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Elucidating the paramagnetic interactions of an inorganic–organic hybrid radical-functionalized Mn-Anderson cluster†

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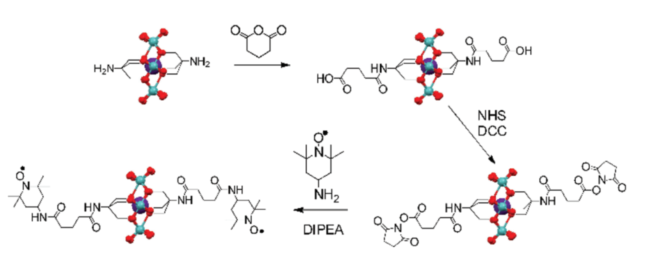
A family of six polyoxometalate-based magnetic compounds were synthesized by anchoring *N*-oxide type TEMPO radicals onto an Anderson type polyoxometalate cluster. The complexes were structurally characterised by single crystal X-ray diffraction and the intramolecular paramagnetic interactions between TEMPO radicals and Mn ions of the resulting hybrids were investigated in detail by electron paramagnetic resonance and the Evans NMR method.

Polyoxometalates (POMs) represent a vast class of negatively charged metal–oxo clusters[1] applicable to catalysis,[2] electronics,[3,4] and magnetism.[5] In particular, it has been reported that a highly redox stable POM, $[PMo_{12}O_{40}(VO)_2]^{n-}$, shows promise for molecular spin-qubit quantum computing, with its molecular magnetism tuneable through electrical manipulation.[6] Besides the fascinating redox properties of POMs, their enormous diversity in both size and structure makes them ideal building blocks to accommodate magnetic ions at specific sites, thus leading to magnetic clusters with definite topology and a tuneable coordination environment.[7,8]

Although big advances have been made in POM-based single molecular magnets, there are currently few examples of such systems based on covalently modified POM clusters. Hence in this context, we envision that it might be interesting to construct POM based magnetic molecules by anchoring stable organic radicals onto a metal–oxo cluster, and investigate the intramolecular magnetic interactions. Here we chose the Mn-Anderson cluster,[9] $[MnMo_6O_{24}\{(CH_2)_3CNH_2\}]^{3-}$, as the platform and covalently attached 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO) radicals on both sides of it. The magnetic properties of the resulting organic–inorganic hybrids were preliminarily monitored by electron paramagnetic resonance (EPR), and the interactions between the TEMPO radicals and the center Mn^{III} ion were investigated systematically using the Evans NMR method, which has rarely been applied in POM chemistry.

The Evans method, first developed in 1959,[10] has become a standard method to measure the magnetic susceptibility and unpaired electrons of inorganic complexes by using a NMR spectrometer.[11–13] Evans NMR is performed in a diamagnetic solvent, and relies on the effect of the dissolved paramagnetic sample on the chemical shift of a reference compound, usually the solvent.[14,15] The data are readily acquired by collecting the ^1H NMR spectrum of the paramagnetic sample that contains a capillary insert of pure solvent as a reference.

The general synthetic procedure for the TEMPO-functionalized Mn-Anderson cluster is depicted in Scheme 1. It contains three steps: first, the carboxylic acid modification of the Mn-Anderson cluster using glutaric anhydride; second, *N*-hydroxysuccinimide (NHS) activation; and third, amidation reaction using 4-amino-TEMPO. The biradical POM hybrid, $[(n\text{-}C_4H_9)_4N]_3[MnMo_6O_{24}\{(CH_2)_3CNHCO(CH_2)_3CONHC_9H_{17}NO\}_2]$, is designated as **1-Mn**. Similarly, an analogous compound **2-Mn**, $[(n\text{-}C_4H_9)_4N]_3[MnMo_6O_{24}\{(CH_2)_3CNHCO(CH_2)_2CONHC_9H_{17}NO\}_2]$, with a shorter alkyl chain, and an Al^{III} centered Anderson hybrid iso-



Scheme 1 General synthetic procedure of **1-Mn**. Colour code: Mo, teal; Mn, violet; and O, red.

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structure **3-Al**, $[(n\text{-}C_4H_9)_4N]_3[AlMo_6O_{24}\{(CH_2)_3CCH_2O\text{-}CO(CH_2)_2CONHC_9H_{17}NO\}_2]$, were prepared for comparison (see the ESI† for details).

The biradical hybrids were characterized by FT-IR, ESI-MS, elemental analysis and single-crystal X-ray diffraction. Taking **1-Mn** as an example, the FT-IR spectrum shows typical bands for an Anderson cluster at 940–890 cm^{-1} (Mo=O) and 650 cm^{-1} (Mo–O–Mo), while the vibration of the amide bonds can be found at 1645 cm^{-1}. The molecular ion peak of **1-Mn** in the ESI-MS spectrum is attributed to m/z = 2174.40 ($\{[\mathbf{1\text{-}Mn}]\text{-}TBA\}^{1-}$). The X-ray structure of **1-Mn** is shown in Fig. 1. It crystallizes in a triclinic system with a $P\bar{1}$ space group. Two unique half molecules (α and β) were found in the asymmetrical unit. The Mn atoms in each half molecule locate on an inversion centre to generate the whole molecule. α and β differ in the conformation of TEMPO with the N–O lengths and related C–N–C angles being very close to each other (Fig. 1A). Though slightly different, these geometrical parameters are all within the range of six-membered ring nitroxide.[16] In crystal packing mode, each α molecule is surrounded by four β molecules at the ac plane, giving rise to a radical layer which further stacks along the b axis (Fig. 1B). No intermolecular contacts of TEMPO radicals are observed within the packing layer, or between layers. Any two N–O groups in the crystal packing are separated by more than 5 Å.

The magnetic properties of these organic–inorganic biradicals were first investigated by EPR spectroscopy. As shown in Fig. 2, all the compounds exhibit the typical three-line signal of TEMPO due to the hyperfine splitting of the radical electrons with the nitrogen nucleus (I = 1),[17] which indicates the absence of spin coupling between the two TEMPO groups within the biradical hybrid. This behaviour is expected since the N···N distance of the two TEMPO radicals within a molecule is too far (*ca.* 25 Å) to allow for strong *J*-coupling between the unpaired electrons.[18,19] High-spin manganese(III) (d^4, S = 2) is archetypical of non-Kramers ions resulting in Mn^{III} centres, which are "EPR-silent" due to a zero-field-splitting with an energy splitting higher than the microwave frequency used (X-Band).[20,21] The possible signals resulting from the excited state could not be detected, due to the strong signal of the TEMPO radical. However, comparison of the EPR spectra of **1-Mn** and **2-Mn** with that of **3-Al** allowed us to conclude that the paramagnetic Mn^{III} has no effect on TEMPO radicals. To further confirm this, the Evans NMR method was adopted to explore the magnetic properties of these biradical hybrids.

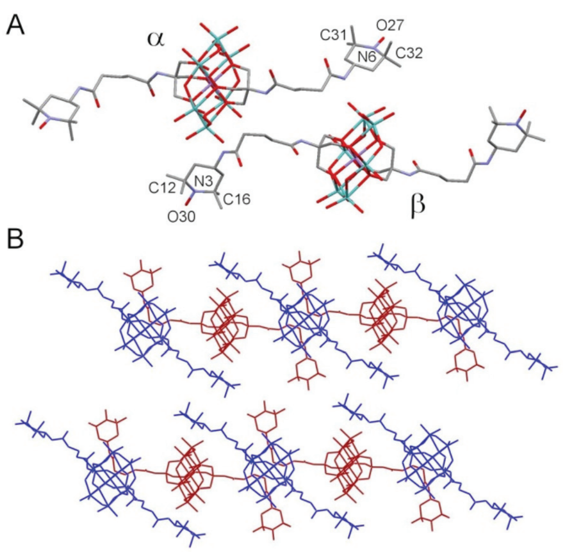

Fig. 1 (A) The single-crystal structure of **1-Mn**, and (B) the crystal packing mode of **1-Mn** viewed along the *a* axis: the α molecule is shown in red and the β molecule in blue. Colour code: Mo, teal; Mn, violet; and O, red; N, blue; and C, grey. H atoms, TBA counter cations, and solvent molecules are omitted for clarity.

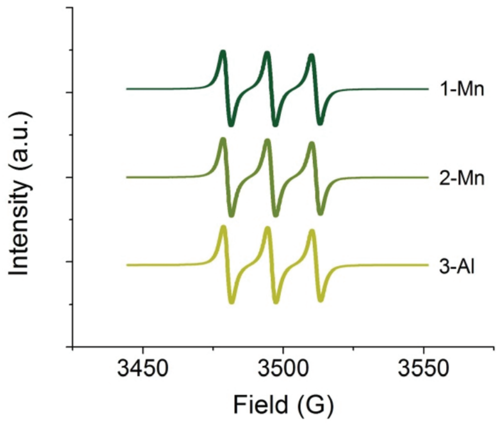

Fig. 2 The EPR spectra of **1-Mn**, **2-Mn** and **3-Al** obtained in acetonitrile solutions (1×10^{-4} M) at room temperature.

Even though Evans NMR has been proved to be an effective method to study the solution state magnetic susceptibility of coordination complexes, attempts to extend it in metal–oxo clusters, including the organically modified ones, have to our knowledge not been explored. Thus, in our first trial the paramagnetic properties of the Mn-Anderson cluster were examined (see the ESI† for experimental details). The calculation of the magnetic moment is given by eqn (1):

$$\mu_{\exp} = 2.828\sqrt{\frac{3 \times T}{4\pi \times 10^6} \times \left[\left(\frac{\Delta_{\text{ppm}}}{c}\right)^{\text{para}} - \left(\frac{\Delta_{\text{ppm}}}{c}\right)^{\text{dia}}\right]} \qquad (1)$$

where Δ_{ppm} is the chemical shift of DMSO-d_6 in ppm, c is the molar concentration of the solute (mol mL^{-1}), T is the probe temperature (K), and the *para* and *dia* superscripts stand for the paramagnetic and diamagnetic contributions, respectively. According to Piguet's work,[15] the diamagnetic contribution of large paramagnetic assembly, here in our case the Mn-Anderson cluster, can be eliminated by deducting the diamagnetic contribution of an analogous assembly, where the paramagnetic metal ion is replaced by a proper diamagnetic one. Therefore, the Al^{III} centered Anderson cluster $[(n\text{-}C_4H_9)_4N]_3[AlMo_6O_{24}\{(CH_2)_3C\text{-}CH_2OH\}_2]$ (**3a**) and $[(n\text{-}C_4H_9)_4N]_3[AlMo_6O_{24}\{(CH_2)_3CCH_2OCO\text{-}(CH_2)_2COOH\}_2]$ (**3b**) were used. However, neither of these two Al^{III} analogues produced solvent chemical shifts; thus the diamagnetic contribution can be taken as zero (Fig. S6†). Thereafter, the magnetic moment (μ_{exp}) of the Mn-Anderson cluster is found to be 4.69, which coincides with the theoretical result (4.90) obtained using eqn (2):

$$\mu_{\text{theo}} = \sqrt{n(n+2)} \tag{2}$$

where n is the number of unpaired electrons.

The implementation of the Evans method in the Mn-Anderson cluster inspired us to go further for biradical hybrids. As shown in Fig. 3, the solvent chemical shifts in both **1-Mn** and **3-Al** are observed. The corresponding magnetic moments are thus calculated based on eqn (1), and the results are listed in Table 1. The μ_{exp} value of **1-Mn** is found to be very close to μ_{theo} (low spin), suggesting that Mn^{III} might adopt a low spin state, that is, two unpaired electrons at the outer 3d orbital.

However, this finding is contradictory to that suggested by X-ray diffraction, as all the Mn–O bond lengths of **1-Mn** are similar to those of previously reported Mn-Anderson POMs (Fig. S1†), which strongly indicates that the Mn^{III} ion in the biradical hybrid is still at its high spin state.[9] Similar phenomena are also observed in the case of **2-Mn**. As for **3-Al**, μ_{calc} is much smaller than μ_{theo}, which implies a weak antiferromagnetic coupling of the magnetic centres.

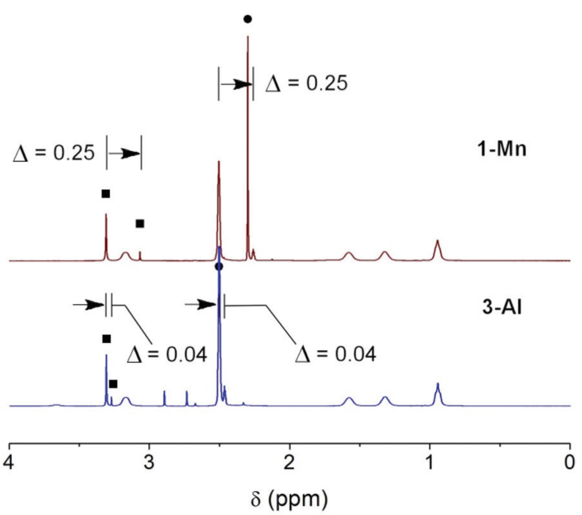

Fig. 3 The Evans NMR spectra of **1-Mn** and **3-Al**. Square and round dots indicate the solvent peaks of H_2O and DMSO, respectively. The chemical shifts of these solvents are labelled in the graph.

Table 1 Magnetic moments calculated by the Evans NMR method

	μ_{exp}	μ_{theo} (high)	μ_{theo} (low)
Mn-Anderson clusters[9]	4.69 ± 0.04	4.90 (4)	—
1-Mn	5.22 ± 0.13	6.93 (6)	4.90 (4)
2-Mn	5.16 ± 0.15	6.93 (6)	4.90 (4)
3-Al	2.23 ± 0.09	2.83 (2)	—
Mn^{III} in **1-Mn**	4.72 ± 0.14	4.90 (4)	2.83 (2)
Mn^{III} in **2-Mn**	4.65 ± 0.16	4.90 (4)	2.83 (2)

The last two columns are the theoretical magnetic moments with the number of unpaired electrons given in brackets.

As such, in order to obtain the magnetic moment of Mn^{III} in **1-Mn**, we hypothesize that the paramagnetic contribution of TEMPO may be eliminated by using **3-Al** as a reference compound, since these biradical hybrids are similar in both structure and molecular mass.[15] To prove this, a modified equation (eqn (3)) is used to calculate the magnetic moment of the Mn^{III} ion in **1-Mn**.

$$\mu_{\text{exp}}^{\text{Mn}} = 2.828\sqrt{\frac{3 \times T}{4\pi \times 10^{6}} \times \left[\left(\frac{\Delta_{\text{ppm}}}{c}\right)^{\text{1-Mn}} - \left(\frac{\Delta_{\text{ppm}}}{c}\right)^{\text{3-Al}}\right]} \tag{3}$$

As listed in Table 1, the μ_{calc} of Mn^{III} in **1-Mn** is found to be 4.72, which is very close to that of the Mn-Anderson cluster (4.69). This result is in agreement with the EPR (non-Kramers ion) and X-ray data and indicates a high spin state of Mn^{III}. In the case of **2-Mn**, the μ_{exp} of Mn^{III} is calculated as 4.65, which further validates that there is no spin coupling between Mn^{III} and the TEMPO radicals.

Conclusions

In conclusion, we have presented here an example of magnetic molecules that are prepared by covalently anchoring TEMPO radicals onto Anderson clusters. The resulting organic–inorganic biradicals have been fully characterized by various techniques such as ESI-MS and single-crystal X-ray diffraction. The solution state magnetic interactions between the TEMPO radicals and Mn^{III} ions have been investigated by EPR spectroscopy and Evans NMR. Though it seems that there might exist some spin coupling, close investigation reveals that such 'false' interaction is due to the magnetic susceptibility calculation of TEMPO radicals using the Evans method, which turns out to be unsuitable. Therefore, the paramagnetic contribution of TEMPO in such biradical hybrids should be taken into account to get the actual spin state of Mn^{III}.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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