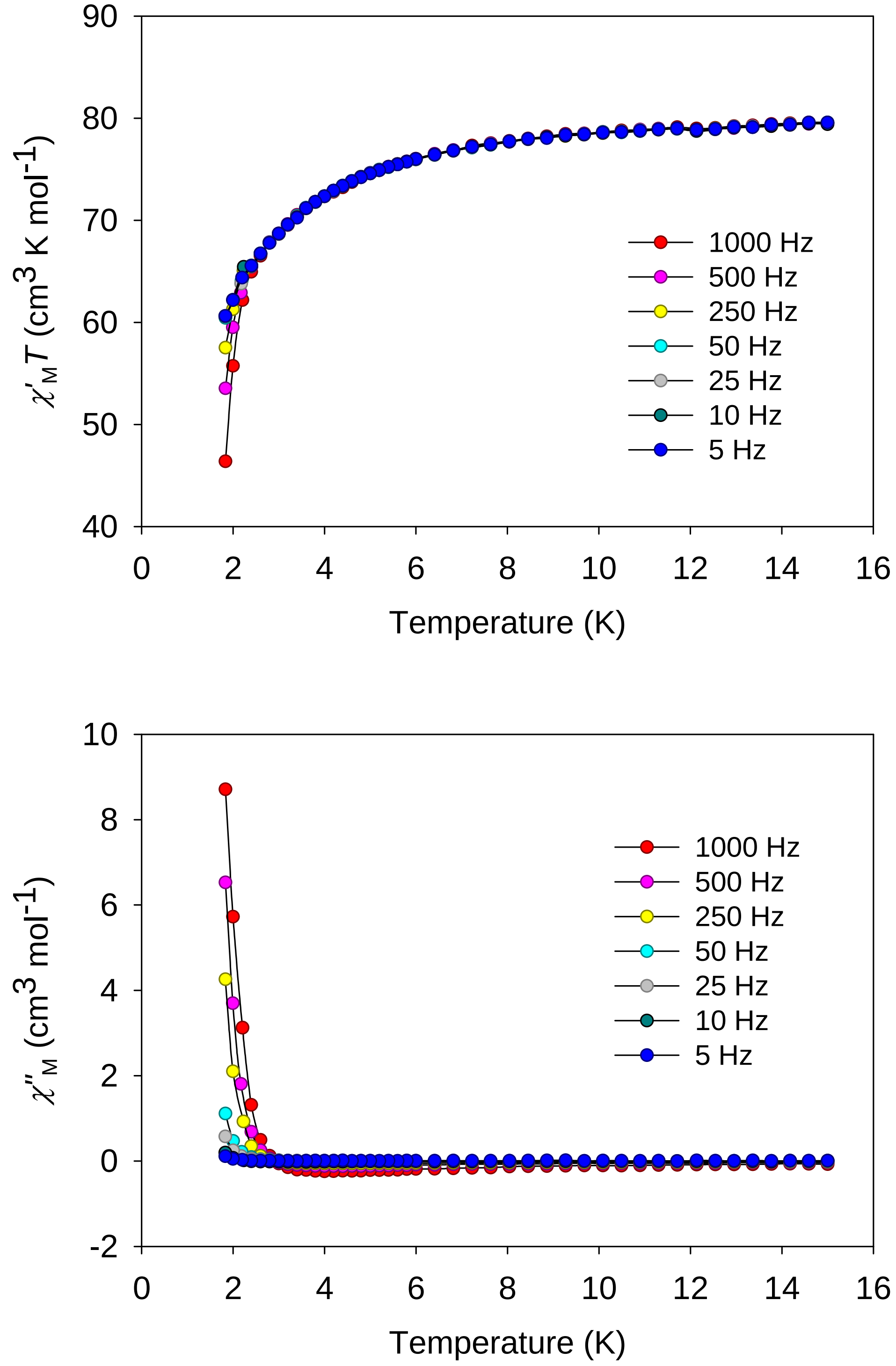


**Figure S13**. Plot of in-phase ($\chi'_M$, as $\chi'_M T$) and out of-phase ($\chi''$) ac susceptibility signal versus temperature for a micro crystalline sample of complex **6** in a 3.5G field oscillating at the indicated frequencies.

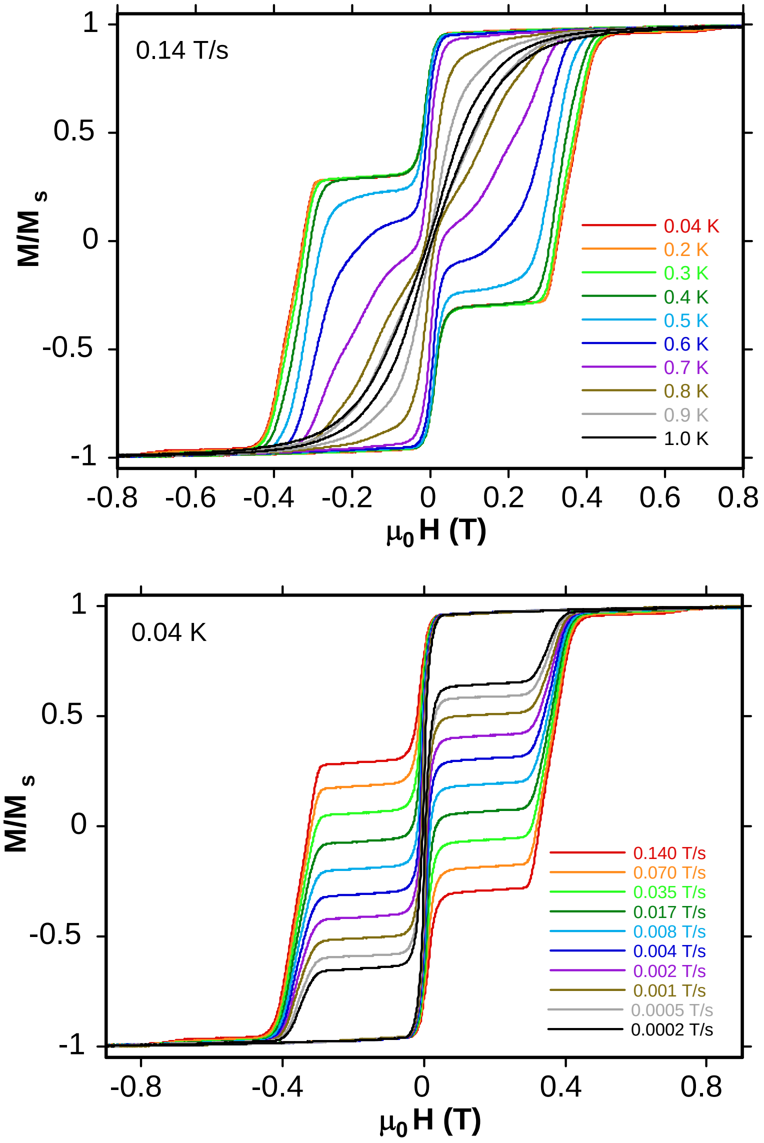
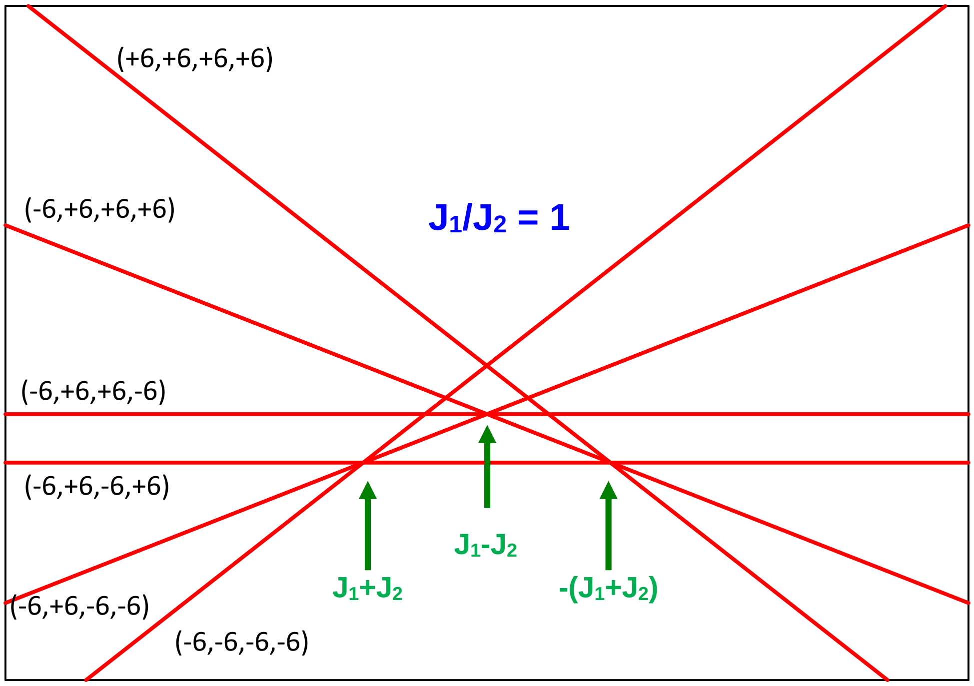


**Figure S14**. Hysteresis loops for monomer **2**·3CH$_2$Cl$_2$ at the indicated temperatures and field sweep rates; reproduced from ref. 75.



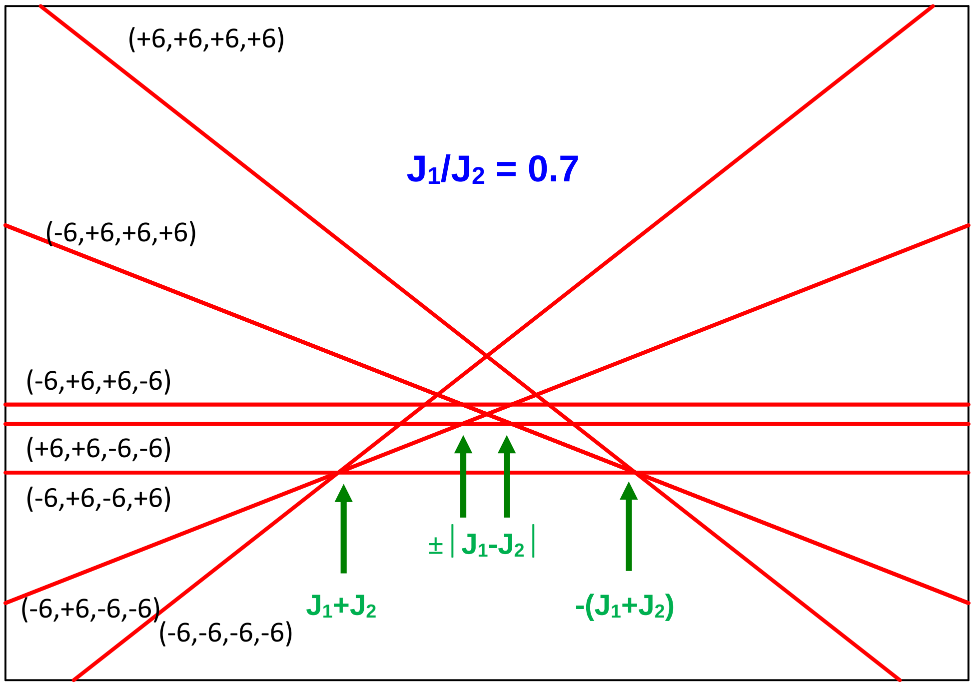


**Figure S15**. Spin state energy plot calculated for the rectangular $[Mn_3]_4$ tetramer with the indicated $J_1/J_2$ ratios

**UV spectroscopy**

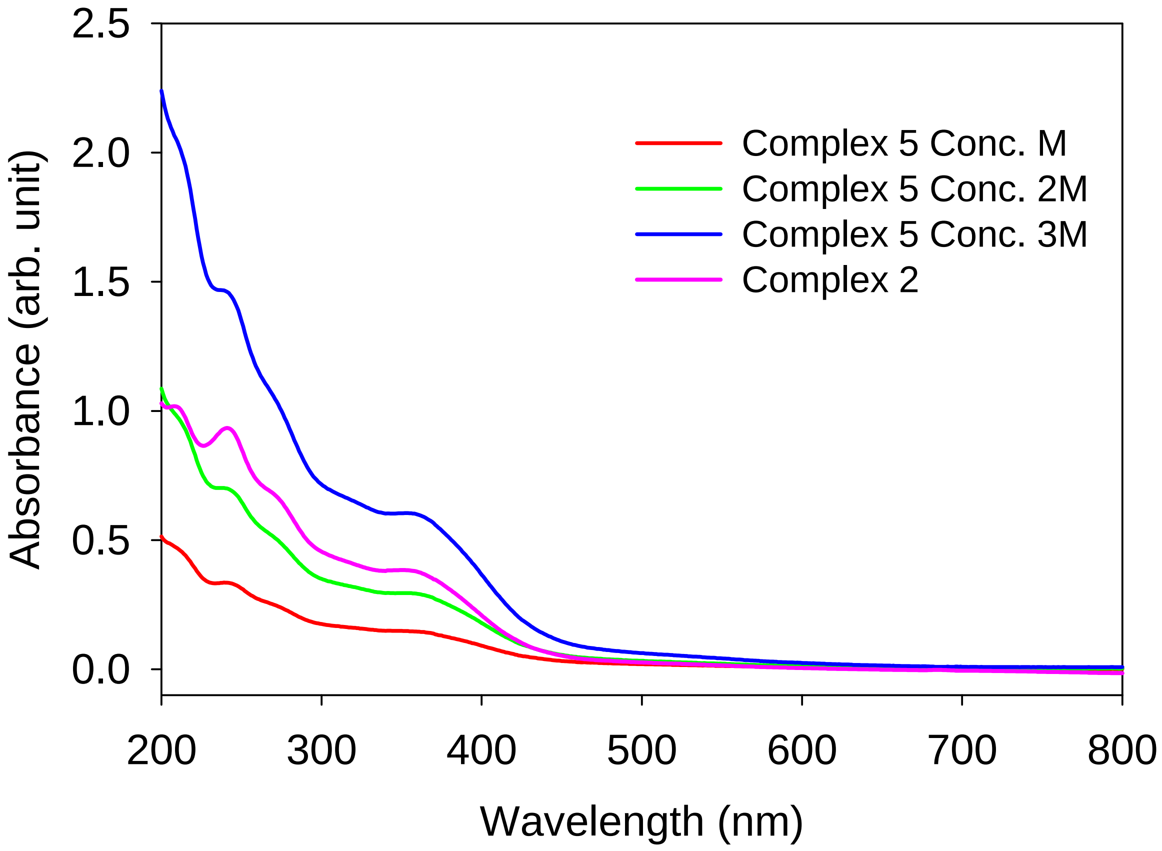


**Figure S20**. UV-Vis spectra of complexes **2** and **5** in acetonitrile. The data were collected with three different concentrations of complex **5**