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Transitions of Two Magnetic Interaction States in Dinuclear Dy(III) Complexes via Subtle Structural Variations

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Herein we explored the transitions of two magnetic interaction states (antiferromagnetic or ferromagnetic) upon structural variations in two dinuclear Dy(III) complexes.

Among the most important aspects in the chemistry of molecular magnetism is the relationship between their structures and magnetic properties.¹ In fact, efforts to rationalize the sign and magnitude of the parameters that describe the magnetic interactions between paramagnetic centres continues, and great achievements have been made to establish qualitative and quantitative relationships between magnetism and structure.² For example, a linear relationship exists between the magnetic interaction parameter and the [Cu-O-Cu] angle in planar {Cu₂O₂} dimers, and an angle of approximately 97.5° represents the boundary for a transition between ferromagnetic and antiferromagnetic interactions.³ In addition, the relationships between magnetic interactions and structures have been also probed for the systems of other transition metals.⁴

These achievements and theoretical analysis of the relationships between magnetic interactions and structures will make it possible to predict and synthesize novel transition metal complexes that have desirable magnetic properties.⁵ However, no such understanding is currently available for systems based on lanthanide complexes, and the occurrence of the transitions between antiferromagnetic and ferromagnetic states is not yet fully clear.⁶ Owing to the efficient shielding of the unpaired electrons in the 4f orbitals, it is difficult to promote magnetic interactions by overlapping bridging ligand orbitals with the 4f orbitals of ions; as a result, the interactions between the lanthanide ions are weak. In

addition, unlike the regular d-block transition metal complexes, the influence of structural variations on the magnetic behaviours of lanthanide complexes is hard to predict. Taken together, these drawbacks complicate the modelling of magnetic interactions among lanthanides, and additional research will be required to understand the relationship between the transition of the two magnetic interaction states (antiferromagnetic and ferromagnetic) and structural variations in lanthanide complexes remains an exciting challenge.

Due to the significant magnetic anisotropy and the large magnetic moment, combined with that the ground states will always be bistable irrespective of the ligand-field symmetry, the Kramers ion, dysprosium(III), is the most widely utilized to construct lanthanide molecular magnets.⁷ Among them, dinuclear Dy(III) complexes represent the simplest molecular unit that allows the study of magnetic interactions between two spin carriers. By investigating such systems, one could expect to understand the nature and strength of the interactions between Dy(III) ions, which was well demonstrated in some elegant {Dy2O2} SMMs systems.8 Unfortunately, it is still lack good {Dy₂} systems in which similar structures exhibit different magnetic interaction properties and could therefore be suitable for probing the relationship between the transitions of the magnetic interactions and structural variations.

This challenge could be addressed through the judicious choice of periphery ligands, which should be able to build a robust molecular motif where the coordination geometries of the metal centers are preserved, while also allowing for the systematic fine-tuning of their coordination geometry to generate structurally related derivatives with different magnetic properties.⁹ Among the pre-organized organic moieties, we were interested in tridentate Schiff-base ligands, which would allow Dy(III) ion incorporating into compartmental acyclic coordination sites to forming robust six-membered rings where the rest coordination environment would possible be fine-tuned.¹⁰ Notably, previous studies have done very well with the modification of the axial coordination

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environment by varying diketone or high coordinating ability solvent ligands to generate structurally related derivatives with different magnetic properties.¹¹

In this contribution, we demonstrate how the magnetic interaction states (antiferromagnetic or ferromagnetic) arise and can be tuned through structural variations in Dy(III) complexes. Specifically, a good magnetism example including two structural closely related dinuclear dysprosium complexes, $[Dy_2(L)_2(DBM)_2(DMA)_2] \cdot 2DMA \cdot 2CH_3CN$ namelv (1) and $Dy_2(L)_2(DBM)_2(DMF)_2$] (2) (H₂L = 2-(2-hydroxy-3methoxybenzylideneamino)phenol, HDBM dibenzoylmethane, DMA = dimethylacetamide, CH_3CN = acetonitrile and DMF = dimethylformamide), is introduced and investigated for structure -dependent magnetic properties. By slightly changing the Dy-O-Dy angle and the related Dy-Dy distance in $\{Dy_2O_2\}$ core of the two related complexes, we were able to cause the transition between antiferromagnetic in complex 1 and ferromagnetic interaction in complex 2. As demonstrated using ab initio calculations, the transition between two magnetic interaction states (antiferromagnetic or ferromagnetic) is a result of the different sensitivities of the dipolar interaction and the exchange interaction between the Dy(III) ions to the structural variations.



Fig. 1 Molecular structures of complexes 1 (a) and 2 (b), with the hydrogen atoms and solvent molecules omitted for clarity.

Single-crystal X-ray structural analysis revealed that the two complexes are centrosymmetric and crystallize in the monoclinic $P2_1/n$ space group for 1 and $P2_1/c$ for 2 (Table S1). Figure 1 shows that the key features of both complexes are neutral dinuclear clusters with nearly identical structures, consisting of two Dy(III) ions, two dianionic Schiff baseligands, two bidentate monoanionic DBM⁻ ligands and two terminal solvent molecules of DMA for complex 1 or DMF for complex 2. The two symmetry-related Dy(III) ions are bridged by phenoxide groups of the two Schiff base ligands. Besides the bidentate DBM⁻ ligand and the terminal DMA or DMF, each metal ion is further coordinated with the methoxide group from one Schiff base ligand, and with N(imine)-O (phenoxide) atoms from the other ligand, generating an NO7 coordination environment with a square-antiprismatic coordination geometry. Table S2 shows only slight structural variations in the Dy-O1 (the bridging phenoxo oxygen) bond lengths, Dy-O1-Dy angles, and Dy-Dy separations in the central rhomboidal {Dy₂O₂} cores of the two complexes. It is important to note that, besides the fact that DMA contains an additional carbon, the different orientation of the DMA and DMF

made the O6–C30–Dy1 angle in complex **2** is considerably smaller, with a value of 132.4 (2)°, when compared to the corresponding angle in complex **1** of 156.3 (3)°. Such changes would change the coordination geometry of the metal centre, and may thus impacting the orientation of the anisotropy axes and the generation of slow magnetic relaxation. The shortest intermolecular $Dy\cdots Dy$ distances are 11.766 Å in complex **1** and 8.905 Å in complex **2**, indicating spatial isolation of the dinuclear units (Fig. S2). In addition, the difference in the shortest intermolecular $Dy\cdots Dy$ distance may produce different intermolecular dipole-dipole interactions, which may also result in the different magnetic behavior of the two complexes.

The program SHAPE 2.0 was used to analyze exact geometry of the octacoordinated dysprosium ions.¹² Close analysis of the resulting data reveals that the values obtained differ from zero (which represents the case of the ideal geometry considered). Therefore, a geometry of triangular dodecahedron (D_{2a}) is observed for the two complexes with a minimum *CShM* value of 1.099 and 0.870, respectively for **1** and **2** (Table S3), which indicated the metal centre of complex **2** with higher local symmetry.



Fig. 2 Plots of the $\chi_M T$ versus temperature for complexes **1** and **2** in an applied magnetic field of 500 Oe. The solid lines correspond to calculated fits to the data by exchange Hamiltonian considered within the Lines model.

Despite their structural similarities, complexes 1 and 2 display different static magnetic properties. Direct current magnetic susceptibility measurements of polycrystalline samples of complexes 1 and 2 are performed to probe their magnetic behaviours and its temperature response (Fig. 2). The room-temperature $\chi_M T$ values of 28.15 for complex 1 and 28.23 cm^3 K mol⁻¹ for complex **2** are in good agreement with the expected value of 28.34 cm³ K mol⁻¹ for two uncoupled Dy(III) (${}^{6}H_{15/2}$, $g = {}^{4}/_{3}$) ions. Upon cooling, the value of $\chi_{M}T$ for complex 1 decreases first slowly and then more rapidly below 50 K, reaching a minimum value of *ca.* 20.56 cm³ K mol⁻¹ at 1.9 K. The observed decrease of $\chi_M T$ at high temperatures results from the depopulation of the excited Stark sublevels, and the low-temperature behaviours mainly results from intramolecular antiferromagnetic interactions between Dy ions.

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Fig. 3 Top: Temperature dependence of the in-phase χ' (a for complex **1**, b for complex **2**) and out-of-phase χ'' (c for complex **1**, d for complex **2**) components of the AC magnetic susceptibility under zero dc field. Bottom: Frequency dependence under zero dc field of the in-phase (χ' , e) and the out-of-phase (χ'' , f) at different temperatures and the Cole-Cole plot (g) for complex **2**; the solid lines are the best fit obtained with a generalized Debye model. (h) Plot of $\ln(\tau)$, where τ is the relaxation time of the magnetization, vs 1/T, where τ is the temperature (K), for complex **2**. The red line represents the best fit to the Arrhenius equation for the thermally activated region. The effective energy barriers (U_{eff}) obtained from the fits are indicated.

For complex **2**, the $\chi_M T$ curve is similar to that of complex **1** at high temperature, reaching a minimum value of 25.46 cm³ K mol⁻¹ at 27 K. However, when the temperature was lowered further, $\chi_M T$ increased rapidly to a maximum of 35.08 cm³ Kmol⁻¹ at 1.9 K, which suggests the presence of intramolecular ferromagnetic interactions between the metal centres. The magnetization (M) plots as a function of field (H) for complexes **1** and **2** below 5 K (Fig. S4) reveals a relatively rapid increase of the magnetization at low fields followed by a slow linear increase at high fields without a clear complete saturation. The high-field linear variation of the magnetization suggests the presence of significant magnetic anisotropy as expected for Dy(III) ions. This is also supported by the observation that, while plotting the M vs HT⁻¹ at different fields (Fig. S5), the curves are not all superimposed on a single master-curve.¹⁰

To further compare the dynamic magnetic properties of complexes 1 and 2, both the temperature dependency and the frequency dependency of magnetic susceptibility measurements under alternating current were measured under zero dc field. Fig. 3 shows that both complexes display temperature-dependent χ'' signal, which indicates a kind of slow relaxation of the magnetization. However, no maximum value was observed above 2 K for complex 1, even under a series of externally applied dc fields at 2 K (Fig. S7), suggesting the block temperature should be lower than 2 K. In contrast, complex 2 shows different behaviours; the maximum χ'' value at 1488 Hz is observed at approximately 4 K, which is higher than that of complex 1 (Fig. 3). In addition, below 3.5 K, the χ'' plot for the complex **2** displays a rapid increase at lower temperatures, but does not show a clear peak at any measured frequency, which indicates that a quantum tunnelling mechanism is gradually replacing thermally activated spin reversal. The anisotropic barrier can be determined from both the χ'' vs. T diagram and the Cole-Cole (χ'' vs. χ') diagrams by fitting with the Arrhenius equation: $\tau = \tau_0 \exp(U_{\text{eff}}/k_{\text{B}}T)$, where τ is the relaxation

time of the magnetization, τ_0 is the attempt time, U_{eff} is the effective spin-reversal barrier, k_B is the Boltzmann constant, and *T* is the temperature (K).¹³ At high temperatures, the best fitting of the ln(τ) versus 1/*T* plot gives $\tau_0 = 2.8 \times 10^{11}$ s and $U_{eff} = 63$ K for complex 2 (Fig. 3 e-h). The χ'' vs. χ' diagram for complex 2 can be fitted to a generalized Debye model with the α parameter in the range from 0.312 to 0.414, which confirms again the mix of quantum tunnelling mechanism (Table S4). It is known that higher local symmetries would efficiently suppress the QTM of lanthanide ions, resulting in the increase of energy barriers, which corresponds to higher local symmetry of **2** with higher higher energy barrier.¹⁴

To elucidate the origins of the divergences, we performed *ab initio* calculations for the two complexes. Local properties of the Dy(III) centers were investigated by means of the CASSCF/SO-RASSI/SINGLE_ANISO methodology using Molcas 8.0 program.¹⁵ The X-ray-determined structures were used in all calculations by replacing the neighbouring Dy(III) ions with the Lu(III) ion,. Because of the presence of an inversion centre in both complexes, only one Dy(III) centre per complex has to be calculated. The calculated low-lying spectra of the Kramers doublets (KDs) of the Dy-fragments are shown in Table S4-S8. We can see that the ground KD is well separated from the excited states in both complexes. Table S5-S9 also shows that the transversal components of the g-tensor of the ground KDs in complex **1**, which will cause the different SMM behaviours for complexes **1** and **2**.

The total magnetic interactions (dipolar + exchange) between the Dy(III) centres in complexes **1** and **2** were taken into account within the Lines model by using the POLY_ANISO program.¹⁶ Because of the high axiality of the ground KDs and the high energies of the local excitations of Dy(III), the interaction reduces to the Ising Hamiltonian form:

$$\widehat{H}_{exch} = -(J_{dip} + J_{exch})\widetilde{s}_{Dy1z} \cdot \widetilde{s}_{Dy2z}$$

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Table 2 The Ising parameters for the magnetic interactions in
complexes 1 and 2

Complex J_{dip} (cm ⁻¹)	1 (cm ⁻¹)	J _{exch} (cm⁻¹)
	J _{dip} (CIII)	Fitted (POLY_ANISO)
1	+6.03	-7.33
2	+5.86	-3.40

The dipolar interaction was calculated directly, while the exchange-coupling parameters were determined by the fitting of the magnetic susceptibility data (Fig. 2). The best fit is given by the parameters shown in Table 2. This data shows that in both complexes, the dipolar interaction (J_{dip}) is ferromagnetic, whereas the exchange interaction (J_{exch}) is antiferromagnetic. In complex 1, the exchange interaction is stronger than the dipolar interaction, so the total magnetic interaction is antiferromagnetic. In contrast, the dipolar interaction in complex 2 is stronger than the exchange interaction and the total interaction is ferromagnetic. This agrees with the experimental data, in which complex 1 shows antiferromagnetic and complex 2 shows ferromagnetic behaviour (Fig. 2). Thus, it can be concluded that the different magnetic behaviours of complexes 1 and 2, despite their very similar structures, result from the different sensitivities of the dipolar interaction and the exchange interaction to the structural variations, more specifically, from the different magnitudes of the exchange interaction. Although the subtle structural variations cannot change the sign of the exchange interaction, they significantly change its magnitude, which is enough to make the dipolar interaction stronger and, as a result, changes the sign of the total magnetic interaction. This confirms that in lanthanide complexes, the magnetic interactions can be tuned through even minor structural variations. In addition, Table S10 shows the calculated low-lying exchange levels. The exchange splitting is only 0.3 cm⁻¹ in complex 1 and 1.4 cm^{-1} in complex **2**. This explains why these two complexes do not show a clear peak in the out-of-phase AC susceptibility at 2 K (Fig. 3b, d). However, complex 2 has a more axial ground state (Table S5-S9), which shows that the observed SMM behaviour in complex 2 originates from a single Dy(III) ion, since at 4 K, the exchange interaction does not play any role due to the small exchange splitting of only 1.4 cm⁻¹.

In summary, slight structural variations within two structurally similar dinuclear Dy(III) single molecule magnets has been demonstrated to impart major changes in the magnetic interactions states. The combination of our experimental observations with *Ab initio* calculations improves our understanding about how the transition between the two magnetic interaction states (antiferromagnetic or ferromagnetic) could be triggered by structural variations, which offers an illuminating insight into the magneto-structural correlation for lanthanide complexes.

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