

Magnetic coupling in oximate bridged $\{\text{Mn}^{\text{III}}_6\}$ clusters bridged by diamagnetic dicyano-metallato linkers: A theoretical perspective[☆]

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ARTICLE INFO

Keywords:

Mn₆ clusters
Single Molecule Magnets
DFT calculations
Intracluster Exchange coupling
Magnetic coupling

ABSTRACT

Oximate bridged $\{\text{Mn}^{\text{III}}_6\}$ clusters are among the best known SMMs for transition metal clusters that exhibit a very large barrier height for magnetization reversal and decent blocking temperatures. Several attempts were made to improve the magnetic properties of this family, among others, employing dicyano-metallato linkers such as $[\text{Au}/\text{Ag}(\text{CN})_2]^-$ to link two $\{\text{Mn}^{\text{III}}_6\}$ clusters gained attention as this paves the way forward to construct supramolecular architecture based on $\{\text{Mn}^{\text{III}}_6\}$ units and also facilitate a way to control the intercluster exchange coupling – a parameter vital to Qubit application. In this work, we have employed DFT calculations to estimate various exchange coupling constants within the $\{\text{Mn}^{\text{III}}_6\}$ clusters ($[\text{Mn}^{\text{III}}_6(\mu_3\text{-O})_2(\text{Et-sao})_6(3\text{-py})_2(\text{MeOH})_2(\text{M}(\text{CN})_2)_2]$ M = Au (1), Ag (2) here sao^{2-} is the dianion of salicylaldehyde oxime or 2-hydroxybenzaldehyde oxime). We have identified four different J s within the cluster based on the orientation of the Jahn-Teller axes and the Mn–N–O–M dihedral angles. The computed J values within the clusters are in the borderline of ferro and antiferromagnetic coupling, leading to a competing interaction within the cluster, and for this reason, several spin states are found to lie close to each other. The computed J s reproduce the experimental susceptibility data and yield very small/negligible $\{\text{Mn}^{\text{III}}_6\text{-M}^{\text{I}}\text{-Mn}^{\text{III}}_6\}$ intercluster interaction. The reason for such weak couplings was analysed, and a search for stronger exchange coupling was undertaken by studying in detail the J values in $[\{\text{Mn}(\text{salen})(\text{EtOH})\}_3\{\text{M}(\text{CN})_6\}]$ (here M = Fe^{III} (3), Cr^{III} (4); Salen = N,N'-bis(salicylidene)ethylenediamine) clusters. This predictive strategy suggests that incorporating a metal ion such as Cr^{III} could be a game-changer as this promotes a very strong ferromagnetic coupling between two Mn^{III} centers. If this prediction is attempted for oximate bridged $\{\text{Mn}^{\text{III}}_6\}$ clusters, it could be very rewarding.

1. Introduction

The long-range coupling between single-molecule magnets (SMMs) has drawn wide attention over past decades due to their potential applications as a building block for a quantum computer, magnetic qubits, spintronic devices, etc., as their electronic spin can serve as an obvious choice for quantum information processing.[1-3] The prospect for improvements in the entanglement as well as strength of interaction towards higher distances remains a challenge in this area. In order to address these challenges, a systematic exploration is required for SMMs in terms of their metal identity, diversity of ligand design, and topology. The synthesis of polynuclear complexes with a large spin ground state and anisotropy remains a hurdle as it depends largely on the exchange interaction that governs the ground state of the complex, which is controlled by several structural parameters.

The keen interest in understanding the effect of structural factors in magnetic exchange (J) came into light when Hatfield and Hodgson explored the impact of Cu-OH-Cu angle on the magnetic exchange in the family of hydroxo bridged dimeric copper complexes.[4-8] This study further led to the magneto-structural correlations studies of dimers and polynuclear complexes comprising different first-row transition metal ions.[9-14] Investigating different structural factors that alter the sign and strength of J is essential and offers a better way for understanding the magnetic behavior of polynuclear clusters. Along with experimental observations from a large family of complexes, density functional theory (DFT) based methods are important in understanding the mechanism of the magnetic exchange and for developing magneto structural correlations.

Among the first-row transition metal ions, the Mn^{III} ion is the perfect choice for synthesizing novel SMMs based on transition metal ions as

[☆] Part of the special issue dedicated to the element manganese, entitled Manganese: A Tribute to chemical Diversity.

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they often exhibit large negative single-ion zero-field splitting parameter D (easy-axis), which is essential to stabilize larger M_S state as the ground state to facilitate slow relaxation of magnetization. The inherent structural distortions favoring Jahn-Teller elongation render a negative D value for this ion in most cases studied. In polynuclear framework, a ferromagnetic interaction is essential to obtain a large ground state S value, and numerous studies reported in Mn^{III} complexes reveal that exchange is often very weak and in the borderline of ferro-antiferromagnetic exchange, which offers a rare choice of fine-tuning the sign of J using a minimal structural distortion.[15-37] Although extensive studies on the magnetic coupling between the magnetic rings bridged by organic ligands are carried out, the studies employing metallic linkers are less explored.[1] The design and understanding of polynuclear complexes connected through metallic linkers can provide a way forward to connect various large clusters that exhibit superior magnetic characteristics. If the coupling is mediated by metallic linkers such as $[Au(CN)_2]^-$ or $[Ag(CN)_2]^-$ they can serve as a promising functional material that offers a way to modulate the intercluster exchange coupling and also propose a viable way to control long-range interactions. [1,38-43]

Although several Mn^{III} clusters are reported, oximate bridged $\{Mn^{III}_6\}$ clusters stand apart as they have varying S value from $S = 4$ to 12 and with $[Mn^{III}_6O_2(sao)_6(O_2CPh)_2(EtOH)_4]$ ($Et-sao^{2-} = 2$ -hydroxyphenylpropanone oxime) reported to have a record barrier height of magnetization reversal value $U_{eff} = 86$ K with $TB \sim 4.5$ K—one of the rarest SMMs based on Mn^{III} ion to show such a large barrier height and blocking temperatures. For this family of $\{Mn^{III}_6\}$ complexes, several magneto structural correlations were developed to rationalize the variation in the observed S value and way to fine-tune the S value using $Mn-N-O-Mn$ dihedral was also proposed. [44-47]

What happens if two $\{Mn^{III}_6\}$ units are linked together? Recently,

Brechin and co-workers have synthesized 1-D chains of $\{Mn^{III}_6\}$ SMMs using dicyanoaurate and dicyanoargentate $\{[M(CN)_2]^- M = Au^I, Ag^I\}$ units, $\{[Mn^{III}_6(\mu_3-O)_2(Et-sao)_6(3-py)_2(MeOH)_2(Au(CN)_2)_2] 2MeOH\}_n$ (1, see Fig. 1a), $\{[Mn^{III}_6(\mu_3-O)_2(Et-sao)_6(3-py)_2(MeOH)_2(Ag(CN)_2)_2]\}_n$ (2, see Fig. 1b) with an aim to improve the SMM characteristics.[48] The fitting of magnetic data (susceptibility curves) shows the presence of antiferro and ferromagnetic interactions between Mn^{III} ions in $\{Mn^{III}_6\}$ units resulting in an $S = 4$ ground state. Ac susceptibility measurements on 1 and 2 show frequency dependency and their U_{eff} barrier for magnetization reversal calculated from the Arrhenius plot as 39.9 K, 50.7 K for 1 and 2, respectively.[48] In this work, we aim to utilize DFT calculations to compute the J values within this $\{Mn_6\}$ cluster and compute the intermolecular J to assess and analyze how this strategy of linking such larger clusters could help in the design of multi-qubit systems.

2. Computational details

All calculations were performed using the hybrid B3LYP [49] functional with Alrich[50] triple- ζ basis set as implemented in the Gaussian 09[51] suite of programs. The percentage of HF in DFT functional is found to play a crucial role in estimating the exchange values in the polynuclear cluster. The hybrid functional, B3LYP, computes the accurate exchange values for non-mixed valence systems, and HSE06 functional tends to be an appropriate choice for mixed-valence clusters.[52] The J values were computed from the energy differences between the high spin (E_{HS}) state calculated using single determinant wave functions and the low spin (E_{LS}) state determined using the Broken Symmetry (BS) approach developed by Noodleman.[53,54] This methodology has a proven track record of yielding a good numerical estimate of J for various clusters, including several structurally similar $\{Mn^{III}_6\}$ motifs.

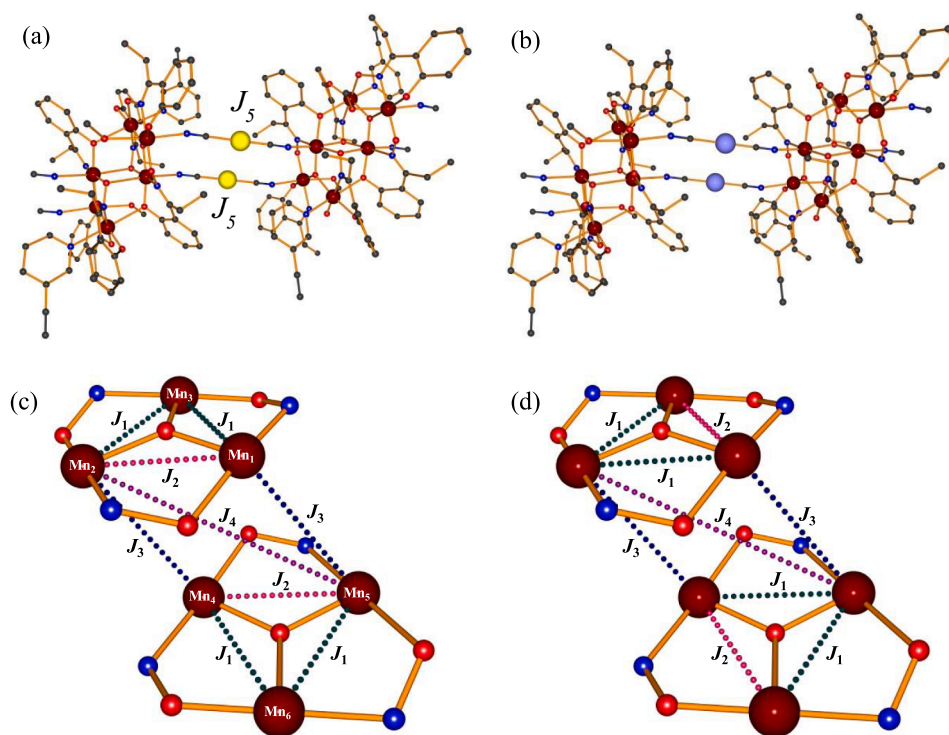


Fig. 1. Molecular structures of (a) 1 and (b) 2 along with J_5 interaction. The different exchange pathways designed within $\{Mn^{III}_6\}$ framework of complex c) 1 and d) 2.

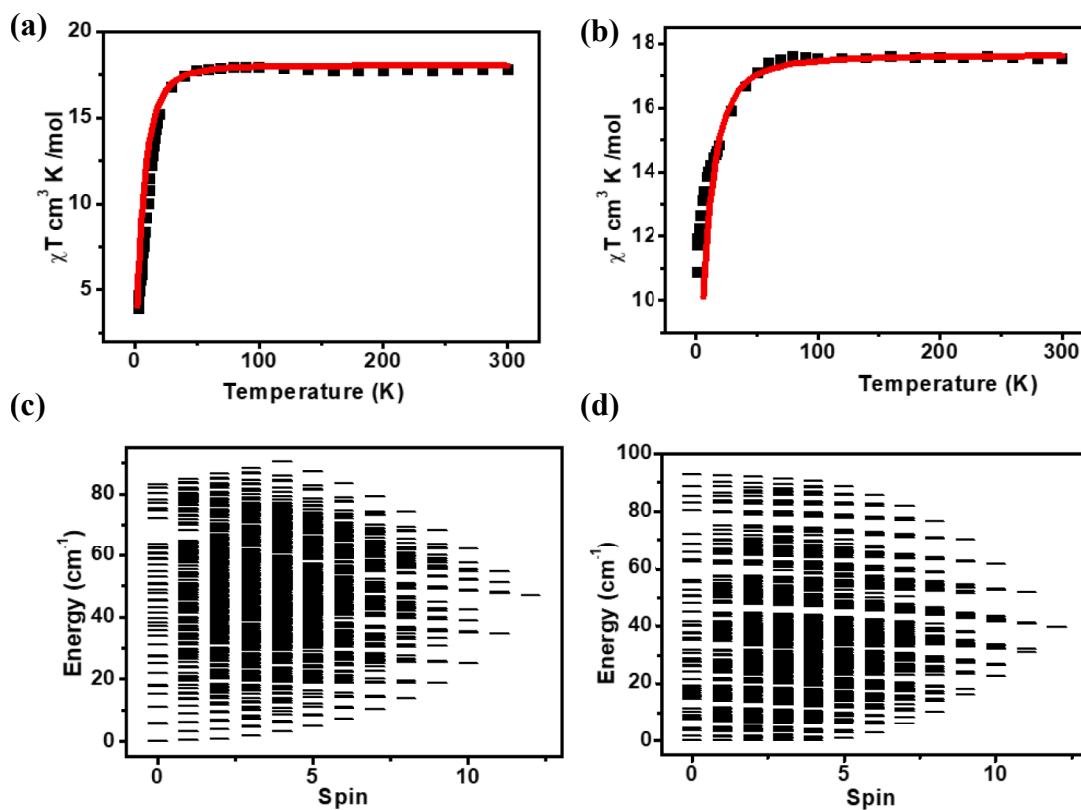


Fig. 2. (a) Simulated $\chi_m T$ versus T curve using the calculated DFT J values (red line) and experimental data (black squares) for 1; (b) Simulated $\chi_m T$ versus T curve using the calculated DFT J values (red line) and experimental data (black squares) for 2; Eigen plots for 1 (c) and 2 (d). ((Colour online.))

[55] The computed broken symmetry solutions are corresponding to some of the Eigen-states shown in Fig. 2. Negative and positive values for J correspond to antiferromagnetic and ferromagnetic interactions, respectively. A tight convergence criterion is employed to obtain a good numerical estimate of J , and details of the computational method employed to compute the exchange interaction are discussed elsewhere. [56-62].

3. Results and discussion

In complexes 1 and 2, $\{\text{Mn}^{\text{III}}_6\}$ units are analogous to each other, which comprise of two oxo bridged $\{\text{Mn}^{\text{III}}_3\}$ triangles. Within the $\{\text{Mn}^{\text{III}}_3\}$ units, the Mn^{III} ions are linked through one oxo and three oxime bridges. Di-oxo bridges interconnect these two $\{\text{Mn}^{\text{III}}_3\}$ triangles. The JT axis of Mn^{III} ions in distorted octahedral geometry is aligned perpendicular to the $\{\text{Mn}^{\text{III}}_3\}$ triangles. Previously we have computed exchange interactions in several Mn^{III} dimers with different bridging ligands

ranging from di-alkoxide bridges, combined oxo and oxime bridges, and di-oxime bridges.[63-65] Apart from validating exchange parameters, we have performed magneto-structural correlation in the dimer complexes to gain insights into the influence of several parameters such as distance, angle, and dihedral angles on the sign and strength of magnetic coupling.

For the $\{\text{Mn}^{\text{III}}_6\}$ motif, four exchange pathways ($J_1 - J_4$) between Mn^{III} ions were identified, as shown in Fig. 1 (c) and (d). We have employed Noodleman's broken symmetry method[53] for evaluating J values using the Hamiltonian shown below. For complexes 1 and 2: J_1 and J_2 represent the magnetic coupling between Mn^{III} centers within $\{\text{Mn}^{\text{III}}_3\}$ units, whereas J_3 and J_4 interactions correspond to exchange values across two $\{\text{Mn}^{\text{III}}_3\}$ units. Additionally, one more exchange denoted as J_5 interaction was identified, which describes inter $\{\text{Mn}^{\text{III}}_6\}$ cluster interaction, and this is calculated in a larger cluster model independently (see Table 1).

Table 1

The survey on various $\{\text{Mn}^{\text{III}}_6\}$ units and their J values along with 1 and 2 studied here.

MolecularFormula	J_{DFT}	J_{Exp}	Reference
$\{[\text{Mn}^{\text{III}}_6(\mu_3\text{-O})_2(\text{Et-sao})_6(3\text{-py})_2(\text{MeOH})_2(\text{Au}(\text{CN})_2)_2] 2\text{MeOH}\}_n$	$J_1 = -0.17, J_2 = 0.37, J_3 = 1.04, J_4 = -1.95,$	$J_1 = 2.56, J_2 = -5.25, J_3 = 2.56,$ $J_4 = 2.56$	This work
$\{[\text{Mn}^{\text{III}}_6(\mu_3\text{-O})_2(\text{Et-sao})_6(3\text{-py})_2(\text{MeOH})_2 \text{Ag}(\text{CN})_2)_2\}_n$	$J_1 = 0.13, J_2 = -1.60, J_3 = 0.62, J_4 = 1.28$	$J_1 = 2.77, J_2 = -6.17, J_3 = 2.77,$ $J_4 = 2.77$	This work
$[\text{Mn}_6\text{O}_2(\text{H-sao})_6(\text{O}_2\text{CH}_2)(\text{MeOH})_4]$	$J_1 = -10.5, J_2 = -3.1, J_3 = 1.3, J_4 = -0.5,$ $J_5 = 2.9$	$J_1 = -4.6, J_2 = -1.8, J_3 = J_4 = 1.25$	[60]
$[\text{Mn}_6\text{O}_2(\text{Me-sao})_6(\text{O}_2\text{CCPh}_3)_2(\text{EtOH})_4]$	$J_1 = 1.2, J_2 = -1.6, J_3 = -1.5, J_4 = -0.8, J_5 = 3.2$	$J_1 = 1.2, J_2 = -1.95$	[60]
$[\text{Mn}_6\text{O}_2(\text{Et-sao})_6(\text{O}_2\text{CPh}_2 \text{OPh})_2(\text{EtOH})_4]$	$J_1 = 47.6, J_2 = 23.7, J_3 = 31.8$	$J_1 = 47.6, J_2 = 23.7, J_3 = 31.8$	[60]
$[\text{Mn}_6\text{O}_2(\text{Et-sao})_6(\text{O}_2\text{CPh}(\text{Me})_2)(\text{EtOH})_6]$	$J_1 = 43.1, J_2 = 39.1, J_3 = 34.9$	$J_1 = 43.1, J_2 = 39.1, J_3 = 34.9$	[60]
$[\text{Mn}_6\text{O}_2(\text{Me-sao})_6(\text{O}_2\text{C-th})_2(\text{EtOH})_4(\text{H}_2\text{O})_2]$	$J_1 = 31.1, J_2 = 36.3, J_3 = 27.4$	$J_1 = 31.1, J_2 = 36.3, J_3 = 27.4$	[60]
$[\text{Mn}_6\text{O}_2(\text{Et-sao})_6(\text{O}_2\text{CCMe}_3)_2(\text{EtOH})_5]$	$J_1 = 1.39, J_2 = -1.92$	-	[44]
$[\text{Mn}_6\text{O}_2(\text{Me-sao})_6(\text{O}_2\text{CPhBr})_2(\text{EtOH})_6]$	$J_1 = 1.15, J_2 = -0.73$	-	[44]
$[\text{Mn}_6\text{O}_2(\text{Et-sao})_6(\text{O}_2\text{C}_{11}\text{H}_{15})_2(\text{EtOH})_6]$	$J_1 = 1.60$	-	[44]

$$\hat{H}_{Ex} = -[2J_1(\hat{S}_{Mn1}\hat{S}_{Mn3} + \hat{S}_{Mn2}\hat{S}_{Mn3} + \hat{S}_{Mn4}\hat{S}_{Mn6} + \hat{S}_{Mn5}\hat{S}_{Mn6}) + 2J_2(\hat{S}_{Mn1}\hat{S}_{Mn2} + \hat{S}_{Mn4}\hat{S}_{Mn5}) + 2J_3(\hat{S}_{Mn2}\hat{S}_{Mn4} + \hat{S}_{Mn1}\hat{S}_{Mn5}) + 2J_4(\hat{S}_{Mn2}\hat{S}_{Mn5})] \quad (1)$$

$$\hat{H}_{Ex} = -[2J_1(\hat{S}_{Mn1}\hat{S}_{Mn2} + \hat{S}_{Mn2}\hat{S}_{Mn3} + \hat{S}_{Mn4}\hat{S}_{Mn5} + \hat{S}_{Mn5}\hat{S}_{Mn6}) + 2J_2(\hat{S}_{Mn1}\hat{S}_{Mn3} + \hat{S}_{Mn4}\hat{S}_{Mn6}) + 2J_3(\hat{S}_{Mn2}\hat{S}_{Mn4} + \hat{S}_{Mn1}\hat{S}_{Mn5}) + 2J_4(\hat{S}_{Mn2}\hat{S}_{Mn5})] \quad (2)$$

To compute these exchange coupling, five different spin configurations (Tables, ST1-2 in [supporting information](#)) were computed to extract the J values in $\{\text{Mn}^{\text{III}}_6\}$ units of 1 and 2. Here J represents the isotropic exchange coupling constant, and S_{Mn} defines the spins on Mn^{III} ions ($S = 2$).

Here, we have designed exchange pathways (J_1 - J_3) in 1 and 2 depending on the variation in the Mn—O—N—Mn dihedral angles (equations (1) and (2), [Table 2](#)) based on the insights from Mn^{III} dimer complexes study.[\[44,45,55,66\]](#) The dihedral angles are found to vary from 29.5° to 64.6° in 1 and 23.7° to 70.3° in 2. In the case of complex 1, J_1 - J_3 interaction corresponds to dihedral angles (a) 29.5° to 31.8° (b) 39.4° to 39.5° (c) 64.5° to 64.6°, respectively ([Fig. 1](#) (c) and (d)). In the case of complex 2, the dihedral angles vary from (a) 35° to 36.6° are labeled as J_1 interaction; (b) 23.7° to 23.8° as J_2 interaction; (c) 69.8° to 70.3° as J_3 interaction.

The J_4 interaction corresponds to the exchange between Mn^{III} ions via μ_2 -oximate bridges, and here the dihedral angle between two JT axes decides the sign and magnitude of exchange as evidenced in $[\text{Mn}^{\text{III}}(\text{OR})_2]$.[\[67\]](#) The calculated DFT J values (See [Table 1](#)) show a mixture of weak ferro and antiferromagnetic interactions in $\{\text{Mn}^{\text{III}}_6\}$ units of 1 and 2. The computed J values reproduce experimental susceptibility curves adding confidence to our chosen methodology. In previous magneto structural correlation developed by Brechin and co-workers in $\{\text{Mn}^{\text{III}}_6\}$ complexes revealed the role of dihedral angle (Mn—O—N—Mn) in switching the nature of exchange interaction and the dihedral angle, 31° is noted to be the critical point where the nature of interaction changes from antiferro to ferromagnetic interaction. The dihedral angles of J_1 interaction in 1 and J_2 interaction in 2 lies in the margin of 31° leading to antiferromagnetic interaction, whereas J_2 , J_3 interactions of 1 and J_1 , J_3 interactions of 2 corresponds to dihedral angles varying from 35° to 70° leading to ferromagnetic coupling.

The computed Eigen plots for $\{\text{Mn}^{\text{III}}_6\}$ units in 1 and 2 are shown in [Fig. 2](#) (c) and (d). For complex 1, calculations reveal $S = 0, 1$, and 2 are nearly degenerate, while for complex 2, $S = 0, 1, 2, 3$, and 4 states are absolutely degenerate within the given set of J values. As the magnetic

properties are likely to be influenced by the intercluster and intermolecular interactions, a small change in these J s could alter the spin ground states. Due to the presence of competing interactions within the $\{\text{Mn}^{\text{III}}_6\}$ units, the energy levels of different spin states are close-lying in energy, which is likely to facilitate faster relaxation of magnetization as observed for the original $\{\text{Mn}^{\text{III}}_6\}$ cluster.[\[68\]](#)

To assess the intercluster interaction J_5 , we have performed calculations on the full dimeric structure of 1 with all the Mn centers intact. The magnetic exchange coupling between the two $\{\text{Mn}^{\text{III}}_6\}$ unit that mediated by the $\{\text{Au}(\text{CN})_2\}$ bridges were then estimated. Our calculation yield a negligible ferromagnetic J value ($1.0 \times 10^{-4} \text{ cm}^{-1}$), suggesting extremely weak interaction between the two units via this bridge. This metallic linker was found to offer not a strong exchange, and this is essentially due to the $\{\text{Au}(\text{CN})_2\}$ bridge that lies along the JT axis with a very long Mn-N bond distance of 2.26 Å, this facilitates relatively weaker exchange between the two Mn_6 motifs. Further, the closed-shell nature of the $\text{Au}^{\text{I}}/\text{Ag}^{\text{I}}$ ions is responsible for weaker exchange as the completely-filled d-orbitals of these ions do not efficiently transmit the spin-densities via delocalization/polarization mechanisms. AC susceptibility measurement performed on this cluster also suggest a weaker exchange interaction with the k value estimated to be 0.14 and 0.15 for complexes 1 and 2, respectively (here $k = \Delta T_B / (T_B \Delta \log f)$ with T_B describes blocking temperature and f the ac frequency). As the intra-cluster exchange couplings are already small, even a very small exchange can offer a superparamagnet-like behaviour, as witnessed in the experiments. [\[48\]](#)

As this linker did not offer a very strong intercluster exchange coupling as expected, we carry out a theoretical search for finding the best linkers that could offer strong exchange coupling between two units. Our interest is to choose first-row transition elements containing $\text{Fe}^{\text{III}}/\text{Cr}^{\text{III}}$ ions that have vacant d-orbitals to facilitate stronger exchange interactions. Among various clusters reported, tetranuclear clusters, $[\{\text{Mn}(\text{salen})(\text{EtOH})\}_3\{\text{M}(\text{CN})_6\}]$ reported by Nojiri and co-workers fits our ambit. These clusters consist of three Mn^{III} ions connected to central Fe^{III} (3) or Cr^{III} ions (4) via cyanide bridges.[\[69\]](#) The exchange Hamiltonian adapted here is given below,

$$\hat{H}_{Ex} = -[2J_1(\hat{S}_{Fe1}\hat{S}_{Mn2} + \hat{S}_{Fe1}\hat{S}_{Mn3} + \hat{S}_{Fe1}\hat{S}_{Mn4}) + 2J_2(\hat{S}_{Mn2}\hat{S}_{Mn3} + \hat{S}_{Mn3}\hat{S}_{Mn4}) + 2J_3(\hat{S}_{Mn2}\hat{S}_{Mn4})] \dots \quad (3)$$

$$\hat{H}_{Ex} = -[2J_1(\hat{S}_{Cr1}\hat{S}_{Mn2} + \hat{S}_{Cr1}\hat{S}_{Mn3} + \hat{S}_{Cr1}\hat{S}_{Mn4}) + 2J_2(\hat{S}_{Mn2}\hat{S}_{Mn3} + \hat{S}_{Mn3}\hat{S}_{Mn4}) + 2J_3(\hat{S}_{Mn2}\hat{S}_{Mn4})] \quad (4)$$

Table 2

The various Mn—O—N—Mn dihedral angles within $\{\text{Mn}^{\text{III}}_6\}$ units of 1 and 2 are listed.

Exchange labels	Mn—O—N—Mn dihedral angles (°) in $\{\text{Mn}^{\text{III}}_6\}$ units	
	1	2
J_1	29.5, 30.2, 30.2, 31.8	34.9, 35.0, 36.1, 36.2
J_2	39.4, 39.5	23.7, 23.8
J_3	64.5, 64.6	69.8, 70.3

Here, we have modelled three exchange pathways (for equations (3), (4), and [Table ST3-4](#) in [supporting information](#) for spin configurations) between the Mn^{III} and Fe^{III} ions to understand the impact of Mn^{III} ions on the *cis* and *trans* positions. The tetranuclear structures chosen for our study are shown in [Fig. 3](#) (a) and (b). The computed J values are summarized in [Table 3](#). The DFT computed J values are able to reproduce the experimental magnetic data ([Fig. 3](#)(c) and (d)). The exchange

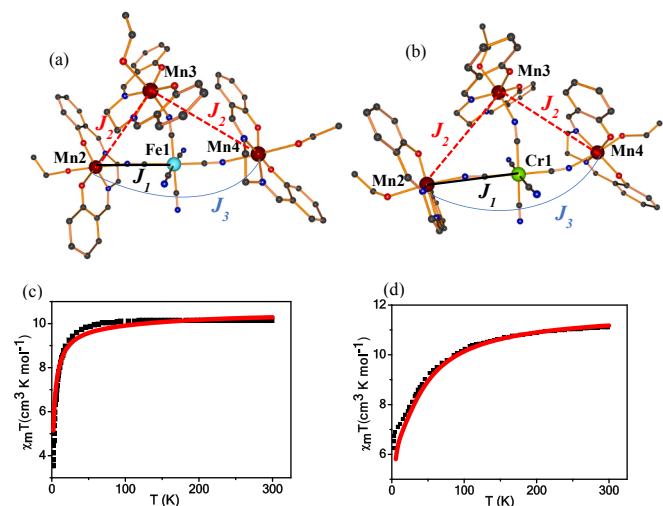


Fig. 3. Crystal structures of (a) 3 and (b) 4; Simulated $\chi_m T$ versus T curve using the calculated DFT J values (red line) and experimental data (black squares) for 3 (c); (b) Simulated $\chi_m T$ versus T curve using the calculated DFT J values (red line) and experimental data (black squares) for 4 (d). ((Colour online.))

Table 3

Computed and Experimental J values (cm^{-1}) for complexes 3 and 4.

Exchange Parameter J	3		4	
	J_{DFT}	J_{Exp}	J_{DFT}	J_{Exp}
J_1	3.75	3.33	-2.49	-1.59
J_2	-0.51	-	-0.94	-
J_3	-0.31	-	1.66	-

interaction between the Fe^{III} and Mn^{III} ions in 3 is found to be ferromagnetic in nature, whereas the exchange interaction pathways between Mn^{III} ions are weakly antiferromagnetic for both *cis* and *trans* isomers.

In the case of complex 4, the magnetic exchange computed between Cr^{III} and Mn^{III} ions is found to be antiferromagnetic in nature, contrary to the observance in 3. Interestingly, ferromagnetic interaction is observed between Mn^{III} ions at the *trans* positions, whereas very weak antiferromagnetic exchange at *cis* positions. Our model studies predict the existence of ferromagnetic exchange between the Mn^{III} ions at the *trans* positions for 4 and could be extended to the $\{\text{Mn}^{\text{III}}_6\text{-M}^{\text{III}}\text{-Mn}^{\text{III}}_6\}$ polynuclear clusters to offer strong exchange coupling that could improve the existing SMM characteristics of the popular oximate bridged $\{\text{Mn}^{\text{III}}_6\}$ motifs.

4. Conclusions

To summarise, we have performed DFT calculations on two oximate $\{\text{Mn}^{\text{III}}_6\}$ clusters that are bridged by $[\text{Au}(\text{CN})_2]^-$ and $[\text{Ag}(\text{CN})_2]^-$ linkers ($[\text{Mn}^{\text{III}}_6(\mu_3\text{-O})_2(\text{Et-sao})_6(3\text{-py})_2(\text{MeOH})_2(\text{M}(\text{CN})_2)_2]$ $\text{M} = \text{Au}$ (1), Ag (2)). Four different exchange coupling constants were identified within the $\{\text{Mn}^{\text{III}}_6\}$ units, and these were computed explicitly. These calculations yield weak ferro and antiferromagnetic coupling leading to very small ground state S values. Further, we have also computed the $\{\text{Mn}^{\text{III}}_6\text{-M}^{\text{I}}\text{-Mn}^{\text{III}}_6\}$ intercluster exchange, which is extremely small. This is essentially due to the nature and position of the linker unit that is placed in the $\{\text{Mn}^{\text{III}}_6\}$ motif. A theoretical search undertaken to predict a stronger exchange between Mn^{III} ions leads to two tetranuclear clusters $[\{\text{Mn}(\text{salen})(\text{EtOH})\}_3\{\text{M}(\text{CN})_6\}]$ (here $\text{M} = \text{Fe}^{\text{III}}$ (3), Cr^{III} (4)) where stronger exchange couplings are detected. Particularly the Cr^{III} ion as linker found to offer a strong ferromagnetic exchange between two Mn^{III}

ions located in the *trans* position, an idea, if extrapolated to $\{\text{Mn}^{\text{III}}_6\}$, could be very rewarding.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

We thank the DST and SERB (DST/SJF/CAS-03/2018-19; SB/SJF/2019-20/12; CRG/2018/000430) New Delhi, India, for financial support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2021.115346>.

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