Supplementary Material (ESI) for Dalton Transactions
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Supporting Information:

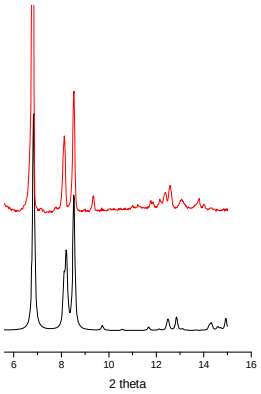
Comments to the syntheses and characterization.

Air oxidation of a methanolic solution containing 1 mmol of $[Mn(hfacac)_2]$, $saloxH_2$ and sodium azide in basic Et_3N (1:1:1:1 ratio, final volume 20 mL), gives a green solution after one hour. Layering this solution with Et_2O dark green crystalline product was obtained in three days. Yield 30%. Anal. Calc. for $C_{94}H_{108}Mn_{12}N_{24}O_{42}$, C, 38.86%, N, 11.57%, H, 3.75%; found C, 39.3%, N, 11.24%, H, 3.64%

Trials to extend the equivalent syntheses to other R-$saloxH_2$ derivatives have been unsuccessful until now. Reaction with $MesaloxH_2$ yield the octanuclear complex reported in *Chem. Commun*. **2007**, 2738-2740 (III, Scheme 1), whereas with EtsaloxH allows to the $Mn^{III}_4Mn^{IV}_2$ complex reported by Brechin et al in Dalton Trans. 2008, 6205-6210.

In addition to the probable equilibrium of more than one compound in the mother solution, slow basic solvolysis of the hexafluoroacetylacetonate molecule produces new and undesired ligands in the reaction medium and then, co-products can appear. One of them, obtained from solutions kept at room temperature for some weeks, is the conventional $[Mn_6]$ complex containing CF_3-COO^- as axial ligand.
Our experience in the syntheses of this $[Mn_{12}]$ complex indicates that the complex should be carefully synthesized and characterized and some key points should be taken into account to correctly reproduce the results:

- The syntheses of the $[Mn_{12}]$ complex often gives impure samples!
- Old solutions should be discarded because hfacac in basic medium suffer solvolysis processes and allows to non-desired co-products.
- IR spectrum is poorly sensitive to the impurities and IT IS NOT a good criterion of characterization.
- Excess of sodium azide in the medium gives non desired co-products containing an high N ratio (non characterized)
- χ''_M peaks should be “clean”. The presence of lower T (around 2.5 K) out of phase AC signals, as well double peaks or any asymmetry or shoulder for the peaks in the 4 K region, indicate the presence of impurities.
- In spite of the slow loss of crystallinity of the product, control of the main peaks of the powder X-ray spectrum is strongly encouraged as optimal criterion of characterization. The peaks at 8.23 and 8.53 are very sensitive and for a typical impure sample shift to larger angles (around 10º).



Powder spectrum of the measured sample. Black, calculated, red, experimental.

Figure S1 Detail of the intermolecular H-bonds (involving the Mn(6) atoms of neighbour molecules), which generates the 1D chain of clusters.

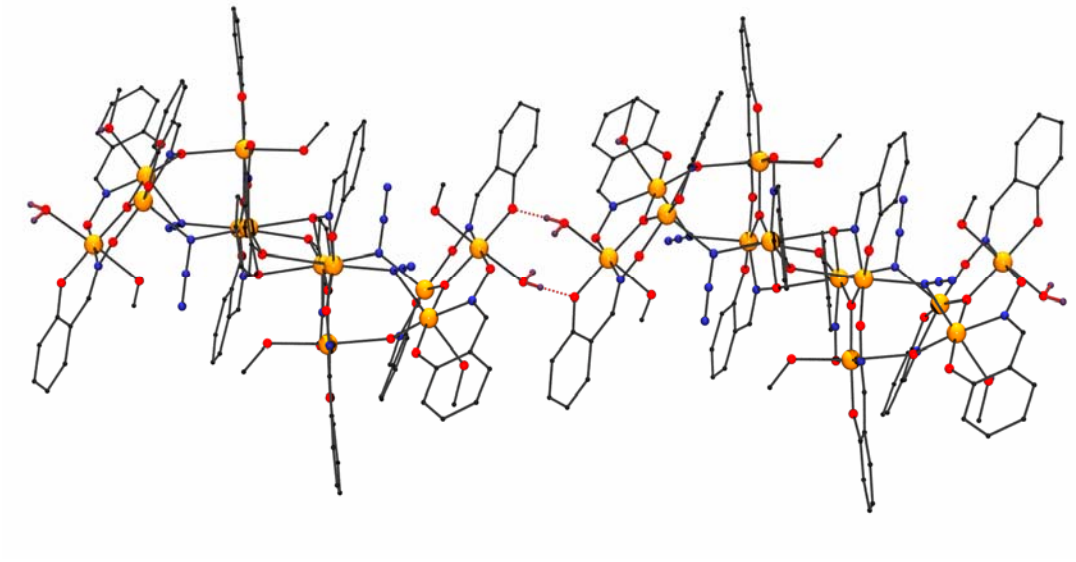


Figure S2 χ'_M vs T plot for variable frequencies (50, 135, 223, 367, 604, 997 and 1302 Hz).