Is a radical bridge a route to strong exchange interactions in lanthanide complexes? A computational examination†

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The origin of very strong antiferromagnetic exchange in $N_2^{3−}$-bridged complex, $[\{(Me_3Si)_2N\}_2Gd(THF)]_2(\mu-\eta^2:\eta^2-N_2)$ (1) has been probed using density functional theory (DFT) combined with molecular orbital (MO) and natural bond orbital (NBO) analysis. The analysis helps us to propose a generic mechanism of coupling for a (2p–4f) class of compounds.

The requirement of high anisotropy to enhance the barrier height in Single Molecule Magnets (SMMs) has led researchers to focus their attention on the 4f-ion based clusters and their combination with transition metals {3d–4f} or radicals {2p–4f}. This synthetic strategy has tremendous success in producing novel SMMs in a short span of time.4,5 The 4f-ion based clusters have also yielded several novel SMMs, for example Wippeny et al. reported a {Dy$^{III}_2$} cluster possessing the largest barrier height for any cluster compounds.5 It is however to be noted that the observed SMM characteristics of these complexes are essentially due to the single-ion anisotropy of Dy$^{III}$ ions and a primary challenge in such clusters is the ever to be noted that the observed SMM characteristics of these complexes are essentially due to the single-ion anisotropy of Dy$^{III}$ ions and a primary challenge in such clusters is the very weak exchange interaction leading to close lying excited states and a fast quantum tunnelling of magnetization.6,7 A recent study on a {Dy$^{III}_2$} dinuclear complex by Powell et al. reveals that the Ising type exchange coupling between the Dy$^{III}$ ions suppresses the quantum tunnelling of magnetization at zero-field.8 This emphasises the importance of the exchange interaction in developing new generation SMMs. The (2p–4f) class of compounds, on the other hand, are slightly superior to 4f- and {3d–4f} systems as moderate to strong exchange interactions have been observed in this class of compounds and the magnitude can be tuned at will.4

Recently, Long et al. reported a new class of Gd$^{III}$ dimeric complexes containing $N_2^{3−}$-radical anionic bridging $[\{(Me_3Si)_2N\}_2Gd(THF)]_2(\mu-\eta^2:\eta^2-N_2)$ (1) and $N_2^{2−}$-anionic bridging $[\{(Me_3Si)_2N\}_2Gd(THF)]_2(\mu-\eta^2:\eta^2-N_3)$ (2) complexes (See Fig. 1). Complex 1 exhibits the strongest antiferromagnetic interaction reported for any 4f- ion based cluster.3 The Gd$^{III}$ and the radical $N_2^{3−}$ interaction is reported to be $-27$ cm$^{-1}$ (see Table 1). On the other hand, complex 2 exhibits a weak antiferromagnetic exchange between two Gd$^{III}$ atoms ($J_{Gd-Gd} = -0.49$ cm$^{-1}$). Given the importance of achieving large $J$ values in 4f-ion based clusters and the fact that the $J$ value of 1 is larger than any {3d–4f} class of compound reported,5 we were motivated to explore the origin of the magnetic interaction in complex 1.

Here, we applied DFT methods to compute magnetic exchange interactions in 1 and 2 and performed MO and NBO analysis to gain insight into the mechanism of magnetic coupling. Magneto-structural correlations have also been developed to offer a way to further enhance the $J$ values in this class of compounds. The Gd$^{III}$ ions in 1 and 2 are five-coordinate with average Gd–N distances of 2.237 and 2.340 Å, respectively. The bridging N–N distances are distinctly different with a longer N–N (1.40 Å) for for 1 and a relatively shorter one for 2 (1.278 Å). The [Gd$^{III}N_2$] core lies in a plane with a Gd–N–Gd–N dihedral angle of 0° in both the complexes. For complex 1 the following exchange Hamiltonian Hamiltonian has been adopted for the computation of $J$ values:

$$H = -2J_1(\hat{S}_{GdA}\hat{S}_{rad} + \hat{S}_{GdB}\hat{S}_{rad}) - 2J_2\hat{S}_{GdA}\hat{S}_{GdB}$$

Here, $J_1$ describes interactions between Gd$^{III}$ ions and $N_2^{3−}$ radicals, while $J_2$ denotes the Gd–Gd non-neighbour interaction. For complex 2, only the Gd–Gd interaction is applicable and this has been computed. A pair-wise interaction model has been employed to compute multiple $J$ values within this cluster (see the ESI for an elaborate discussion†).

The DFT calculations$^3$ yield $J_1 = -23.7$ cm$^{-1}$ and $J_2 = -0.53$ cm$^{-1}$ for complex 1. For complex 2, a $J_{Gd-Gd}$ interaction of $-0.51$ cm$^{-1}$ has been obtained. A strong antiferromagnetic $J_1$ in 1 supports experimental observations and the computed magnitude is in good accord with the experimental value.
Table 1: Experimental and DFT computed exchange coupling constants of different GdIII-radical complexes reported in the literature.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>J_{exp}/cm(^{-1})</th>
<th>J_{cal}/cm(^{-1})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(Me3Si)2N(_2)Gd(THF)](_2^+) (I)</td>
<td>-27</td>
<td>-23.7/-0.53</td>
<td>9</td>
</tr>
<tr>
<td>[Gd(Hbpp)(_2)-(dbsq)]</td>
<td>-5.7</td>
<td>-6.18</td>
<td>4b</td>
</tr>
<tr>
<td>[Gd (NITBzImH(_2))(NO(<em>3)</em>)(_3)]</td>
<td>-4.05</td>
<td>-2.85</td>
<td>4d</td>
</tr>
<tr>
<td><a href="ClO(_4)">Gd(NITMeBzImH)(_4)</a>(_3)</td>
<td>-3.8</td>
<td>-4.0</td>
<td>4d</td>
</tr>
<tr>
<td><a href="Me(_2)py">Gd(thf)(_3)</a>(_2)]</td>
<td>-3</td>
<td>-2.26</td>
<td>4e</td>
</tr>
<tr>
<td><a href="MBzimH">Gd(thf)(_2)</a></td>
<td>-2.6</td>
<td>-4</td>
<td>4e</td>
</tr>
<tr>
<td>[Gd(NITBzImH(_2))(ClO(_4))]</td>
<td>-1.8</td>
<td>-1.28</td>
<td>4d</td>
</tr>
<tr>
<td>[Gd(thf)(imidv)]</td>
<td>-1.58</td>
<td>-4</td>
<td>4f</td>
</tr>
<tr>
<td><a href="CCl(_4)">Gd(THQSF)(_2)</a>(_2)]</td>
<td>-1.4</td>
<td>-4</td>
<td>4g</td>
</tr>
<tr>
<td>[(Me3Si)2N(_2)Gd(THF)](_2^+)(μ-η(_2)-η(_2)-N(_2))</td>
<td>-0.49</td>
<td>-0.51</td>
<td>10</td>
</tr>
<tr>
<td>[Gd(TCNE)(_3)](x(MeCN)]</td>
<td>-0.05</td>
<td>-4</td>
<td>4h</td>
</tr>
</tbody>
</table>

(see Table 1). Although the \(J_2\) interaction has not been estimated experimentally for complex I, the estimate obtained for 2 serves the purpose of comparison and our calculations reveal that a weak non-neighbour Gd-Gd antiferromagnetic interaction is operational in both the complexes. This set of \(J\) values leads to an \(S = 13/2\) ground state with the \(S = 11/2\) and \(9/2\) excited states at 8.2 and 16.9 cm\(^{-1}\), respectively for 1. We have also extended our studies to other antiferromagnetically coupled GdIII-radical systems reported in the literature and this has been done primarily for comparison and also to depict a generalised picture of the coupling mechanism in the \(2p-4f\) class of compounds. In all the computed cases, the \(J_{cal}\) is in excellent agreement with the \(J_{exp}\) reported. From Table 1 it is also clear that the \(J\) value calculated for complex I is highest of all the \(2p-4f\) class of compounds (see ESI, Table S4 for a comparison with other classes of compounds).

The computed ground state spin density plots for 1 and 2 are shown in Fig. 2a-b. The GdIII atoms have a spherical spin distribution, having spin densities of 7.01 and 7.04 for 1 and 2 respectively. The nitrogen atoms of the N\(_2\)\(^{3-}\) bridge in I have spin densities of 0.47 and 0.48 and this indicates a near symmetrical distribution of spin densities on both the nitrogen atoms. The magnitude of the spin densities on the nitrogen atoms in I is the largest, among the \(2p-4f\) class of compounds, computed (see Table S2 and S3 and Fig. S1) revealing a large localization of spin densities on the N\(_2\)\(^{3-}\) moiety. The unpaired electron in the N\(_2\)\(^{3-}\) moiety is found to be located in a \(\pi^*\) orbital (\(\pi_{py}\)), which is perpendicular to the [Gd\(_2\)N\(_2\)] plane (see Fig. 2a and Fig. S3 for a qualitative MO diagram).

In general, there are two contributions to the magnetic coupling in \(2p-4f\) based systems, the first one being a direct overlap of the 4f- magnetic orbitals with the radical orbital of the N\(_2\)\(^{3-}\) unit. The second is an indirect contribution where partial charge transfer (CT) from N\(_2\)\(^{3-}\) to 5d/6s orbitals of GdIII takes places. Here, the former will have both ferromagnetic, as well antiferromagnetic, contributions to the net exchange, while the latter contributes exclusively to the ferromagnetic part of the net exchange.13 The sign and magnitude of the net exchange interaction is decided by these two competing contributions. Recently, using DFT methods, we have proposed that these two contributions can be qualitatively analysed using computation of overlap integrals \(S_{ab}\) (direct) between the magnetic orbitals and NBO analysis (indirect). The computed \(S_{ab}\) values between the GdIII 4f-orbitals and the \(\pi_{py}\) orbital of N\(_2\)\(^{3-}\) are given in Table S4.13 Interestingly, a significant overlap between the \(\pi_{py}\) orbital of the N\(_2\)\(^{3-}\) moiety and two 4f orbitals of the GdIII (see ESI for orbital labels) has been observed. These two orbital lobes are aligned with the \(\pi_{py}\) orbital and this essentially leads to a strong overlap (see Fig. 2c). For the Gd-Gd interaction, one non-negligible 4f–4f overlap between two orbitals (\(f_xz^2–f_xz^2\)) have been detected and the \(S_{ab}\) values computed are ca. the same in both 1 and 2. This indicates that the unpaired electron in the \(\pi_{py}\) orbital is not playing an important role in the Gd-Gd coupling (Note: similar \(J_2\) strength in 1 and 2).

NBO analysis has been carried out to gain insight into the mechanism, which is charge transfer in nature (indirect). Quite interestingly, the \(\pi_{py}\) orbital is found to interact with the 6 type \(d_{xy}\) orbital (see Fig. S3 of the ESI†). This interaction is rather weak as revealed by the NBO second order-perturbation analysis. Besides, only a small increase in 5d occupation has been noted for 1 compared to 2 (0.48; 0.49 for 1 and 0.46; 0.46 for 2 for two GdIII atoms in each case). All this essentially indicates that the \(\pi_{py}\) orbital in 1 does not play a proactive role in the charge transfer mechanism. This suggests that the ferromagnetic contribution, which generally dominates in \{3d–4f\} pairs, is significantly weak in complex 1. On the other hand, two \(\pi_{py}-4f\) interactions (see Fig. 2c-d) have been detected in the NBO second order perturbation analysis and this reinforces the significant \(\pi_{py}-4f\)-orbital interaction previously suggested from the overlap integral calculations.

The \(\pi_{py}\) orbital is strongly antibonding in character and has a large anionic charge, thus the lobes are very much diffused. This makes it ideal for overlap with 4f-orbitals and this interaction is very significant compared to any \{3d–4f\} pair computed earlier.13 A significant \(\pi_{py}-4f\)-orbital interaction and a less significant charge transfer mechanism essentially lead to a very large anti-ferromagnetic \(J\) in 1. Moreover, the \{2p–4f\} class of compounds enjoy close proximity to the lanthanide ions as the radical centres are directly coordinated to the metal ions. This essentially leads to significant direct interactions between the radical magnetic orbitals and the 4f-orbitals. On the other hand, in the \{3d–4f\} class, such overlap is super-exchange in nature, which eventually diminishes this contribution. Due to these mechanistic differences, the majority of the \{3d–4f\} complexes exhibit ferromagnetic coupling\(^{5d-f}\) while the \{2p–4f\} class of compounds exhibit antiferromagnetic coupling. Although all the analysis has been performed on complex 1, a similar trend has been noted for other \{2p–4f\} complexes calculated in Table 1. This suggests that the proposed mechanism of coupling is generic for a \{2p-GdIII\} class of compounds and we are confident that a similar mechanism is operational for the Ising type of exchange exhibited by other 4f-elements.
We have developed some magneto-structural correlations to 1 to offer a way to enhance the magnitude of the J value. One of the large structural differences observed among the reported \([\text{La}_2\text{N}_2]^{12+}\) core structures\(^{14}\) are the N–N bond lengths of the bridging unit. The N–N length varies with respect to the charge of the N\(_2\) moiety and the ligand crowding surrounding the lanthanide ions. To underpin the effect of N–N distance on the magnetic coupling, the N–N distance was varied\(^{13}\) from 1.40 Å to 1.22 Å in 1 and the developed correlation is shown in Fig. 3a. As the N–N distance increases, there is a considerable increase in \(J_1\) and \(J_2\) interactions. A rationale for this comes from the computed \(S_{ab}\) values, where a larger \(S_{ab}\) has been detected as the N–N length elongates (See Table S6 and S8 of the ESI\(^{1}\)). Quite interestingly, below 1.27 Å, the interaction switches from antiferro to ferromagnetic. For the antiferromagnetic part, as the N–N distance elongates (compresses), the relative energy of the \(\pi_{by}\) orbital decreases (increases) and the net charge on the nitrogen atom increases (decreases) and this essentially leads to a strong (weak) Gd–radical interaction. The correlation essentially increases (decreases) and this essentially leads to a strong (weak) Gd–radical interaction. The correlation essentially increases (decreases) and this essentially leads to a strong (weak) Gd–radical interaction. The correlation essentially increases (decreases) and this essentially leads to a strong (weak) Gd–radical interaction.

Notes and references

12. Note: treating the two \(J_{1}\) interactions in 1 differently leads to \(J_{1a} = -23.8\) cm\(^{-1}\) and \(J_{1b} = -23.5\) cm\(^{-1}\).
15. Note here that modifying the N–N distance also leads to very small changes in other geometrical parameters such as Gd–N distance and Gd–N–Gd angles.

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