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COMMUNICATION

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 the 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 clusters¹ applicable to catalysis,² electronics,³,⁴ and magnetism.⁵ In particular, it has been reported that a highly redox stable POM, [PMO₁₂O₄₀(VO₂)]⁶⁻, 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 tuneable coordination environment.⁷,⁸

Although big advances have been made on POM-based single molecular magnets, there currently is 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 bases magnetic molecules by anchoring stable organic radicals onto the metal-oxo cluster, and investigate the intramolecular magnetic interactions. Here we choose the Mn-Anderson cluster,⁹ [MnMo₆O₃₄(CH₃CNHCO(CH₂)₃CONH-C₄H₄NO₂)]²⁻, as the platform and covalently attach 2,2,6,6-tetramethyl-piperidin-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 Mn²⁺ 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.¹¹¹² The 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.¹³,¹⁴ The data is readily acquired by collecting the ³H NMR spectrum of the paramagnetic sample that contains a capillary insert of pure solvent as 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 Mn-Anderson cluster using glutaric anhydride; second, N-hydroxsuccinimide (NHS) activation; and third, amidation reaction using 4-amino-TEMPO. The biradical POM hybrid, [(n-C₄H₉)₄N][MnMo₆O₃₄(CH₃CNHCO(CH₂)₃CONH-C₄H₄NO₂)], is designated as 1-Mn. Similarly, an analogue compound 2-Mn, [(n-C₄H₉)₄N][MnMo₆O₃₄(CH₃CNHCO(CH₂)₃CONH-C₄H₄NO₂)], with shorter alkyl chain, and an Al₈ centered Anderson hybrids isostucture 3-Al, [(n-C₄H₉)₄N][AlMo₆O₃₄(CH₂)₃CC≡CH-O-CO(CH₂)₃CONH-C₄H₄NO₂], were prepared for comparisons (See SI for details).

Scheme 1 General synthetic procedure of 1-Mn. Colour code: Mo, Teal; Mn, Violet; and O, Red.

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

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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 ESI-MS spectrum is attributed to \(m/z = 2174.40\) ([1-Mn] TBA\(^+\)). The X-ray structure of 1-Mn is shown in Fig. 1. It crystallizes in a triclinic system with P-1 space group. Two unique half molecules (α and β) found in the asymmetrical unit. The Mn atoms in each half molecule locate on an inversion centre that is 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 very close to each other (Fig. 1A). Though slightly different, these geometrical parameters are all within the range of six-membered ring nitrooxide.\(^{16}\) In crystal packing mode, each α molecule is surrounded by four β molecules at the \(c\) 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 distant more than 5 Å.

However, comparison of the EPR spectra of 1-Mn and 2-Mn with that of 3-Al allow 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 view along \(a\) axis: a molecule in red and 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.

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).\(^{20,21}\) Possible signals resulting from the excited state could not be detected, due to the strong signal of the TEMPO radical.

Even though the Evans NMR has been proved to be an effective method to study the solution state magnetic susceptibility of coordination complexes, the 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 Mn-Anderson cluster were examined (See SI for experimental details). The calculation of the magnetic moment is given by Equation 1:

\[
\mu_{\text{exp}} = 2.824 \sqrt[3]{\frac{3\pi}{4n}} 10^{-6} \left[ \frac{\Delta_{\text{ppm}}}{\text{catom}} \text{para} - \frac{\Delta_{\text{ppm}}}{\text{cdiam}} \text{dia} \right] \tag{1}
\]

where \(\Delta_{\text{ppm}}\) is the chemical shift of DMSO-\(d_6\) in ppm, c is the molar concentration of the solute (mol/L), \(T\) is the probe temperature (K), and the para and dia superscripts stand for the paramagnetic and diamagnetic contributions, respectively. According to Piquet’s work,\(^{15}\) the diamagnetic contribution of large paramagnetic assembly, here in our case Mn-Anderson, 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 \([n-C_3H_7]_n\)[AlMo\(_6\)O\(_{19}\)(\(CH_3\)\(_2\)C-\(CH_3\)OH)]\(_3\) (3a) and \([n-C_3H_7]_n\)[AlMo\(_6\)O\(_{19}\)(\(CH_3\)\(_2\)CCH\(_2\)C(OH)\(_2\))]\(_3\) (3b) were used. However, neither of these two Al\(^{III}\) analogues produce shifts in solvent chemical shift, thus the diamagnetic contribution can be taken as zero (Fig. 56). Thereafter, the magnetic moment (\(\mu_{\text{exp}}\)) of Mn-Anderson is measured to be 4.69, which coincides with the theoretic result (4.90) obtained by Equation 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 Mn-Anderson inspired us to go further for the 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 Equation 1, and the results are listed in Table 1. The $\mu_{\text{exp}}$ value of 1-Mn is found to be very close to $\mu_{\text{theo}}$ (low spin), suggesting the Mn$^{III}$ might adopt a low spin state, that is, two unpaired electrons at the outer 3d orbital.

As listed in Table 1, the $\mu_{\text{calc}}$ of Mn$^{III}$ in 1-Mn is found to be 4.72, which is very close to that of Mn-Anderson (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 $\mu_{\text{exp}}$ 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 represented here an example of magnetic molecules that are prepared by covalently anchoring TEMPO radicals onto the 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 TEMPO radicals and the Mn$^{III}$ ions have been investigated by EPR spectroscopy and Evans NMR. Though it seems 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.

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Notes and references


