

Supplementary information for

Magnetic properties of a manganese(III) chain with mono-atomic bridges: *catena*-MnF(salen)

Torben Birk, Kasper S. Pedersen, Stergios Piligkos, Christian Aa. Thuesen, Högni Weihe and Jesper Bendix

Experimental procedures:

All chemicals and solvents were purchased from Sigma-Aldrich or Fluka and used as received. The Schiff base ligand $H_2(\text{salen})$ (*N,N'*-ethylene-bis-salicylideneimine or 2,2'-[ethane-1,2-diylbis(azanylylidenemethanylyl-idene)]diphenol) was synthesized as described in Mason, T. *Ber. Dtsch. Chem. Ges.*, **1887**, 20(1), 267.

Synthesis: $H_2(\text{salen})$ (10 mmol, prepared by literature procedure) was treated with methanol (80 mL) and added solid MnF_3 (10 mmol, Aldrich) and Et_3N (20 mmol). The reaction mixture was heated to reflux for 35 min. added water (5 mL) followed by 5 min. of heating. The reaction mixture was allowed to cool slowly to room temperature before being filtered through a filter of paper and then added $tBuOMe$ (500 mL) drop-wise with simultaneous stirring. The brown crystalline product was isolated by filtration. Yield 68%. The product was recrystallized from methanol by diffusion of $tBuOMe$ over a period of several days. Elemental analysis: Elemental analysis calcd. (%) for $H_{14}C_{16}N_2O_2FMn$: H 4.15, C 56.48, N 8.23, F 5.58, Mn 16.15; found H 4.00, C 56.38, N 8.15, F 5.38, Mn 16.41.

The magnetic characterisation was performed on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 5 T dc magnet. Susceptibility measurements were conducted at $H_{dc} = 1$ kOe in the temperature range 1.8–300 K on a polycrystalline sample in a polycarbonate capsule. The susceptibility was corrected for diamagnetic contributions by means of Pascal constants. For magnetization measurements the field was swept to ± 5 T at 1.8 K at an average rate of 160 Oe min^{-1} . Ac experiments were conducted at selected frequencies between 50 Hz and 1500 Hz with $H_{ac} = 3.8$ Oe in the absence of a dc field.

Elemental analysis for C, H and N was performed with a CE Instrument: FLASH 1112 series EA, at the microanalytical laboratory, University of Copenhagen. Whereas F and Mn analysis was performed at the Mikroanalytisches Laboratorium KOLBE, Höhenweg 17, D-45470 Mülheim an der Ruhr.

UV/vis spectra were measured in a 1cm path-length quartz cell using a Perkin Elmer UV/vis lambda 2 spectrophotometer. Mid-range FTIR spectra of the compounds were recorded as KBr-pellets using a Bio-Rad Excalibur Series FTS 30000MX FT-IR spectrometer within the range of 4400–450 cm^{-1} . Fast atom bombardment (FAB, Xe ions, accelerated by 6 kV) mass spectra were recorded on a JEOL JMS-HX/HX110A tandem mass spectrometer (positive and negative ion detection). Matrix for FAB: *m*-nitrobenzyl alcohol (*m*-NBA).

Experimental data from X-ray structure determination

Mn(F)(salen) $M_r = 340.237$, $T = 122(1)$ K, Triclinic, Space group $P-1$, $a = 10.0400(9)$, $b = 15.4490(12)$, $c = 16.0420(17)$ Å, $\alpha = 108.164(9)$, $\beta = 103.874(10)$, $\gamma = 101.140(7)^\circ$, $V = 2196.3(3)$ Å³, $Z = 6$, $D_c = 1.543 \text{ g}\cdot\text{cm}^{-3}$, 123564 measured reflections of which 23068 ($R_{\text{int}} = 0.0506$), $R[F^2 > 2 \sigma(F^2)] = 0.0384$, $wR(F^2) = 0.0815$, CCDC 796782.

Supplementary data:

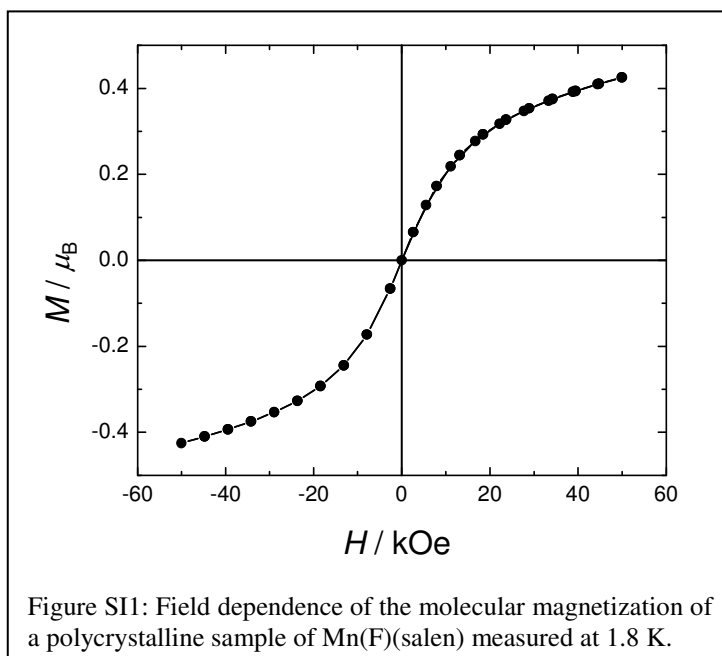
FT-IR (cm^{-1}): 3428(broad), 1649(s) $\nu_{\text{str}}(\text{C}=\text{N})$, 1599(s), 1541(s), 1446(s), 1334(m), 1297(s) $\nu_{\text{str}}(\text{C}-\text{O})$, 1195(m), 1147(m), 1127(m), 1029(m), 902(m), 744(s), 732(s), 630(m), 584(m), 460(s) $\nu_{\text{str}}(\text{Mn}-\text{N}/\text{O})$. Assignment based on: J. Chakraborty, B. Samanta, G. Pilet, S. Mitra, *Struct. Chem.*, 2006, **17**, 585.

UV/vis (MeOH): $\lambda[\text{nm}] \epsilon[10^3 \text{ M}^{-1}\cdot\text{cm}^{-1}]$: 216 (33.57), 236 (37.58), 281 (17.08), 307 (12.35), 349 (60.45), 397 (46.76). MS(FAB+): *m*-NBA $m/z = 340.04$ [M^+], 321.08[M-F]. MS(FBA-): *m*-NBA $m/z = 339.42$ [M-H].

Crystals grown for X-ray by: Mn(F)(salen) in MeOH (0.090 g / 20 mL) is placed together with Et₂O in a vacuum dessicator.

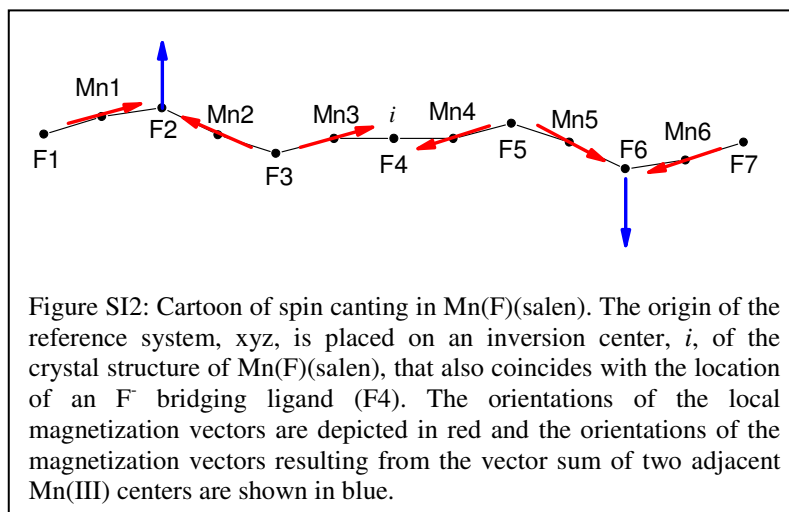
Field-dependence of the magnetic moment of Mn(F)(salen):

The fast rise of the residual molecular magnetization of Mn(F)(salen) with magnetic field at 1.8 K shown in Figure ESI1, indicates the presence of a paramagnetic impurity in the measured polycrystalline sample. Assuming that the magnetic moment saturates at $0.15 \mu_B$ at a magnetic field of about 1 T (linear region) at 1.8 K, this leads to a χT product of the order of $0.17 \text{ cm}^3 \text{ K mol}^{-1}$ at this field and temperature. This is about 5 % of that expected for a Mn(III) paramagnetic species ($3 \text{ cm}^3 \text{ K mol}^{-1}$). In the case that the detected residual magnetization came from the thermal population of excited spin states of total spin different than zero, the molecular magnetization would rise slowly with the magnetic field, eventually presenting a step behavior, in contrast to what observed for Mn(F)(salen).



Spin canting in Mn(F)(salen):

In Mn(F)(salen), the Mn(III) centers are tetragonally elongated by Jahn-Teller distortion, as discussed in the main manuscript text. Assuming that the local magnetic moment vectors are aligned with the Jahn-Teller distortion axes, there are two possible orientations for the local magnetic moments of the Mn(III) sites. These two directions are defined by the Mn-F bonds. The assumed orientations of the



local magnetic moments of the Mn(III) centers in Mn(F)(salen) are depicted in red in Figure SI2. The vector sums of the local magnetic moments of two adjacent Mn(III) sites are depicted in blue in Figure ESI2. One can easily see that the vector sum of the two Mn(III) centers located in the immediate proximity of the inversion center is null. The same is true for the vector sum of the summed magnetic moments resulting from centers Mn1 and Mn2 and centers Mn5 and Mn6. Thus, the macroscopic

magnetic moment in the chain structure of Mn(F)(salen) is zero because of the existence of the inversion center in conjunction with the topology of the Mn(III) centers.

In Figure ESI2 we have assumed some particular orientations for the local magnetic moments. In principle these can be oriented along arbitrary orientations, that have however to be related by the inversion center. Thus, the arguments presented above are also valid for arbitrary orientations of the local magnetic moments. These symmetry considerations also rationalize the absence of ordering in Mn(F)(salen), which is observed for some Mn(III) chains with longer Mn-Mn distances.^[1]

High-temperature expansions

For large spin systems, it is computationally impossible to diagonalise the full energy matrix. A useful method to extract spin Hamiltonian parameters from experimental data is instead through the high temperature expansion (HTE).^[2-5] In general, the partition function Z can be rewritten^[2]:

$$Z = \sum_i \exp(-\beta E_i) = \text{tr} \left\{ \exp(-\beta \hat{H}) \right\}$$

Where $\beta = (k_B T)^{-1}$. The summation is over all states and “tr” stands for the trace of the matrix representation. To avoid any diagonalisation, in the HTE, the exponential is evaluated as a power series around $\beta = 0$:

$$Z = \sum_{n=0}^{\infty} \frac{(-\beta)^n}{n!} \text{tr} \{ \hat{H}^n \}$$

From this, the susceptibility may be calculated in the usual way^[3]:

$$\chi_m = \mu_0 N_A \beta^{-1} \frac{\partial^2}{\partial B^2} \ln Z$$

Via in-house software^[4], we have calculated the expansion up to order 13 for rings with 2 to 13 centers. Large J makes the expansion-based susceptibilities diverge at rather high temperatures. As increased nuclearity has the same effect, it was not possible to model rings with higher nuclearity in

the temperature region where experimental data were available. The calculated expressions for χ_m/N were fit to the experimental susceptibility per ion in the temperature region 250 – 370 K. g was fixed to 2.

1. Arthur, J. L.; Moore, C. E. ; Rheingold, A. L.; Miller, J.S. *Inorg. Chem.*, **2011**, *50* , 2735–2737.
2. Rushbrooke, G. S.; Wood, P. *J. Mol. Phys.*, **1958**, *1*, 257-283.
3. Eifert, T.; Hüning, F.; Lueken, H.; Schmidt, P.; Thiele, G. *Chem. Phys. Lett.*, **2002**, *364*, 69-74.
4. Thuesen, C. A.; Weihe, H.; Bendix, J.; Piligkos, S.; Mønsted, O. *Dalton Trans.* **2010**, *39*, 4882-4885.
5. Schmidt, H.-J.; Schnack, J.; Luban, M. *Phys. Rev. B*, **2001**, *64*, 224415.