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Jahn-Teller beads on a string:
Synthesis and magnetic properties of one-dimensional fluoride-bridged manganese(ɪɪɪ)-systems

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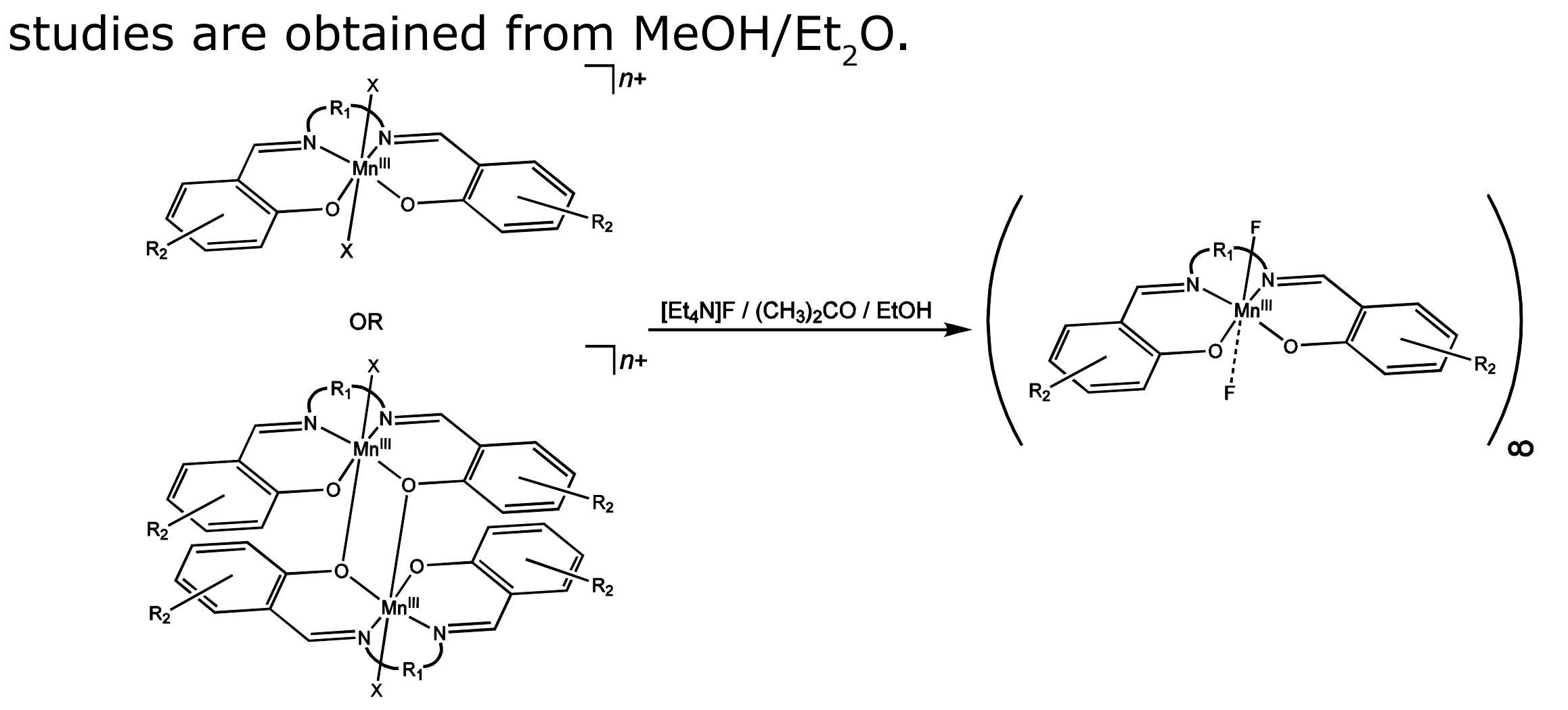
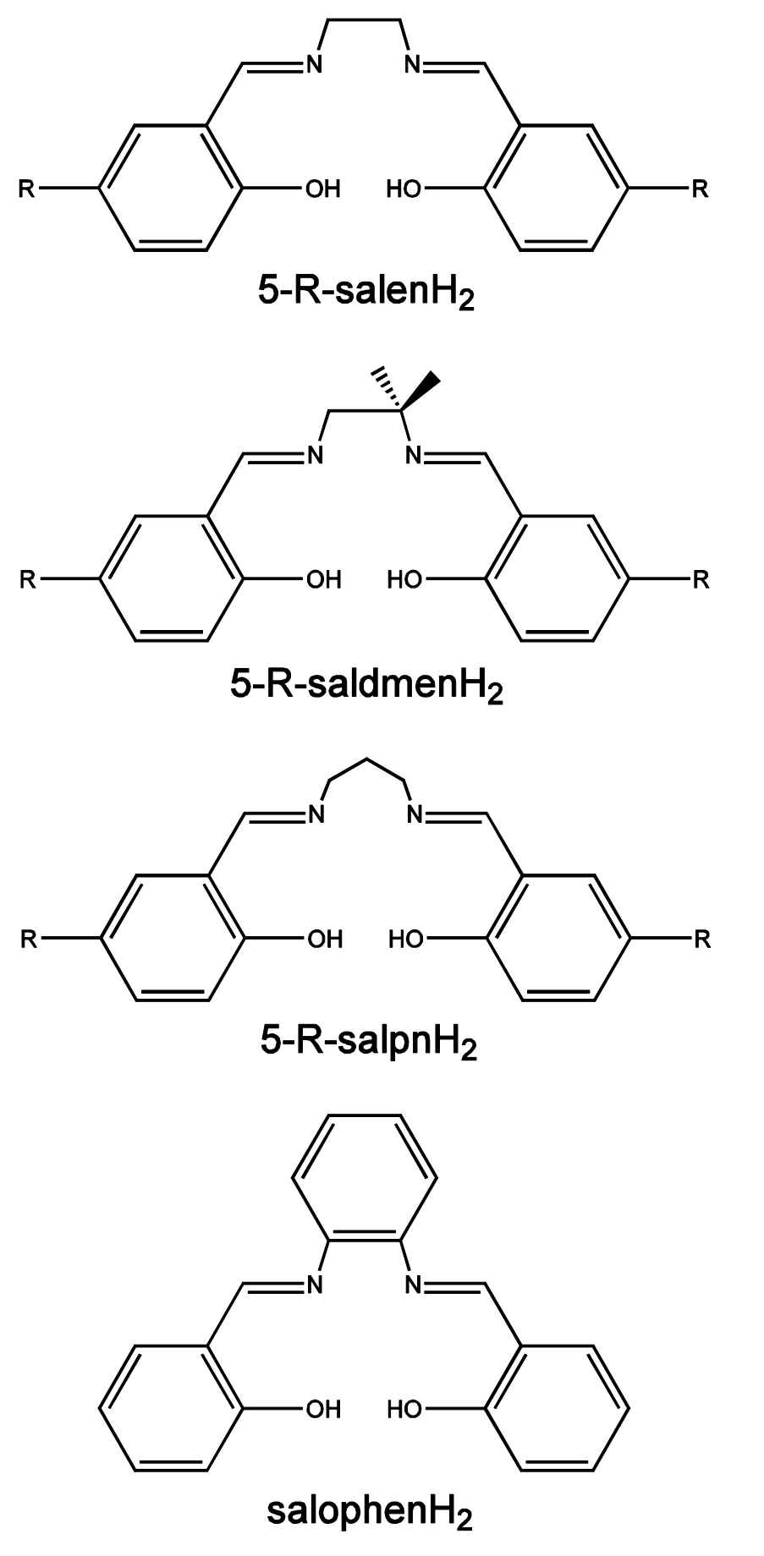
Introduction

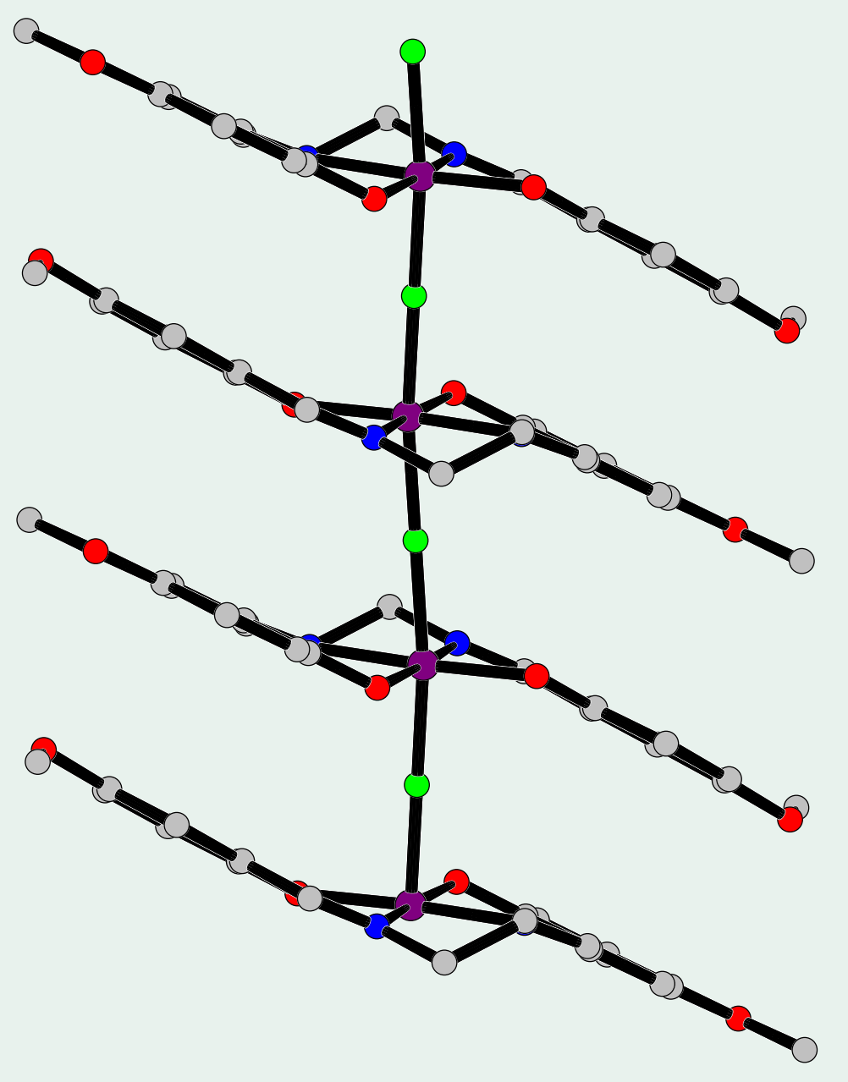
The system *catena*-[Mn^{III}(F)(salen)] (salenH$_2$ = *N*,*N'*-bis(salicylidene)ethylenediamine), as published by Birk *et al.*, [1], presented the first example of a fluoride-bridged chain based on the ubiquitous [Mn^{III}(salen)]$^+$-unit. To expand this class of compounds, a new and more general route to *catena*-[Mn(F)(Schiff base)]-systems has been developed. By varying the Schiff base ligand, systems with both strictly linear bridges as in *catena*-[Mn^{III}(F)(5-MeO-salen)]·½MeOH·½H$_2$O (**1**), somewhat bent bridges as in *catena*-[Mn^{III}(F)(5-Me-saldmen)]·MeOH (**2**) (164°), and even quite bent bridges as in *catena*-[Mn^{III}(F)(salpn)] (**3**) (146°) and *catena*-[Mn^{III}(F)(5-MeO-salpn)] (**4**) (144°), have been synthesized. In these compounds, the Jahn-Teller axis is along the Mn-F bonds, providing sufficient basicity of the fluoride ligand to make fluoride-bridging the structure-directing motif. Sizeable antiferromagnetic intrachain exchange interactions are found in all the compounds, emphasizing the potential of fluoride as a good mediator of magnetic exchange interaction in polynuclear complexes. By tuning the bridging angle and crystal packing, interesting magnetic properties arise, and in **3**, slow relaxation of the magnetization is observed. The slow relaxation is a result of a small canting of the spins on neighboring manganese(ɪɪɪ)-centers in the chains.

Synthesis

The synthetic protocol published for *catena*-[Mn^{III}(F)(salen)], [1], fails upon sufficient modification of the Schiff base type ligand. Instead *catena*-[Mn^{III}(F)(Schiff base)] systems can be prepared by addition of fluoride to [Mn^{III}(Schiff base)X$_2$]$^{n+}$ or [Mn$^{III}_2$(Schiff base)$_2$X$_2$]$^{n+}$ precursors (X = solvent molecules or triflate counterions) in acetone/ethanol binary solvents. Crystals suitable for single crystal X-ray diffraction studies are obtained from MeOH/Et$_2$O.







1

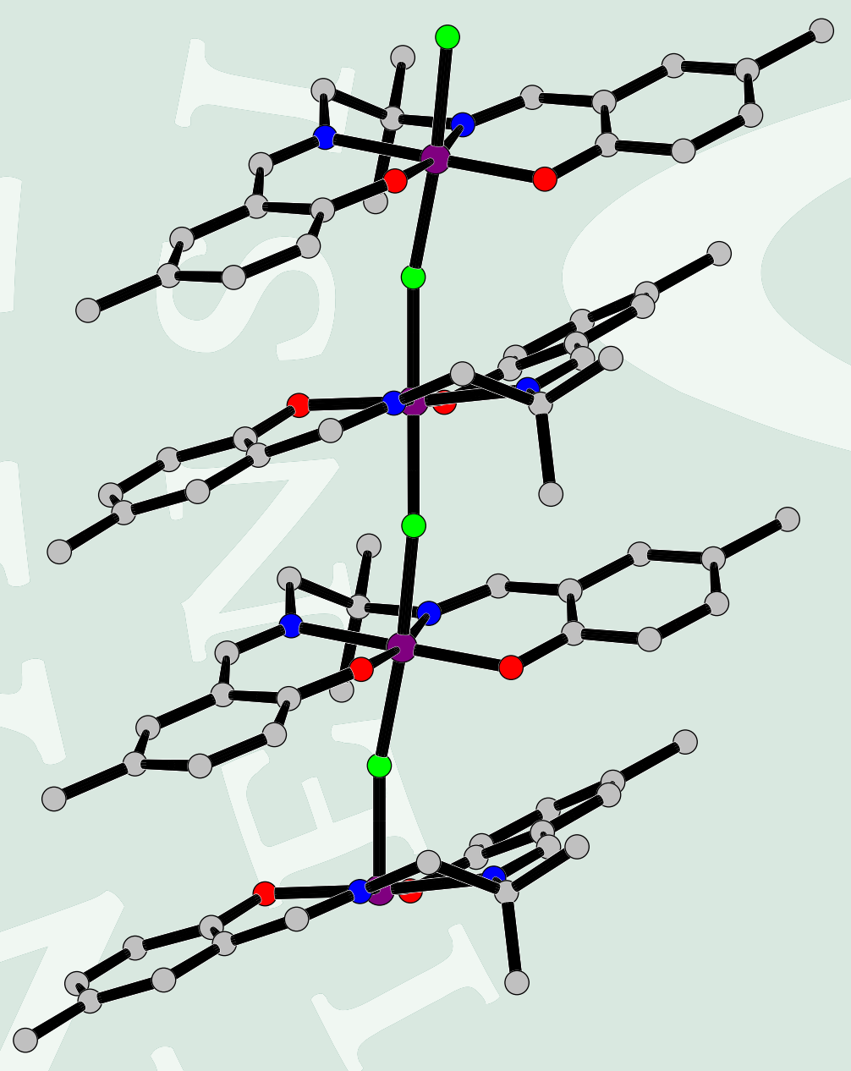
Space group: *P*-1
Mn-F-Mn = 180.00°
F-Mn-F = 169.99°
Mn-F = 2.0318 Å and 2.0329 Å

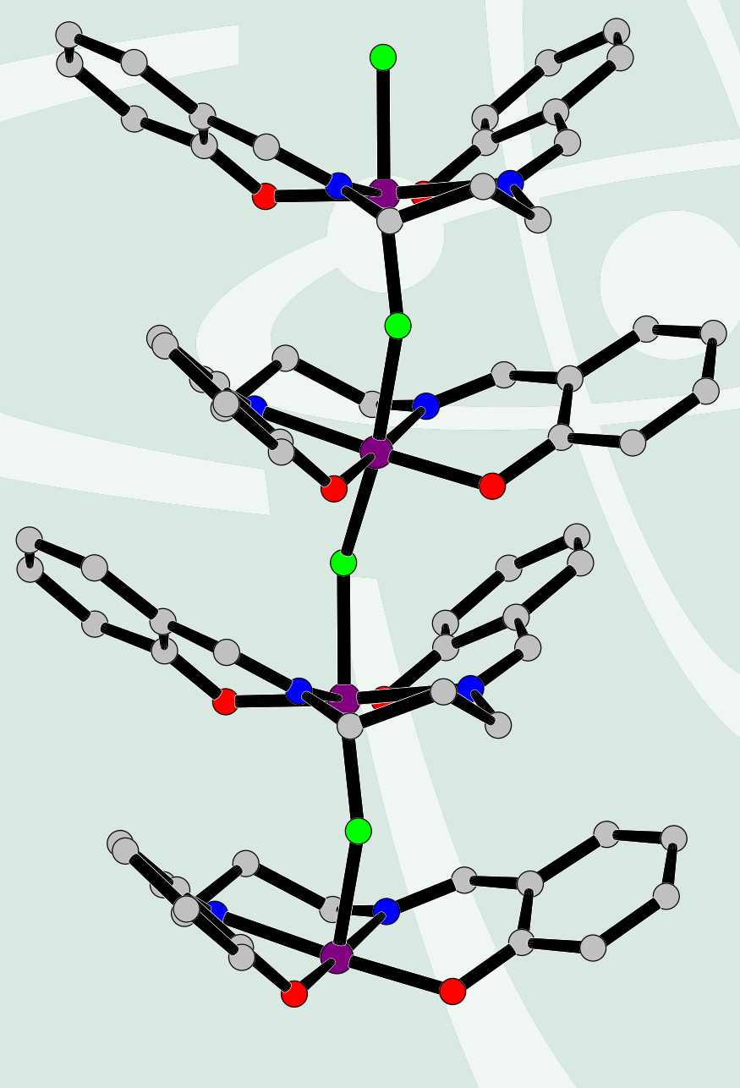
Brown blocks

Light brown needles

Space group: *P*2$_1$/*c*
Mn-F-Mn = 163.61°
F-Mn-F = 174.08°
Mn-F = 2.0678 Å and 2.0731 Å

2





Space group: *P*2$_1$/*m*
Mn-F-Mn = 143.52° and 144.21°
F-Mn-F = 167.60° and 168.28°
Mn-F = 2.0557 Å, 2.0588 Å,
2.0859 Å and 2.0927 Å

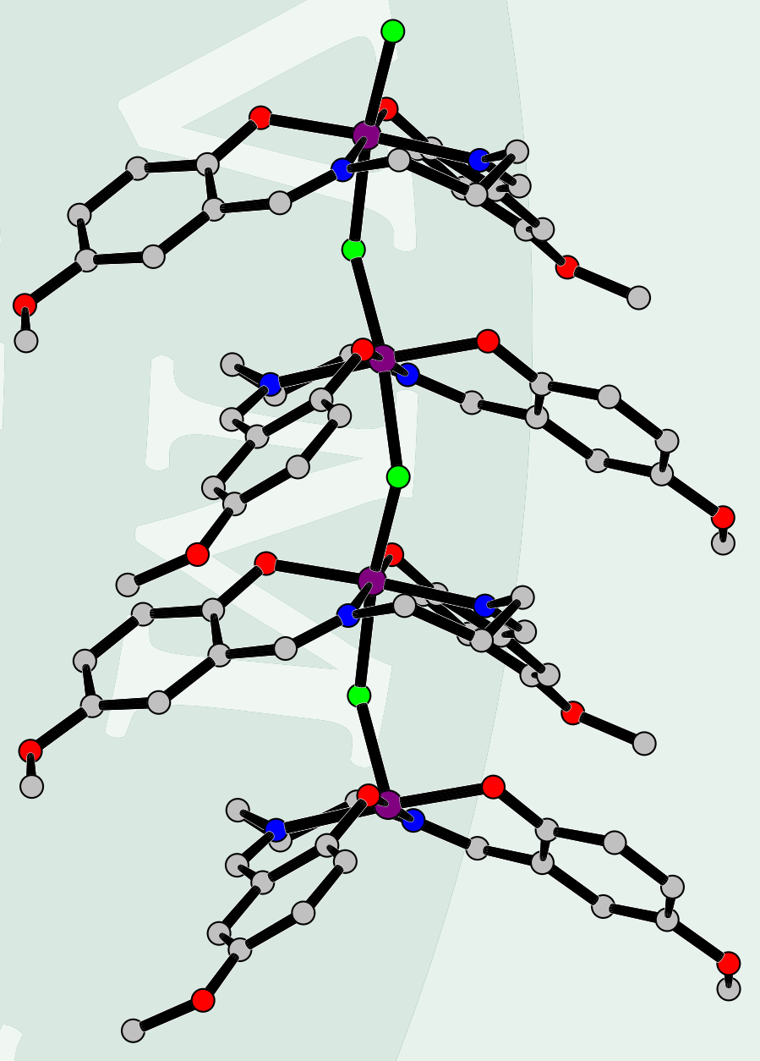
4

Dark green needles

Greenish brown needles

3

Space group: *P*2$_1$2$_1$2$_1$
Mn-F-Mn = 145.82°
F-Mn-F = 167.86°
Mn-F = 2.0530 Å and 2.0856 Å



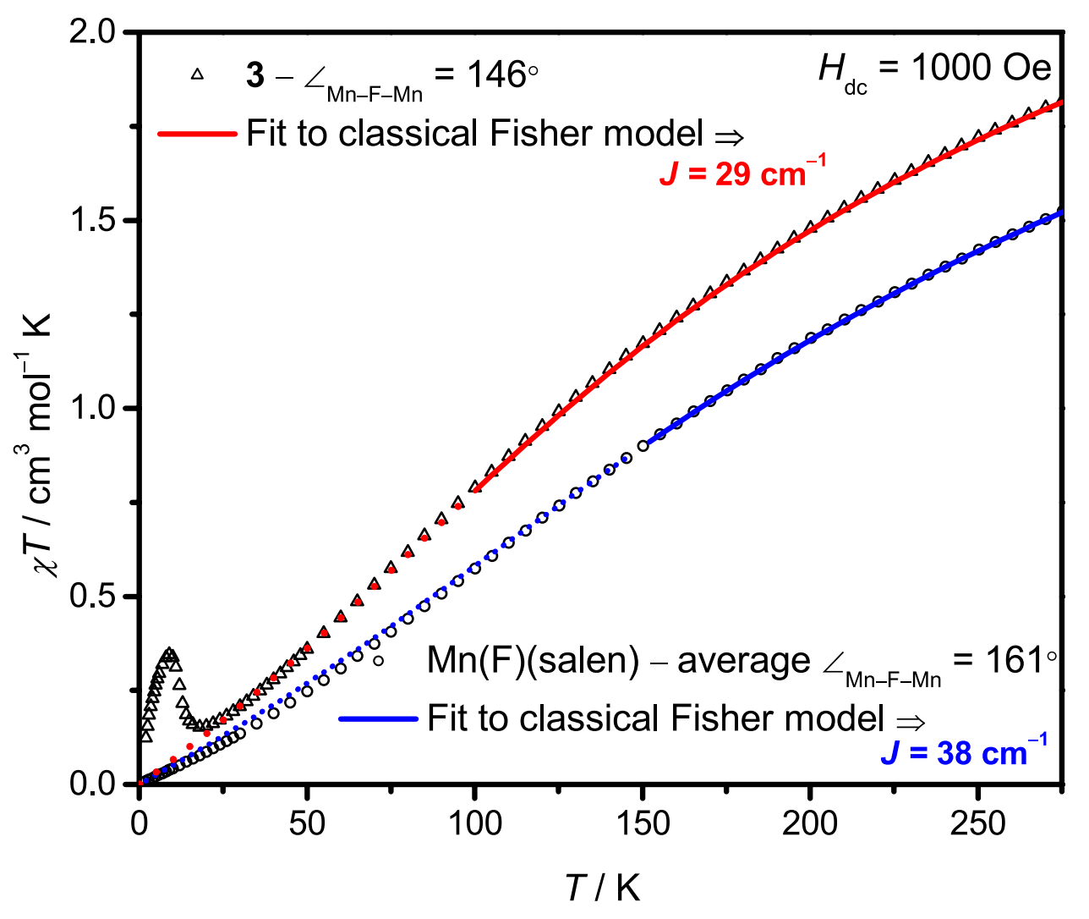
Magnetic hysteresis behavior of 3

In **3**, the bending of the fluoride bridges weakens the antiferromagnetic exchange interaction between neighboring manganese(ɪɪɪ)-centers, as evident from the fitting of the static magnetic susceptibility data to the isotropic Heisenberg Hamiltonian:

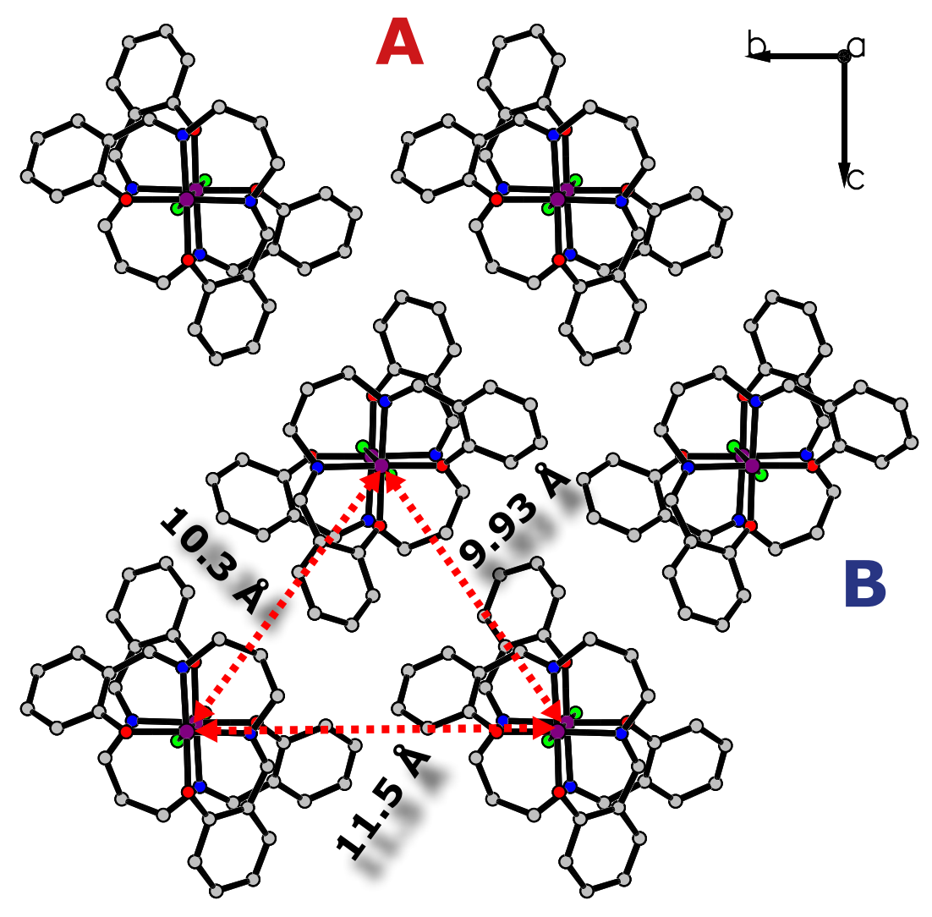
$$\hat{H} = J\sum_i \hat{S}_i\cdot\hat{S}_{i+1} + \mu_B gB\sum_i \hat{S}_i \qquad (1)$$

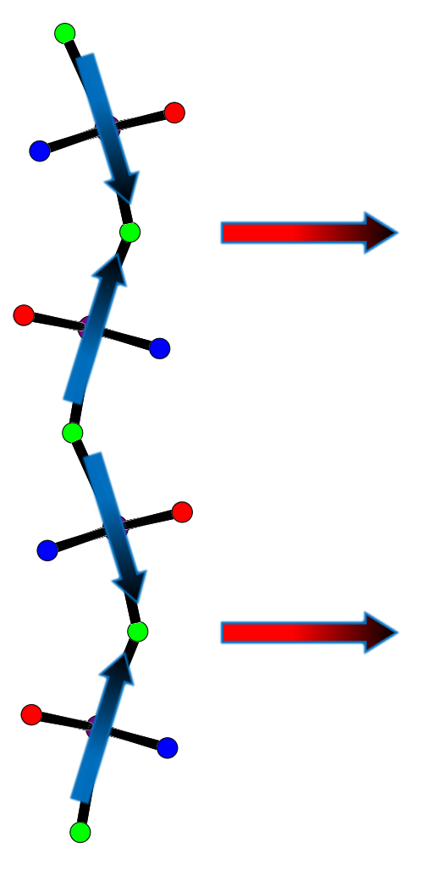
by use of the classical Fisher expression for the magnetic susceptibility of an infinite chain of classical spins, [2]:

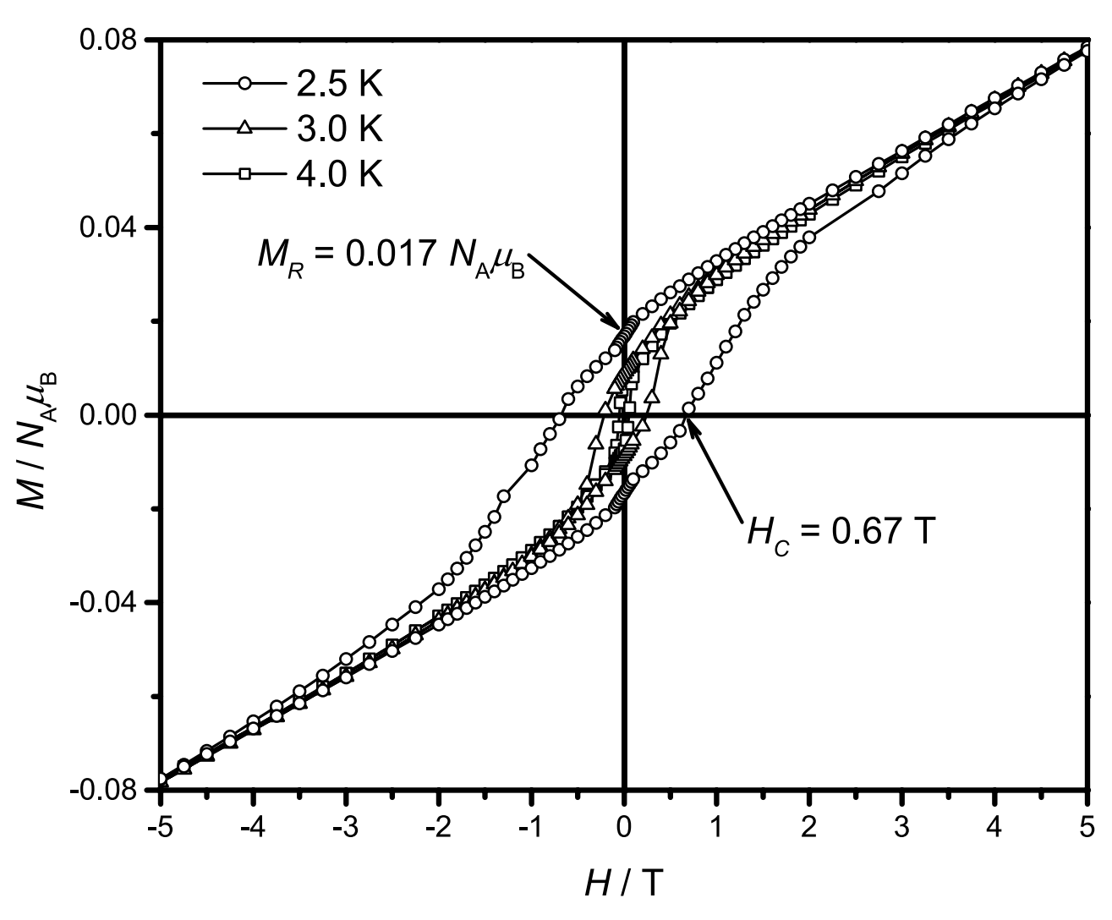
$$\chi = \frac{N_A g^2\mu_B^2 S(S+1)}{3kT}\frac{1+u}{1-u}\quad,\quad u = \left(\frac{kT}{S(S+1)J}\right) - \coth\left(\frac{S(S+1)J}{kT}\right)$$



The chain motif is generated by 2$_1$ screw axes, making neighboring manganese(ɪɪɪ)-centers magnetically inequivalent as well as generating two magnetically inequivalent chains within the unit cell, **A** and **B**. Due to the large local axial anisotropy (*D* ~ -3.5 cm^{-1}), each manganese(ɪɪɪ)-center has a preferred orientation of the magnetization, ➡. From magneto-structural considerations regarding the size of *J*, *D* and the angle between the easy axes and the chain axis, [3], a canting angle of 1.4° is calculated, meaning that each chain has a small uncompensated magnetic moment perpendicular to the chain, ➡. Below *T* = 8 K a phase transition to a phase showing magnetic bistability occurs, with the opening of a hysteresis loop at *T* = 4 K.

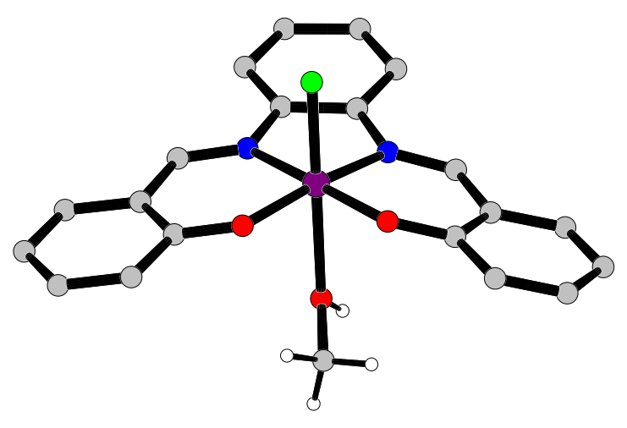




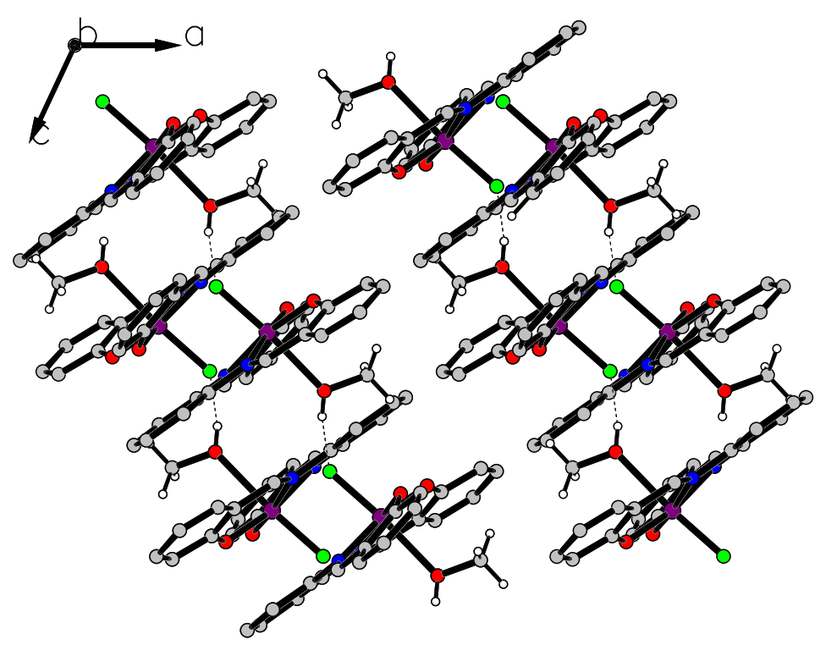


A mononuclear exception

If the general synthetic procedure is followed with [Mn^{III}(salophen)(CF$_3$SO$_3$)] as precursor, the outcome is the mononuclear complex *trans*-[Mn^{III}(F)(MeOH)(salophen)]. The complex forms a one-dimensional network through O-H···F hydrogen-bonding.



Space group: *P*2$_1$/*n*
F-Mn-O$_{MeOH}$ = 175.39°
Mn-F = 2.0546 Å
Mn-O$_{MeOH}$ = 2.4289 Å



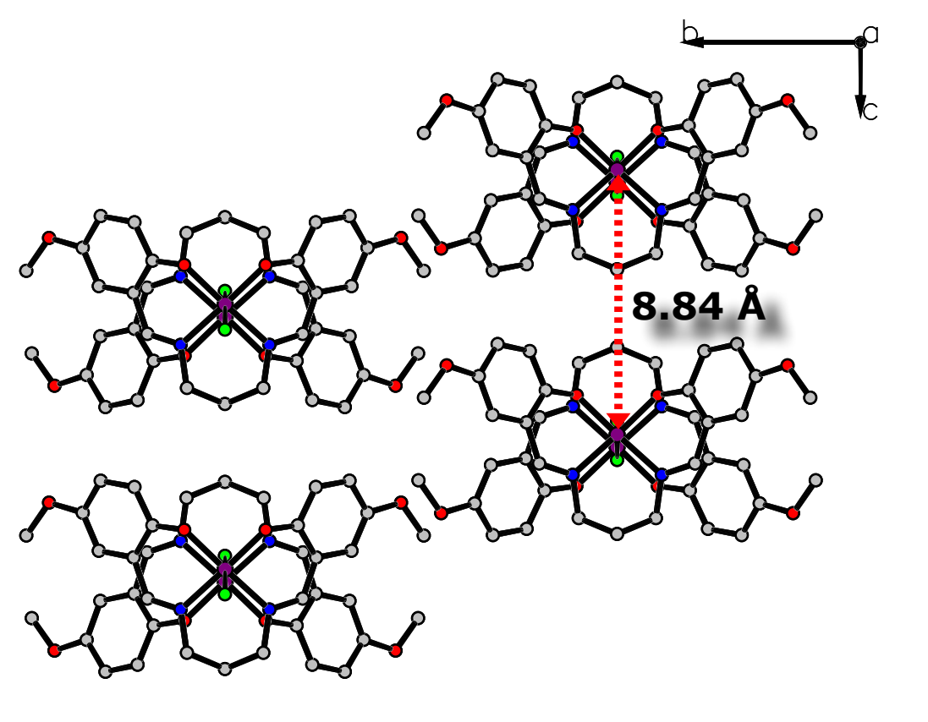
Reddish black blocks

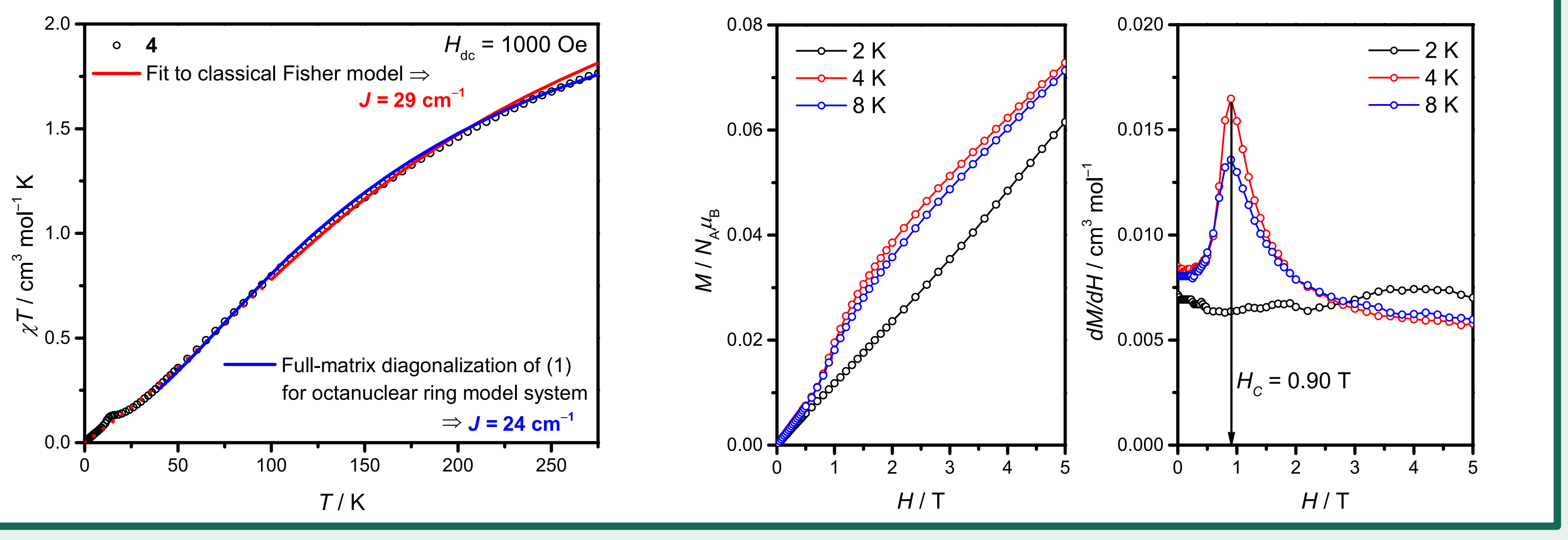
References

[1] Birk, T.; Pedersen, K. S.; Piligkos, S.; Thuesen, C. A.; Weihe, H.; Bendix, J., *Inorg. Chem.*, **2011**, *50*, 5312. [2] Fisher, M. E., *Am. J. Phys.*, **1968**, *32*, 343. [3] Mossin, S.; Weihe, H.; Sørensen, H. O.; Lima, N.; Sessoli, R., *Dalton Trans.*, **2004**, 632.

Antiferromagnetic ordering in 4

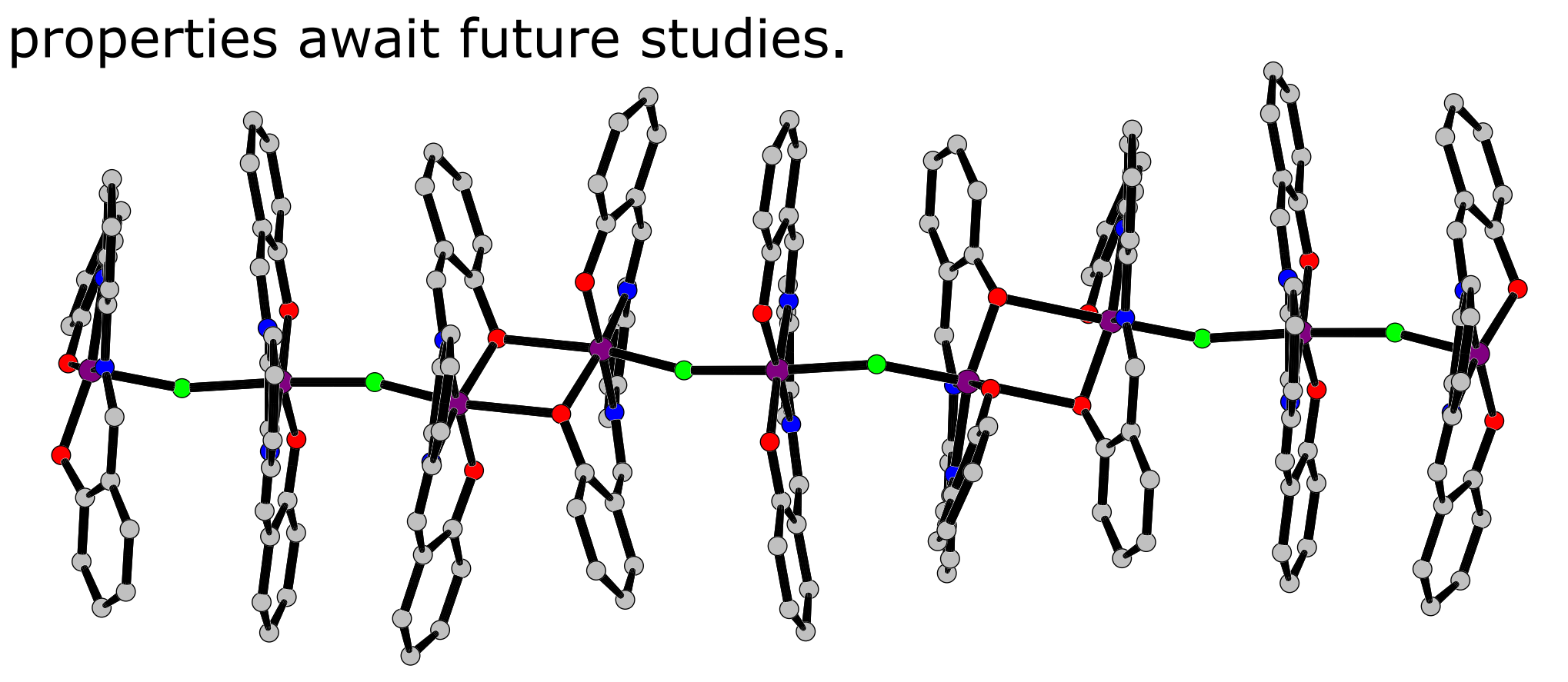
In **4**, a substantial antiferromagnetic intrachain exchange interaction is found, and following similar considerations as for **3**, an uncompensated magnetic moment perpendicular to the chains is expected. From maxima in the numerical field derivative of the magnetization and the low-temperature magnetic susceptibility, a transition to an antiferromagnetically ordered phase with T_N = 13 K and H_C = 0.90 T is concluded. The unusual behavior of *M* at *T* = 2 K might be a result of a transition to a structural phase with much stronger interchain interactions.

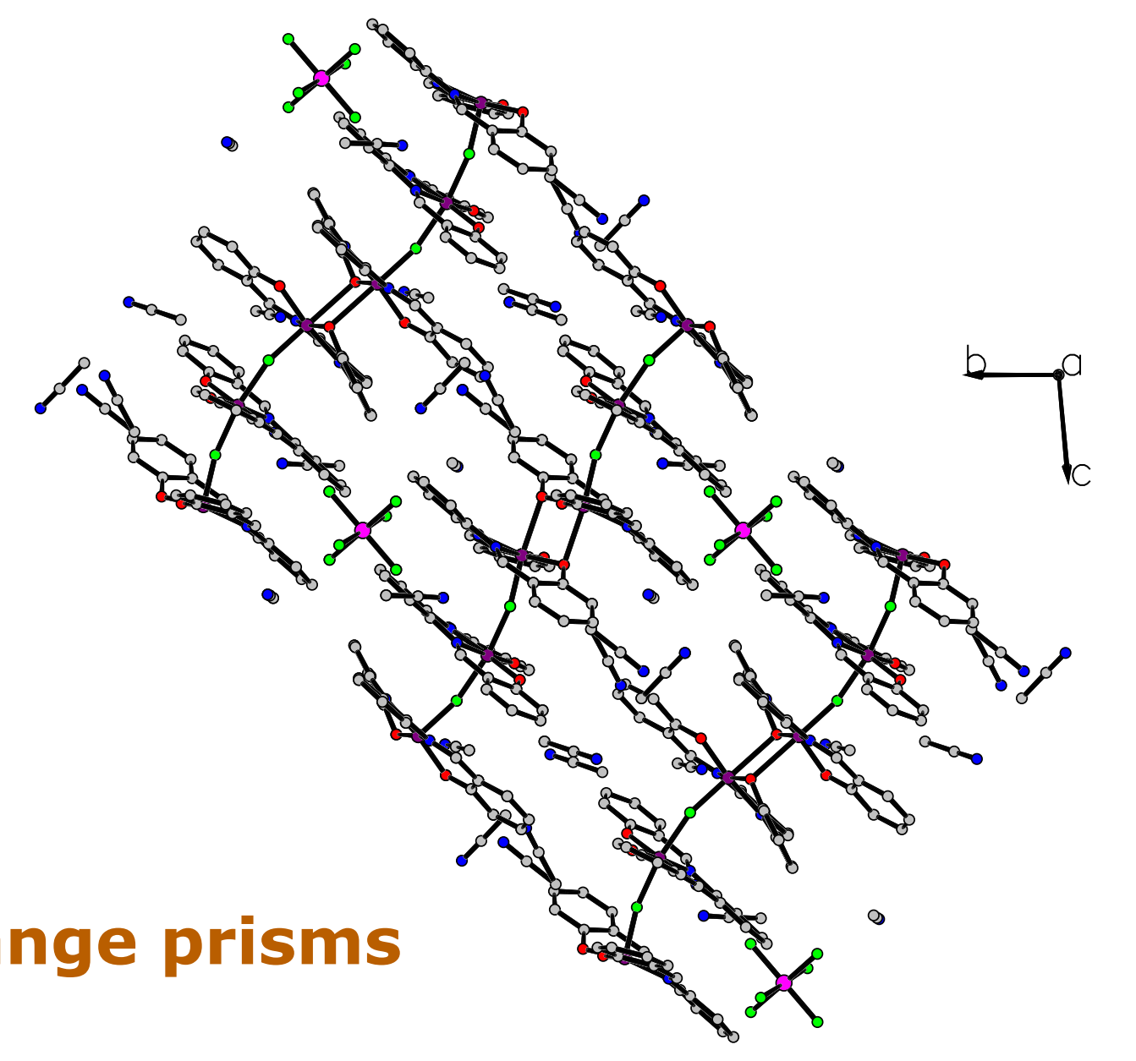




A different kind of chain

The reaction between [Mn^{III}(salophen)(CF$_3$SO$_3$)] and [Re^{IV}F$_6$]$^{2-}$ yields a fluoride-bridged one-dimensional manganese(ɪɪɪ) coordination polymer, consisting of both mononuclear [Mn^{III}(salophen)]$^+$-units and [Mn$^{III}_2$(salophen)$_2$]$^{2+}$ out-of-plane dimers, with octahedral [Re^{IV}F$_6$]$^{2-}$ counterions neutralizing the charge of the chains. The fluoride linkers are believed to stem from a possibly redox promoted fluoride abstraction from the otherwise robust hexafluoridorhenate(ɪᴠ). The magnetic properties await future studies.





Space group: *P*-1
F-Mn-F = 156.67° and 164.44°
Mn-F = 1.9836 Å, 1.9955 Å, 2.0721 Å and 2.1156 Å
(Mn····Mn)$_{\text{out-of-plane dimer}}$ = 3.259 Å and 3.349 Å

Dark orange prisms

Conclusions

This work shows the versatility of fluoride as bridging ligand, and therefore structure-directing motif, in polynuclear coordination compounds. The fluoride ligand mediates relatively strong magnetic exchange interaction with $J_{\text{Mn-Mn}}$ ~ 25 - 40 cm^{-1}. Through minor structural changes, *e.g.* tuning of the bridging angle, systems with highly different properties can be constructed.

Dr. Hab. Rodolphe Clérac (CNRS, Centre de Recherche Paul Pascal, France and University of Bordeaux, France) is thanked for fruitful discussions of the magnetic properties of these chain systems.