

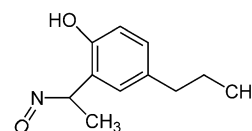
Single-Chain Magnets

Can CH $\cdots\pi$ Interactions Be Used To Design Single-Chain Magnets?Mukesh Kumar Singh and Gopalan Rajaraman^{*[a]}

Abstract: This theoretical study suggests that CH $\cdots\pi$ stacking interactions between monomeric units can be used to design novel single-chain magnets (SCMs), as the sign of coupling is predictable and such chains inherently yield negative axial anisotropy, a condition often difficult to achieve in conventional SCMs.

Despite two decades of research efforts, the potential applications proposed for single-molecule magnets (SMMs) are yet to be achieved.^[1] The two key parameters that control the barrier height for the magnetisation reversal are the spin ground state S and the axial anisotropy D . In many instances these two parameters antagonise each other leading to a smaller barrier height for magnetisation reversal.^[2] Achieving large S and D is intrinsically a challenging task, so another class of one-dimensional chain complexes called single-chain magnets (SCMs) have emerged as an alternative to SMMs. For SCMs, the ground state S value tends to reach infinity and even complexes possessing a smaller negative D value yield relatively larger barrier heights.^[3] Unlike in SMMs, the barrier height in the SCMs is also correlated to the strength of the intra-chain coupling. Ideal SCMs demand a large intra-chain magnetic exchange and negligible inter-chain coupling, and synthesising molecules possessing these characteristics along with the anisotropy is a non-trivial task.^[4] Use of weak stacking interactions (such as π - π and CH $\cdots\pi$) between mononuclear fragments to build one-dimensional SCMs is an attractive idea and already there are some literature examples of SCMs built using such interactions.^[5] By designing SCMs to allow the π - π and/or CH $\cdots\pi$ interactions in a particular direction, this approach offers the advantage of enhancing the intra-chain magnetic coupling and keeping the inter-chain interaction at a minimum and thus can yield better SCMs.

Our initial attempt was to explore the weak π - π interaction as a possible interaction to build SCMs. We chose the dinuclear Cu^{II} ([Cu(L¹)₂] (1), L¹H = 2-hydroxy-5-*n*-propylacetophenone



Scheme 1. Structure of the ligand {L¹H} employed in this study.

oxime, see Scheme 1),^[5d] Cr^{III} ([NBu₄][*trans*-Cr(C₆F₅)₄(L²)₂] (2), L² = cyano *meta*-xylene),^[5f] Mn^{III} ([Mn(L³)] (3), L³ = 5,10,15-tris(pentafluorophenyl)corrole)^[5e] and Ni^{II} ([Ni(L⁴)(L⁴H)] (4), L⁴H = 2,3-dihydroxy benzaldehyde)^[5j] complexes possessing π - π stacking interactions and performed calculations to estimate the exchange coupling constants. Selected structural parameters and crystal structures of the complexes are given in the Supporting Information (see Table S1 and Figure S1 for complexes 1–4). The π - π stacking interaction itself is a challenging task for the conventional exchange-correlation functionals; therefore, computing magnetic exchange mediating through the π - π stacking interaction poses a challenge even to the modern-day functionals.^[6] So we performed a benchmarking with these four complexes with ten different exchange-correlation functionals (see Table S2 in the Supporting Information). Among the tested functionals, B97D^[7] and M06^[8] yield good structures and good numerical estimates of exchange interaction compared with the experimental values/data. Herein, we have chosen to study with the B97D functional as the estimates of J with this functional are slightly superior. All these complexes yield antiferromagnetic coupling (J_{DFT} vs. J_{exptl} = -0.67 vs. -0.98 cm⁻¹, -0.08 vs. -0.09 cm⁻¹, -0.21 vs. -0.28 cm⁻¹ and -0.87 vs. -0.60 cm⁻¹ for complexes 1–4, respectively). The ligand-centred aromatic π^* antibonding molecular orbitals (MOs; see Scheme S1 in the Supporting Information) are found to mediate the coupling in these complexes and antiferromagnetic coupling results due to spin polarisation between the two π^* MOs (see Figure S2 in the Supporting Information). Although the magnitude of the J values tends to increase with some structural alteration, the sign of exchange, which is very important to obtain the effective S value, is found to be antiferromagnetic for all the structural variations studied (see Figure S3 in the Supporting Information). This is also consistent with the literature, in which ferromagnetic coupling mediated by the π - π interaction is extremely rare.^[9] Ferromagnetic coupling is required to obtain a non-zero ground state, so we searched for alternative weak interactions that can be utilised in the design of SCMs.

As the stabilisation due to CH $\cdots\pi$ interactions is found to be on a par with the π - π interaction,^[6b,10] we have studied the CH $\cdots\pi$ interaction as a possible force in the design of SCMs.

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201404853>. It contains optimized structures, spin density plots, magneto-structural plots, and spin density schemes, along with tables and computational details.

The CH $\cdots\pi$ interactions are not completely new to SCMs, as there are several one-dimensional chains reported to possess the weak CH $\cdots\pi$ interactions.^[5a-c,g-i] Herein, we have taken complexes **1** and **2**, and have created six model structures (models **1 a–e** and **2 a**). Models **1 a** and **1 b** describe two possible orientations encountered in complex **1**, in which five and one CH $\cdots\pi$ interactions, respectively, are present (see Figure 1 a and b).

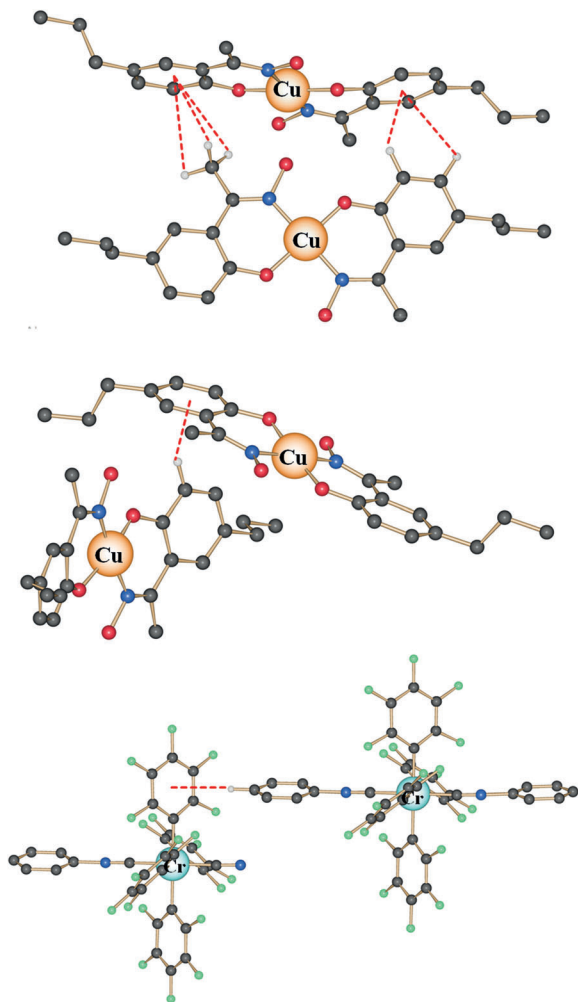


Figure 1. B97D optimised structures of models **1 a** (top), **1 b** (middle) and **2 a** (bottom). Hydrogen atoms except the ones involved in the CH $\cdots\pi$ interactions are omitted for clarity. Colour code: orange, Cu^{II}; cyan, Cr^{III}; green, F; red, O; blue, N; black, C; and white, H.

Models **1 c–1 e** (see Figure S4 in the Supporting Information) describe interaction with different transition-metal ions on the model **1 b** structure (**1 c** is a diiron(III), **1 d** is a dimanganese(III) and **1 e** is a dichromium(III) model possessing one CH $\cdots\pi$ interaction). For completeness we have also taken complex **2** and have modelled **2 a** possessing one CH $\cdots\pi$ interaction (see Figure 1c) to ascertain the nature of exchange interaction with different ligand architectures (see Table S3 in the Supporting Information for selected structural parameters for all models). Here, models **1 a** and **1 b** possess square-planar geometries whereas model **1 d** possesses a distorted square-pyramidal ge-

ometry. All other models (**1 c**, **1 e**, **1 f**) are octahedral in nature. All these models are optimised by using the B97D functional along with the TZV basis set.

All the computed structures are found to be minima with the **1 a** being 1.3 kcal mol⁻¹ (basis set superposition error corrected energy)^[11] stabilised relative to model **1 b**. The calculated *J* values of these model complexes (see Table 1) suggest

Table 1. DFT computed *J* values, *D* and *g* tensors along with M–M distance for models **1 a–e** and **2 a**.

Models	Average CH $\cdots\pi$ distance [Å]	M–M distance [Å]	<i>J</i> [cm ⁻¹]	<i>D</i> [cm ⁻¹]	<i>g</i>
1 a {Cu ^{II} ₂ }	4.3	5.68	4.72	-0.68	2.08
1 b {Cu ^{II} ₂ }	3.4	7.22	0.24	-1.34	2.08
1 c {Fe ^{III} ₂ }	3.4	8.30	0.20	-0.28	2.01
1 d {Mn ^{III} ₂ }	3.5	7.88	0.08	-0.43	2.00
1 e {Cr ^{III} ₂ }	3.4	7.93	-0.03	-	-
2 a {Cr ^{III} ₂ }	3.4	11.83	-0.003	-	-

that the CH $\cdots\pi$ stacking interaction yields ferromagnetic coupling when the unpaired electrons reside either in axial e_g-type orbitals (**1 a,b**) or in both e_g- and t_{2g}-type orbitals (**1 c,d**). However, a weak antiferromagnetic interaction is observed when the unpaired electrons reside only in the t_{2g}-type orbitals (models **1 e** and **2 a**). The energies of e_g orbitals are closer to the empty ligand-centred aromatic π* antibonding MOs (see Scheme S1 in the Supporting Information), so this leads to a stronger mixing and greater delocalisation of the spins to the coordinated atoms. This in turn promotes stronger polarisation leading to large *J* values (see Figure 2 (top) and Figure S5 in the Supporting Information). The t_{2g} orbitals, on the other hand, lie close to the ligand-centred aromatic π MOs (see Scheme S1 in the Supporting Information) and promote direct spin polarisation (see Figure 2 (bottom) and Figure S5 in the Supporting Information). This interaction is relatively weak leading to smaller *J* values.

The spin polarisation is the cause of the sign switching for both ferromagnetic and antiferromagnetic coupling (see Figure 2) and the nature of the coupling can be rationalised based on the observed spin densities (see Figure S6 in the Supporting Information). A strong spin polarisation on the aromatic region was detected for ferromagnetic coupling whereas delocalisation of unpaired electron density was found to be dominant for the antiferromagnetic coupling (see Figure 2). The coupling values are small, so the detected overlap integrals between the SOMOs are also found to be small. To check if dipolar interactions contribute to the magnetic coupling, additional models were created from **1 a** and **1 b** (see Figure S7, Supporting Information), in which the CH $\cdots\pi$ interaction is eliminated thereby keeping the metal–metal distance constant. These models yield *J* values of -0.05 and -0.009 cm⁻¹ for models **1 a** and **1 b**, respectively. These values are antiferromagnetic in nature and are in stark contrast to the *J* values given in Table 1. This indicates that the exchange mediates through the CH $\cdots\pi$ interaction and dipolar contributions to the *J* values are very small.

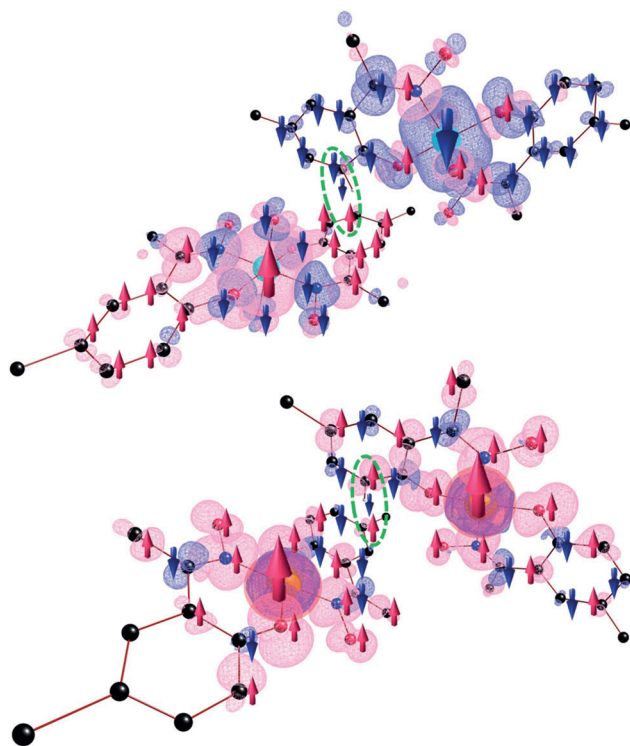


Figure 2. Diagrammatic representation of spin polarisation in model **1b** (bottom) and spin delocalization in model **1e** (top) resulting in ferro- and antiferromagnetic coupling, respectively, with the adjacent molecule connected through CH... π interaction (indicated by green dotted circle).

Although the tested complexes offer a generic way to obtain ferromagnetic coupling, the strength of the magnetic coupling is weak. Our calculations on **1a** suggest that the strength of the magnetic coupling can be fine-tuned by the number of CH... π stacking interactions; with five interactions present in **1a**, the magnitude of the J value was raised to $+4.72\text{ cm}^{-1}$ (from 0.24 cm^{-1} on **1b**). Both ligand design and crystal engineering can be utilised to achieve the maximum number of interactions; thus, this study highlights the potential of this interaction to obtain strong ferromagnetic coupling.

Apart from ferromagnetic coupling, axial anisotropy is another prerequisite for the observance of SCM behaviour. We have calculated the D and g values for models **1a–d** (see Table 1), for which negative D values for all models are obtained, and this encouraged us to explore the interaction further for possible SCM design.

The observation of negative D in all the cases is not surprising. The interaction between the monomeric units is weak, therefore dipolar terms are likely to dominate the D values. Generally, dipolar contributions to D are important compared with its contributions to J values. The largest component of $D_{\text{MM}}^{\text{dip}}$ (here $M = \text{Cu}^{\text{II}}$, Fe^{III} and Mn^{III}) is along the Z direction and the sign of $D_{\text{MM}}^{\text{dip}}(ZZ)$ is always negative for the orbitally degenerate ground state.^[12] Thus, this guarantees the observance of negative D values for these structures, a condition often difficult to meet in conventional exchange-coupled dimers and polynuclear clusters. Note here that the ground-state anisotropy will have multiple contributions, such as single-ion, ex-

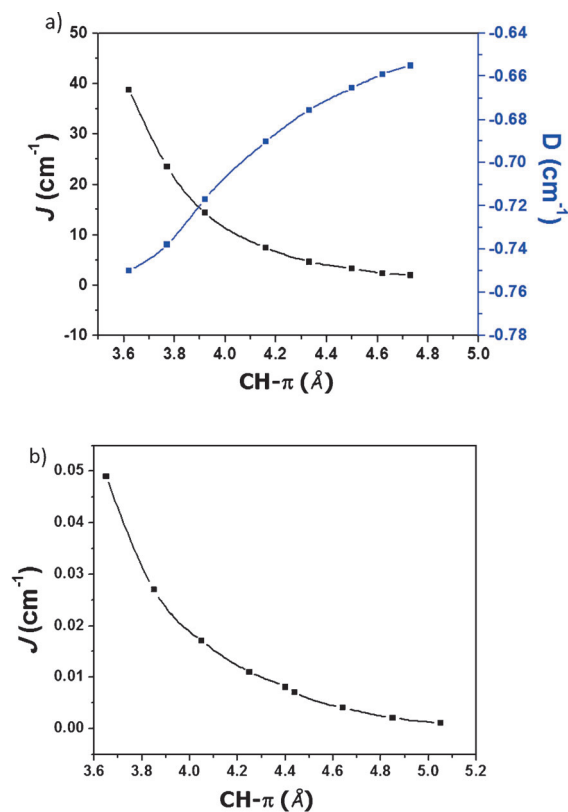


Figure 3. Magneto-structural correlations developed using DFT calculations by varying the CH... π stacking distance of models: a) **1a** and b) **1d**. For each point both J and D values are computed for model **1a**.

change and dipolar, and for metal ions such as Mn^{III} the orientation of the Jahn–Teller axis is an important factor that decides the magnitude of the anisotropy.^[13]

To explore how CH... π stacking distance influences the J values, we have developed magneto-structural correlations in which both the J and D values are computed by varying the CH... π distance for models **1a** and **1d** (see Figure 3). From the magneto-structural studies it is clear that the magnitude of J increases sharply with a decrease in the CH... π stacking distance. In both studied cases, the sign of J is preserved reiterating the fact that the sign is correlated to the electronic configurations of the metal ions, as stated earlier. Besides, the sign of D is found to be negative in all the points computed and this is also in accord with the earlier statement on dipolar interactions.

For model **1a**, large variations in J values are observed, with values as large as 40 cm^{-1} detected for extremely short CH... π interactions.^[14] This is also likely to be the case for other metal ions. For **1a**, as the J increases, the D also tends to be more negative, as expected from the summation of the exchange part to the dipolar contributions.^[12] For **1d**, the change in J is small, so the D value remains constant (-0.43 cm^{-1}). This invariably suggests that larger positive J and larger negative D can be achieved simultaneously in this architecture. This is also hard to achieve in conventional exchange-coupled systems/SCMs.

In summary, our study reveals that the CH $\cdots\pi$ stacking interaction can be utilised to design novel SCMs as the couplings are often ferromagnetic and inherently render negative zero-field splitting. Besides, such interaction can also be utilised to suppress quantum tunnelling of magnetisation observed in SMMs. By fine-tuning the nature of the interactions, stronger interactions than those obtained by ligands, such as carboxylates, phosphonates and so forth,^[15] can be achieved.

Acknowledgements

G.R. would like to acknowledge financial support from DST India (DST/INT/AUS/P-47/11; SR/NM/NS-1119/2011) and IIT Bombay for access to the high-performance computing facility. M.K.S. acknowledges a JRF position from UGC, India.

Keywords: density functional calculations · magnetic properties · pi interactions · single-chain magnets · stacking interactions

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Received: August 14, 2014

Published online on November 27, 2014