Nickel(II)–Lanthanide(III) Magnetic Exchange Coupling Influencing Single-Molecule Magnetic Features in \{Ni_2Ln_2\} Complexes**


Abstract: Four isostructural \[\text{Ni}_2\text{Ln}_2\text{[CH}_2\text{CO}_2\text{]}_2\text{[(HL)}_2\text{]}\text{(H}_2\text{O})_3\] \(^{1+}\) (\(\text{Ln}^{3+}=\text{Dy} (1), \text{Tb} (2), \text{Ho} (3) \text{or Lu} (4)\)) complexes and a dinuclear \[\text{NiGd}[\text{(HL)}_2\text{(NO}_3\text{)}_3\] \(5\) complex are reported (where \(\text{HL}=2\text{-methoxy-6-[(E)-2'-hydroxymethyl-phenyliminomethyl-yl]-phenolate}\)). For compounds \(1-3\) and \(5\), the \(\text{Ni}^{2+}\) ions are ferromagnetically coupled to the respective lanthanide ions. The ferromagnetic coupling in \(1\) suppresses the quantum tunnelling of magnetisation (QTM), resulting in a rare zero dc field Ni–Dy single-molecule magnet, with an anisotropy barrier \(U_{\text{eff}}\) of 19 K.

Following the remarkable observation of single-molecule magnet (SMM) behaviour within a \([\text{Mn}_3\text{OAc}]\) cluster, numerous transition-metal SMM complexes have subsequently been reported.[7] The interest stems from the many potential applications, such as storage of digital information, molecular qubits, and spin valves.[8] The two parameters that govern the effective energy (anisotropy) barrier \(U_{\text{eff}}\) for transition-metal-based SMMs, namely the ground spin state \(S\) and the magnetic anisotropy parameter \(D\), are inversely proportional to each other, hampering efforts to significantly improve properties.[9]

To address this issue, a combination of lanthanides and transition-metal ions has been utilised in an attempt to gain maximal magnetic anisotropy.[10] Promising observations such as the identification of ferromagnetic coupling between \(\text{Cu}^{2+}\) and \(\text{Ni}^{2+}\) ions suggests a beneficial synergy within 3d–4f complexes, offering great potential for SMM study.[11,12] Drawbacks are also found to arise upon incorporation of lanthanide ions, however, such as efficient quantum tunnelling of the magnetisation (QTM), which hampers the improvement of relaxation times and thus the blocking temperature \(T_B\).[13,14,15] Therefore, because \(\text{Ln}^{3+}\)-containing complexes appear to be promising, strategies to overcome this problem need to be developed.

It has previously been identified that enhancing the magnitude of the exchange interaction should inhibit the loss of magnetisation at zero magnetic field through QTM.[16,17] This proposal was adequately confirmed using a family of lanthanide dimers bridged by radical-containing ligands.[18] We have recently shown that the magnitude of the super exchange interaction can also be significant enough to suppress QTM through the incorporation of 3d metal ions such as \(\text{Cr}^{3+}\), with long relaxation times observed in \([\text{Cr}^{3+}\text{Dy}^{3+}]\) complexes.[19] To look for alternate 3d metal ions that may result in strong super-exchange interactions between 3d and 4f ions, we have investigated nickel-based lanthanide complexes, using the Schiff base ligand \(2\text{-methoxy-6-[(E)-2'-hydroxymethyl-phenyliminomethyl-phenol}\)}, \(\text{H}_2\text{L}\); see the Supporting Information for synthesis of ligand). Herein, we report a family of \([\text{Ni}^{2+}\text{Ln}^{3+}]\) complexes (where \(\text{Ln}^{3+}=\text{Dy, Tb, Ho and Gd}\) dimeric compound, with magnetic studies revealing that the Dy, Tb, Ho and Gd derivatives display significant ferromagnetic interactions and the Dy analogue displays fascinating SMM behaviour.

The reaction of \(\text{Ln(NO}_3\text{)}_3\cdot\text{H}_2\text{O}\) (where \(\text{Ln}^{3+}=\text{Dy, Tb, Ho, Lu or Gd}\)) and nickel acetate hydrate with the singly deprotonated Schiff base ligand \(2\text{-methoxy-6-[(E)-2'-hydroxymethyl-phenyliminomethyl-phenol}\}}\), \(\text{H}_2\text{L}\); see the Supporting Information for synthesis of ligand). Herein, we report a family of \([\text{Ni}^{2+}\text{Ln}^{3+}]\) complexes (where \(\text{Ln}^{3+}=\text{Dy, Tb, Ho and Gd}\) dimeric compound, with magnetic studies revealing that the Dy, Tb, Ho and Gd derivatives display significant ferromagnetic interactions and the Dy analogue displays fascinating SMM behaviour.

The crystal structure for \(1\) is shown in Figure 1 (See also Figure S1 in the Supporting Information for the crystal structures of \(2, 3, 4\) and \(5\)). The asymmetric unit (ASU) for \(1-4\) contains half of the molecule with one \(\text{Ni}^{2+}\) and one \(\text{Ln}^{3+}\) ion. The other half of the molecule is generated by axis/mirror plane symmetry within the monoclinic space group \(C2/c\), whereas \(5\) crystallises in the monoclinic space group \(P2_1/n\) (Table S1 in the Supporting Information).

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with a similar bonding perspective, with an average Ni1-O-Gd1 angle of 107.2°. These four atoms (Ni-O11-Ln1-O31) deviate from planarity, reflected by dihedral angles of 8.84°, 8.52°, 8.82°, 9.48° and 7.4° for 1–5, respectively. The two trivalent LnII ions in 1–4 are surrounded by eight oxygen donor atoms and display distorted bicapped trigonal-prismatic geometries, confirmed by continuous shape analysis. This geometry is rare for a LnIII ion, with only one known example reported in the Cambridge structural database (CSD). The average Ln–O bond length is found to be 2.388, 2.406, 2.379 and 2.346 Å, for 1–4, respectively. Four out of the eight coordination sites are provided by oxygen atoms from the two Schiff base ligands (phenoxy and methoxy groups). The remaining four are completed by three acetate ligands and a terminal water molecule. The three acetate groups bridge the Ln ions, displaying the usual μ-η1-η1 mode. In 5, the GdIII ion is ten-coordinate with a distorted bicapped square anti-prism geometry. As with 1–4, four of the coordination sites are occupied by two HL ligands. The remaining sites are, however, now completed by three chelating nitrate ligands, preventing any further growth. The average Gd–O bond length is 2.498 Å. In all five complexes, the divalent nickel ions display distorted octahedral geometries with an (N1O4) coordination environment, with all bonding atoms derived from two Schiff base ligands. Selected bond lengths and angles for 1–5 are given in Table S2 in the Supporting Information. Three nitrate anions reside in the crystal lattice, neutralising the excess cationic charge on the coordination spheres of 1–4. These anions are heavily disordered and facilitate intermolecular hydrogen-bonding interactions (See Table S3 in the Supporting Information).

Direct current (dc) magnetic susceptibility measurements on polycrystalline samples of 1–5 were performed between 2.0 to 300 K with an external magnetic field of 0.1 T (Figure 2). The room-temperature (RT) \( \chi_{MRT} \) values of 30.68, 25.57 and 30.91 cm\(^3\)Kmol\(^{-1}\) for 1–3, respectively, are close to the expected values of 30.33 cm\(^3\)Kmol\(^{-1}\) (\( g_{\text{obs}} = 4/3 \)), 4.7 and 25.63 cm\(^3\)Kmol\(^{-1}\) (\( g_{\text{obs}} = 3/2 \)) and 30.13 cm\(^3\)Kmol\(^{-1}\) (\( g_{\text{obs}} = 5/4 \)) for two uncoupled NiII (\( A_{2g}, g = 2.0 \)) and two LnII ions. The values of 2.39 and 9.35 cm\(^3\)Kmol\(^{-1}\) for 4 and 5, respectively, are slightly larger than those expected for two isolated NiII (\( A_{2g}, g = 2.0 \)) ions in 4 and non-interacting NiII and GdIII ions (\( S; g = 2.0 \)) in 5. Upon reduction of the temperature from RT, the \( \chi_{MRT} \) value decreases gradually down to 29.5 Kmol\(^{-1}\) for 1 and 3, likely due to the depopulation of the Ln Stark levels. Below this temperature, the \( \chi_{MRT} \) product increases, reaching a maximum value of 33.93 and 30.27 cm\(^3\)Kmol\(^{-1}\) at 4.0 K for 1 and 3, respectively, before falling below 4.0 K. The increase in \( \chi_{MRT} \) observed at low temperatures indicates ferromagnetic interactions between the Ni and Ln ions. Interestingly, unlike 1, the \( \chi_{MRT} \) values for 2 and 5 increase steadily as the temperature is lowered from RT, before a steeper increase, reaching a maximum value of 26.9 and 14.45 cm\(^3\)Kmol\(^{-1}\) at 8.6 and 1.9 K for 2 and 5, respectively, again indicating ferromagnetic exchange. For complex 4, there is no appreciable change in the \( \chi_{MRT} \) value (\( \approx 2.39 \) cm\(^3\)Kmol\(^{-1}\)), which remains constant from RT down to 18 K, before decreasing sharply below this temperature. The constant \( \chi_{MRT} \) value signifies that there is no interaction between the two nickel ions through the diamagnetic Lu centres, which is expected, considering the distance between the two nickel ions (9.47 Å). The sharp fall in the \( \chi_{MRT} \) value below 18 K is likely due to single ion anisotropy (zero field splitting) and/or intermolecular antiferromagnetic interactions (the closest Ni–Ni distance found between the molecules is 8.36 Å in 4).

Isothermal field-dependent magnetisation measurements were also performed between 2 to 20 K (see Figure S2 in the Supporting Information and related discussion) for 1–5. The non-overlapping nature of the reduced magnetisation curves confirms the presence of significant magnetic anisotropies for 1–3. The reduced magnetisation plots for 5 reveal overlapping curves, signifying a lack of anisotropy (Figure S2 in the Supporting Information).

The maximum \( \chi_{MRT} \) value (14.4 cm\(^3\)Kmol\(^{-1}\)) of 5 at low temperature corresponds to a total spin ground state of \( S = 9/2 \), which is consistent with its magnetisation saturation value. The magnetic susceptibility data of 5 was fitted using the Heisenberg isotropic exchange Hamiltonian (\( \mathbf{H} = -J \mathbf{S}_{i} \cdot \mathbf{S}_{j} \)). The best fit of the data was obtained using the parameters \( g = 2.08, J_{\text{Ni-Gd}} = 1.31 \) cm\(^{-1}\) and \( zJ = 0.007 \) cm\(^{-1}\) (where \( zJ \) is the intermolecular interaction). The extracted spin Hamiltonian parameters are consistent with other reported Ni–Gd dimeric complexes.[12]

In order to confirm empirically the existence of ferromagnetic interactions between the nickel and the anisotropic lanthanaide ions, and to understand the contributions of the lantha-
nide ions to the observed magnetic behaviour, we have synthesised the isostructural diamagnetic Lu complex (4). Attempts to synthesise the (Zn$_2$Dy$_2$) analogue were unfortunately unsuccessful. We have, however, recently reported a Zn–Dy heterodinuclear complex,\textsuperscript{10} the magnetic core of which closely resembles the asymmetric unit of 1. Hence, for an approximate empirical calculation we have taken into account the $\chi_M T$ value of this Zn–Dy complex. Using the available data, we have applied Equation (1) assuming that $J_{\text{Dy}-\text{Dy}}$ is negligible (see Figure 2b).

$$\Delta(\chi M T) = (\chi_M T)_{\text{Ni}_2\text{Lu}_2} - (\chi_M T)_{\text{Ni}_2\text{Lu}_2} - 2 \times (\chi_M T)_{\text{ZnDy}} = 2J_{\text{Ni}-\text{Dy}}$$

(1)

This exclusively shows the nature of the exchange interaction between the Ni$^{II}$ and Dy$^{III}$ ions in 1. The $\Delta(\chi M T)$ values in Figure 2b are positive over the entire temperature range (2.0 to 300 K), with a marked increase below 75 K. This unambiguously confirms the existence of ferromagnetic coupling between the Ni$^{II}$ and Dy$^{III}$ ions.

In order to investigate the magnetisation relaxation dynamics, alternating current (ac) magnetic susceptibility measurements were performed for complexes 1–3 between 1.8–10.0 K. Using a 3.5 Oe oscillating ac field with a zero external dc magnetic field, complex 1 displayed frequency- and temperature-dependent out-of-phase susceptibility signals ($\chi_M$‘) indicating the blockage of the magnetisation vector, characteristic of a SMM (Figure 3). Observation of such signals for 1 under zero applied dc field is rare for a Ni–Dy complex.\textsuperscript{14} Though many ferromagnetically coupled polynuclear Ni–Dy complexes have previously been reported, it has been found that an external bias field is necessary to observe a $\chi_M$‘ signal in many of those examples (Table S4 in the Supporting Information).

From Figure 3, the relaxation is found to be temperature dependent over the entire frequency range, with a single maximum in $\chi_M$‘ found for each temperature, indicative of a single relaxation process. A single relaxation process is further supported by the Cole–Cole plots, which were fitted to a generalised Debye model, with $\alpha$ parameters in the range 0.23–0.37 (Figure 3b, Table S4 in the Supporting Information). This shows a moderate distribution of relaxation times, which could be due to weak dipolar interactions. The relaxation times obtained from the ac data were fitted to the Arrhenius equation ($\ln \tau = \ln \tau_0 - U_{\text{eff}}/kT$), shown in Figure 3a, inset, which reveals the energy barrier $U_{\text{eff}}$ to be 19 K, with a pre-exponential factor ($\tau_0$) = 4.23×$10^{-7}$ s.

QTM is often the predominant relaxation mechanism in lanthanide-based complexes and the observation of zero-field SMM behaviour in 1 is uncommon. Moreover, when SMM behaviour is observed in a zero field for complexes containing Ln$^{III}$ ions, tunnelling is often still observed in the ac experiment at low temperatures, when the tunnelling rate becomes faster than the thermally activated mechanism. To show that the tunnelling rate is slower than the thermal relaxation process in complex 1, we performed ac measurements in the presence of an external magnetic field of 0.15 T (see Figure S3 in the Supporting Information). The unchanged value of the effective energy barrier compared with the zero field ac measurement unambiguously indicates that resonant QTM is significantly reduced and/or suppressed. This result accentuates that the magnetisation vector relaxes predominantly through an Orbach process, consistent with the non-deviation from Arrhenius behaviour, revealing an absence of tunnelling over the entire temperature range studied. This behaviour is markedly different from other lanthanide-based complexes where QTM and other relaxation mechanisms such as direct and Raman processes are operative.\textsuperscript{15} Comparison of the small number of Ni–Dy examples which display SMM behaviour (ac experiment) in the absence of an applied dc magnetic field; such as (Ni$_2$Dy$_2$) and (Ni$_3$Dy$_3$) complexes, each displays multiple relaxation mechanisms, including QTM, differing from our example.\textsuperscript{14} In those cases, the linkage between the metal centres and geometry around the Dy$^{III}$ ions are distinctly different to those in 1.

As stated above, it has recently been reported that the super-exchange interaction is one of the key parameters enabling the suppression of QTM.\textsuperscript{7a,7b,8} It is, however, difficult to achieve large exchange parameters for Ln$^{III}$ ions due to the shielded nature of the 4f orbitals. The insertion of 3d ions within 4f complexes has helped to some extent, resulting in...
strong exchange between 3d and 4f ions in a small number of cases, allowing for the observation of high blocking temperatures.\textsuperscript{38} It is likely that the suppression of QTM in complex 1 is therefore a consequence of the ferromagnetic interaction between the Ni\textsuperscript{i}\textit{ii} and Dy\textsuperscript{i}\textit{ii} ions.

Although it is difficult to estimate the strength of the exchange interaction in anisotropic metal complexes, the analogous isotropic (Ni\textit{Gd}) complex would, to some extent, be expected to yield the strength of the exchange interaction between the metal centres. Attempts to isolate this complex, utilising similar reaction conditions followed for 1–4 was, however, unsuccessful, instead yielding the dinuclear compound 5. In unrelated work, Matsumoto and co-workers reported an analogous (Ni\textit{Gd}) complex,\textsuperscript{4d} with the Gd\textsuperscript{i}\textit{ii} ions being bridged by carbonate ligands. The magnetic susceptibility data of this isotropic tetraneutral complex were fitted using a Heisenberg–Dirac–Van Vleck (HDVV; $H = -2J_S^\text{Ni} S_\text{Gd}$) Hamiltonian and considering only the Ni–Gd exchange ($U_{\text{Ni-Gd}} = 1.2 \text{ cm}^{-1}$), with $J_{\text{Gd-Gd}}$ set at zero. The extracted $J_{\text{Ni-Gd}}$ value of the discrete Ni–Gd complex 5 is in excellent agreement with this constant (Ni\textit{Gd}) complex and other discrete Ni–Gd dimers reported in the literature.\textsuperscript{5d} This picture signifies that the exchange interaction between the Dy–Dy ions in 1 is likely to be zero or negligible and the SMM behaviour arises due to the Ni–Dy dimeric unit in the molecule. To calculate empirically the exchange between Ni\textit{ii} and Dy\textit{ii} in 1, the obtained exchange coupling constant $J_{\text{Ni-Gd}}$ for 5 was rescaled to the spin of the Dy\textit{ii} ion by multiplying by 5/2 (spin of Dy\textit{iii}) and dividing by 7/2 (spin of Gd\textit{iii}), and was found to be $J_{\text{Ni-Dy}} = 0.94 \text{ cm}^{-1}$. This qualitative approach has proven successful in estimating the exchange between Cr\textit{iii}–Dy\textit{iii} in a (Cr\textit{Dy}) complex reported recently by us.\textsuperscript{6d} As we have rationalised that the SMM behaviour for 1 arises due to the Ni–Dy dimeric unit, to assess the importance of the Ni\textit{i} ion in 1, various hetero-dinuclear Zn–Dy SMMs have been analysed. The majority (> 95%) of reported Zn–Dy complexes are found to display field-induced SMM behaviour, and therefore the QTM is very efficient.\textsuperscript{7d} This strongly supports the theory that the SMM behaviour in 1 is predominantly due to the exchange interaction between the Ni\textit{ii} and the Dy\textit{ii} ion.

In order to investigate why complex 1 displays relatively strong exchange and zero field SMM behaviour without the observation of QTM, contrary to the situation in other ferromagnetically coupled Ni–Ln complexes, we have analysed the structural details of 1 more carefully. Rajaraman and co-workers have predicted, through detailed theoretical studies, that a larger (Gd–O(phenoxo))–Ni bond angle and a smaller dihedral angle (Gd1–O11–Ni1–O31) are requirements for enhancing the ferromagnetic interaction between Ni\textit{ii}–Gd\textsuperscript{i}\textit{ii} ions.\textsuperscript{8d} Although the bond lengths of 1 (Ni–O; Ni–N; Ni–O(phenoxo) and Dy–O) are similar to those of other reported Ni–Dy SMMs, it is significant that the dihedral plane formed by Dy1–O11–Ni1–O31, and the Dy–O–Ni bond angles are distinctly different from other known Ni–Dy SMM complexes, displaying a smaller deviation from planarity and wider angles (see Table S6 in the Supporting Information). We would like to emphasise that the structural parameters of 5, from which the Ni–Dy exchange is derived, are essentially similar to those in the asymmetric unit of 1–4. These structural parameters are presumably the reason for the observed ferromagnetic exchange interaction and also the lack of QTM.\textsuperscript{9d} Moreover, the coordination geometry of the lanthanide ion is also likely to provide a contribution towards the resultant SMM properties;\textsuperscript{10d} however, this contribution can be overridden and/or neglected if the exchange interaction between the 3d–4f ions dominates, which has been recently shown for a (Cr\textit{Dy}) family of complexes.\textsuperscript{11d} In this strong exchange regime, one that appears to be the case with 1, QTM is significantly reduced, especially when the Ln\textsuperscript{i} ion is Dy.

Variable-temperature ac susceptibility measurements were also performed on 2 and 3 and contrary to 1, reveal an absence of $x_{\chi_m}$ signals at all temperatures under zero applied magnetic field, implying that QTM is much faster in these compounds. This is often the case with Tb\textsuperscript{i} and Ho\textsuperscript{i}, considering the non-Kramers nature of the ground state of the ions on top of the nuclear spin-induced QTM (hyperfine interaction), often observed for Ho\textsuperscript{i} ($I_{\text{Ho}} = 7/2$; 100% abundance).\textsuperscript{12d} Upon application of a bias dc field (0.2 T), however, 2 and 3 both display out-of-phase susceptibility signals. The maxima in $x_{\chi_m}$ for both complexes appear below the minimum operating temperature of the instrument (see Figure S4 in the Supporting Information). The field-induced SMM behaviour further reiterates that QTM is dominant in both 2 and 3.

In conclusion, we have reported an isostructural series of (Ni\textit{Ln}) complexes (1–4) and a (NiGd) dinuclear complex using a Schiff base ligand. Dc magnetic susceptibility measurements reveal the existence of ferromagnetic interactions between the Ni and Ln ions (1–3 and 5), and its strength ($J$) is estimated to be 0.94 cm$^{-1}$ and 1.31 cm$^{-1}$ for 1 and 5, respectively. The existence of a ferromagnetic interaction in 1 is empirically validated in the $\Delta\chi_m/T$ plot. Ac susceptibility measurements on complex 1 reveal slow relaxation of the magnetisation and SMM behaviour, with an anisotropy barrier, $U_{\text{an}}$, of 19 K, under a zero applied dc magnetic field. The most fascinating aspect is that the ferromagnetic exchange interactions likely play a key role in suppressing the QTM, a much sought-after goal within the SMM field. The reduced efficiency of the QTM is further validated by the unchanged value of $U_{\text{an}}$ estimated in the presence of an external magnetic field. Compounds 2 and 3 also join the field-induced SMM family. Overall, this study shows the importance of the S = 1 Ni\textsuperscript{i} ion in generating magnetic exchange sufficient enough to quench/suppress QTM in lanthanide-based complexes. It also highlights the role of the bond and dihedral angle in determining the strength of the exchange interaction between Ni\textsuperscript{i} and Gd\textsuperscript{i} ions. A quantitative estimation of the super-exchange interaction between the Ni and Ln ion for 1–3, and a derivation of other possible magneto-structural correlations needed to fine tune the SMM behaviour, are currently in progress through use of HF-EPR and ab initio calculations.

**Experimental Section**

Details of ligand and metal complex syntheses are given in the Supporting Information. Synthesis, relevant dc and ac data figures,
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