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What Controls the Magnetic Interaction in bis- μ -Alkoxo Mn^{III} Dimers? A Combined Experimental and Theoretical Exploration**

Nelly Berg,¹ Thayalan Rajeshkumar,² Stephanie M. Taylor,³ Prof. Euan K. Brechin,³
Dr. Gopalan Rajaraman,^{2,*}, Dr. Leigh F. Jones^{1,*}

^[1]School of Chemistry, NUI Galway, University Road, Galway, Ireland.

^[2]Department of Chemistry, Indian Institute of Technology, Powai, Mumbai, 400 076, India.

^[3]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

^[*]Corresponding authors; G.R. e-mail: rajaraman@chem.iitb.ac.in; L.F.J. e-mail: leigh.jones@nuigalway.ie

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Keywords:

Mn(III) dimers; magneto-structural correlations; molecular magnetism; coordination complexes; DFT

Abstract

The synthesis and magnetic characterisation of a series of bis- μ -alkoxide bridged Mn(III) dinuclear complexes of general formula $[\text{Mn(III)}(\mu\text{-OR})_2(\text{biphen})_2(\text{ROH})_x(\text{L})_y]$ (where R = Me, Et; H_2biphen = 2,2-biphenol and L = terminally bonded N-donor ligand) is described, doubling the literature basis set for this type of complex. Building on these findings we have categorised all known μ -OR bridged Mn(III) dinuclear complexes into one of three classifications with respect to their molecular structures. We have then employed DFT and MO calculations to assess all potential magneto-structural correlations for this class of compound in order to identify the structural requirements for constructing ferromagnetic family members. Our analysis indicates that the most influential parameter which governs the exchange interaction in this class of compounds is the relative orientation of the JT axes of the Mn(III) atoms. A perpendicular orientation of the JT axes leads to a large ferromagnetic contribution to the exchange. These results also suggest that a large ferromagnetic interaction *and* a large anisotropy are unlikely to co-exist in such structural types.

Introduction

The construction of families of polynuclear cluster compounds containing multiple paramagnetic metal centres and the understanding and development of the relationship between structure and magnetism (magneto-structural correlations) is an area of widespread interest.^[1] In practice of course this is not a trivial task, even assuming that a large number of structurally-related compounds can be synthesised, crystallised and characterised, because the super-exchange mechanisms involved are influenced by many structural factors including, for example, the type of metal ion(s) (M) and bridging ligand(s) (L) employed, and the specific M-M and M-L distances and the M-L-M and M-L-L-M angles in the molecule.^[1] Despite these obstacles such studies are extremely important because the ability to control and modulate the type and magnitude of magnetic exchange within a complex has enormous ramifications for materials science and nanotechnology.^[2] Seminal work in this field emerged shortly after the discovery of the apparent anomalous paramagnetism of “monomeric” copper acetate.^[3] The molecular structure was proposed to be dimeric by Bleaney and Bowers in 1952 using EPR spectroscopy^[4] and was later validated via single crystal X-ray diffraction.^[5] These findings coincided with the rapid development of structure determination and soon led to the evolution of magneto-structural correlation studies within other dinuclear Cu(II) species. The first example of a quantitative relationship was developed by Hatfield and Hodgson in a large family of di- $\mu\text{-OH}^-$ bridged $[\text{Cu(II)}_2]$ complexes, in which the magnetic exchange (J) was found to be governed by the magnitude of the Cu-OH-Cu angle.^[6] These observations were then followed by other studies on dimeric cupric complexes containing, for example, symmetric halide bridging ligands,^[7] asymmetric

mixed ligand combinations,^[8] and a family of end-on azide-bridged complexes containing both ferro- and antiferromagnetically coupled siblings in which the magnetic exchange was very elegantly shown to depend on the Cu-N-Cu angle.^[9] Thereafter, magneto-structural correlations were also attempted and established for (dimeric) complexes containing other 1st row transition metal ions such as Fe(III),^[10] Cr(III),^[11] Mn(II)^[12] and Mn(III).^[13]

Understanding the magneto-structural relationship in small compounds, such as dimers and trimers, is also an important step towards understanding the magnetic behaviour of large or very large polymetallic complexes, since the magnetic skeletons of the latter are often made up of the same basic building blocks. Recent trends in molecular magnetism have seen enormous growth in the synthesis of molecules containing tens, if not hundreds, of metal ions because of their potential application in, for example, information storage, magnetic refrigeration, quantum information processing and molecular spintronics.^[14] Such compounds often possess very elaborate topologies comprising multiple M-L-M and / or M-L-L-M exchange pathways that may not be accurately deciphered due to over parameterisation and / or computational limitations.^[15] However, if the magnetic behaviour of the small building blocks that self-assemble to form the larger architecture are known and understood, the magnetic behaviour of the larger molecule can be more easily rationalised. Indeed the last few years have seen both qualitative and quantitative magneto-structural trends established for tri-,^[16] tetra-,^{[15a],[17]} hexa-,^[18] and octanuclear^[19] complexes of 1st row transition metals, as well as with mixed metal 3d-4f species.^[20]

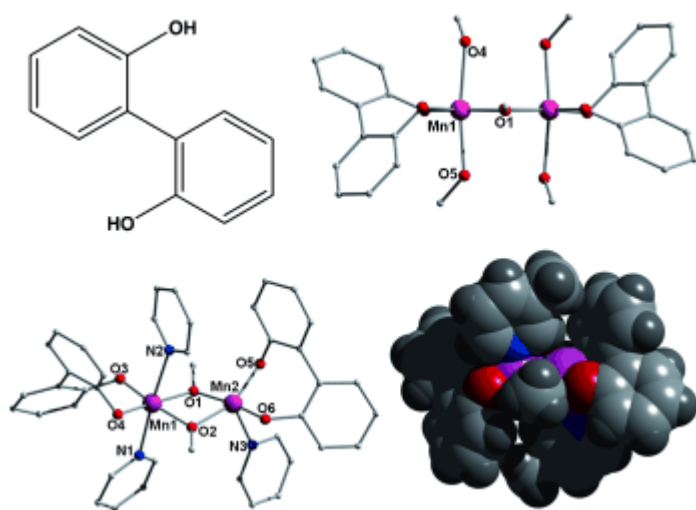
In addition to experimental observations, theoretical methodologies based on density functional theory have become increasingly popular tools with which to compute magnetic exchange interactions and develop magneto-structural correlations.^[21] Established theoretical protocols have provided excellent numerical estimates of J values and of the underlying electronic structure. One major advantage of the theoretical approach is that magneto-structural correlations for a particular structure type can be developed on simplified model complexes in which structural parameters can be modified in a methodical manner, offering insights into the effect of one particular structural change at a time on the sign and magnitude of J .

Due to its large single ion anisotropy the Jahn-Teller distorted Mn(III) ion is often the metal of choice for the synthesis of Single-Molecule Magnets (SMMs), an important class of compounds with potential application in information storage.^{[14],[22]} In order to build such molecules it is preferable to have strong ferromagnetic exchange between neighbouring Mn centres and as such knowledge of what controls the pairwise magnetic exchange is vital. A literature search reveals however that the majority of di- and polynuclear Mn(III) complexes exhibit, with few exceptions,^{[46],[47]} very weak ferro- or antiferromagnetic exchange interactions and that the parameters that control the magnitude and sign of J have not been clearly established - even for simple Mn(III) dimers. The bis-alkoxo

bridged dinuclear Mn(III) compounds reported in the literature to date are collected in Tables 2-4, and have J values (based on the $-2JS_i \cdot S_j$ formalism) ranging from -15.5 cm^{-1} to $+19.7 \text{ cm}^{-1}$. Herein we describe the synthesis and magnetic characterization of a new family of bis- μ -alkoxide bridged Mn(III) dinuclear complexes of general formula $[\text{Mn(III)}(\mu\text{-OR})_2(\text{biphen})_2(\text{ROH})_x(\text{L})_y]$ (where R = Me, Et; H_2biphen = 2,2-biphenol and L = terminally bonded N-donor ligand) and establish a magneto-structural correlation for all known bis-alkoxo bridged dinuclear Mn(III) compounds using a combined experimental and theoretical study.

Results and Discussion

All significant bond distances and angles along with single crystal X-ray diffraction data for complexes **1-5** are given in Tables 1 and S1, respectively. Structural parameters pertinent to our correlation studies are given in Tables 2-4. The first member of this family is $[\text{Mn(III)}_2(\mu\text{-OMe})_2(\text{biphen})_2(\text{MeOH})_4]$ (**1**), formed via the reaction of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2,2-biphenol^[23] and NaOH in alcohol. Complex **1** (Figure 1) crystallizes in the triclinic $P\bar{1}$ space group with an asymmetric unit composed of one dinuclear molecule. The two six-coordinate Mn(III) ions, which lie about an inversion centre (Mn1 and symmetry equivalent (s.e)), are bridged via two $\mu\text{-OMe}$ anions with a $\text{Mn1-O1-Mn1}'$ angle of 103.66° and $\text{Mn1} \cdots \text{Mn1}'$ distance of 3.071 \AA . Each Mn(III) cation is ligated by two oxygen atoms from a chelating, doubly deprotonated 2,2'-biphenolate ligand. The six coordinate distorted octahedral geometries of each metal ion are completed by two terminal methanol molecules which bond on the Jahn-Teller axes at distances of 2.37 \AA (Mn1-O4) and 2.27 \AA (Mn1-O5). The oxidation state of the Mn(III) was confirmed through bond length and charge balance considerations and BVS calculations (as were all others described in this work).



← **Figure 1.** (top left) Schematic of 2,2'-biphenol, (top right) Crystal structure of **1**, (bottom left and right) Crystal structure of **2** viewed as ball-and stick (left) and space-fill (right). Colour code: Pink (Mn), Red (O), Blue (N), Light Grey (C), Dark Grey (H).

	1		2		3
Mn1-O1	1.956(19)	Mn1-O1	1.972(6)	Mn1-O1	1.938(2)
Mn1-O1#	1.950(2)	Mn1-O2	1.936(2)	Mn1-O1#	1.935(2)
Mn1-O2	1.896(2)	Mn1-O3	1.841(6)	Mn1-O2	1.853(2)
Mn1-O3	1.852(2)	Mn1-O4	1.879(6)	Mn1-O3	1.842(2)
Mn1-O4	2.366(3)	Mn1-N1	2.321(7)	Mn1-N1	2.196(2)
Mn1-O5	2.270(2)	Mn1-N2	2.420(8)		
Mn1-O1-Mn1#	103.65(10)	Mn1-O1-Mn1#	101.1(2)	Mn1-O1-Mn1#	104.11(9)
Mn1...Mn1#	3.071	Mn1...Mn1#	3.007(2)	Mn1...Mn1#	3.0537(9)
	4		5		
Mn1-O1	1.9388(14)	Mn1-O1	1.9372(15)		
Mn1-O1#	1.9475(14)	Mn1-O1#	1.9496(15)		
Mn1-O2	1.8363(15)	Mn1-O2	1.8563(14)		
Mn1-O3	1.8645(15)	Mn1-O3	1.8839(15)		
Mn1-N1	2.1847(19)	Mn1-O4	2.3056(16)		
		Mn1-O5	2.2839(16)		
Mn1-O1-Mn1#	103.03(6)	Mn1-O1-Mn1#	102.85(6)		
Mn1...Mn1#	3.0422(8)	Mn1...Mn1#	3.039		

Table 1. Selected bond lengths (Å) and angles (°) for complexes **1-5**.

The introduction of N-donor (pyridine type) ligands into the synthetic procedure used for the formation of **1** gives rise to the remaining members of this family. For instance the addition of pyridine (py) and 3-picoline (3-pic) affords [Mn(III)₂(μ-OMe)₂(biphen)₂(py)₃] (**2**) and [Mn(III)₂(μ-OMe)₂(biphen)₂(3-pic)₂]•2H₂O (**3**), respectively. Complexes **2** and **3** (Figures 1-2) crystallize in the monoclinic space groups *P2₁/c* and *C₂/c* respectively and share many structural similarities with complex **1**. Both contain central μ-OMe⁻ ligands, this time producing Mn(III)-O-Mn(III) angles of

101.14° (Mn1–O1–Mn2) and 100.70° (Mn1–O2–Mn2) in **2** and 104.04 ° (Mn1–O1–Mn1') in **3**. Indeed **2** and **3** differ to complex **1** only in the presence of terminally bonded N-donor ligands rather than terminally bonded alcohol. More specifically, complex **2** contains two pyridine ligands axially coordinated to the Jahn-Teller axis of [distorted octahedral] Mn1 (via N1 and N2), and one pyridine molecule attached (N3) to Mn2. The latter is in a distorted square based pyramidal geometry ($\tau = 0.28$),^[24] presumably due to the steric effects of the rather twisted biphenoxide ligands (Figure 1). The Mn1–N1 and Mn1–N2 bond lengths in **2** are 2.322 Å and 2.420 Å respectively, while the Mn–N3 distance is slightly shorter, at a value of 2.207 Å. The steric constraints present in **2** give rise to a puckering of the {Mn(III)₂(μ -OMe)₂} plane. This core distortion can be quantified via the Mn1–O1–Mn2–O2 torsion angle of 15.08° which can be directly compared to the completely flat {Mn(III)₂(μ -OMe)₂} plane in complex **1** (Mn1–O1–Mn1'–O' = 0.0 °). The individual {Mn₂} units in **1** stack in superimposable rows along the *a* axis of the unit cell (Figure S1). These 1-D rows are stabilised by two symmetry related H-bonding interactions between an O atom of a biphen²⁻ ligand (O2) and a nearby alcoholic proton (H4A–O4) belonging to a terminal EtOH ligand of a juxtaposed {Mn₂} unit (O2⋯H4A(O4) = 1.909 Å). These hydrogen bonded chains arrange in the common brickwork pattern in the remaining two directions. No significant intermolecular interactions are observed between the chains in **1**. The packing arrangement in **2** also comprises superimposable 1-D rows propagating along the *c* axis of the unit cell. These chains are held in position by only weak interactions; however these rows are connected in 3-dimensions via strong C–H... π dipolar interactions at a distance of 2.496 Å ([C24–29]...H4(C4)) emanating from biphenolate and pyridyl aromatic rings on neighbouring dimeric units.

In complex **3** (Figure 2) both Mn(III) ions are five coordinate and adopt square-based pyramidal geometry ($\tau = 0.02$), with one 3-picoline ligand coordinated to each metal centre at a distance of 2.198 Å (Mn1–N1). This change in metal coordination number is presumably due to the presence of the bulkier 3-picoline ligand (Figure 2). This is also true for [Mn(III)₂(μ -OEt)₂(biphen)₂(3-pic)₂] (**4**) (Figure 2), whose structure is essentially analogous to complex **3** but in which the bridging methoxide ions are replaced with bridging ethoxide ligands, as a result of the change of solvent from MeOH to EtOH. **4** crystallises in monoclinic space group *P2₁/n*. The Mn–O–Mn angles in **3** and **4** are given as 104.11 and 103.03 ° resulting in Mn⋯Mn distances of 3.054 and 3.402 Å, respectively. Moreover the Mn–O–Mn–O torsion angles produced in **3** and **4** are both 0 °. The crystal packing in the unit cells of **3** and **4** bear striking similarities. Both comprise 1-D superimposable chains running across (dissecting) the *ab* plane in **3** and along the *b* axis in **4**. The individual {Mn₂} units in these siblings are connected through intra-chain H-bonding interactions via O atoms and methyl protons belonging to biphenolate and 3-picoline ligands, respectively, of nearest neighbour [Mn₂] units (O3⋯H18A(C18) = 2.715 Å in **3**; O2⋯H19(C19) = 2.420 Å in **4**). In terms of 3-D connectivity the 1-D rows in **3** and **4** each alternate in direction along the *c* axis of their unit cells. Inter-chain close contacts were observed in both

structures via interactions between O and H atoms of neighbouring biphen²⁻ bridging ligands (O2 \cdots H9(C9) = 2.550 Å in **3**; O2 \cdots H19(C19) = 2.420 Å in **4**) (Figure S3).

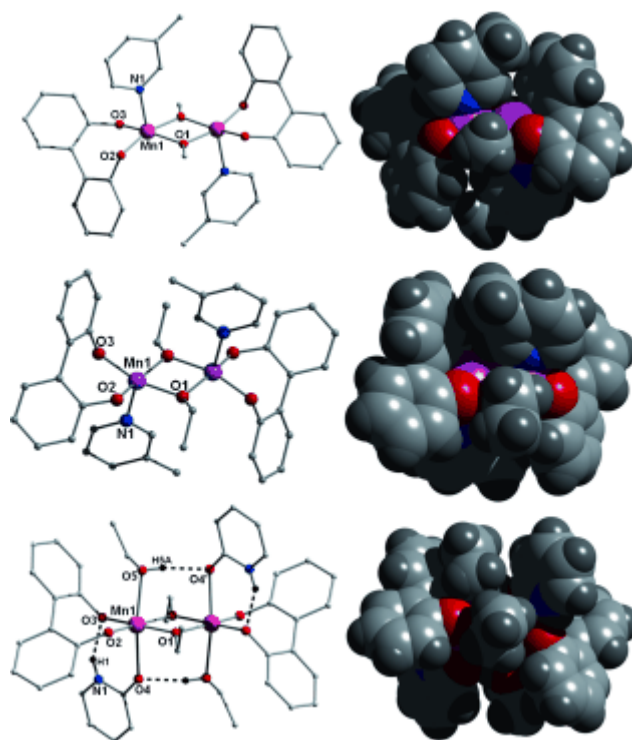


Figure 2. Crystal structures and equivalent space-fill representations of complexes **3-5** (top→bottom). Colour code as in Figure 1. H atoms have been omitted for clarity. Dashed lines represent intra-molecular H-bonding interactions (N1(H1) \cdots O3 = 1.913 Å).

The final member of the family, [Mn(III)₂(μ -OEt)₂(biphen)₂(2-O-pyH)₂] (**5**; Figure 3), is made from the reaction of Mn(ClO₄)₂·6H₂O, 2,2'-biphenol, 2-hydroxypyridine (2-OH-py) and NMe₄OH in EtOH. The common central {Mn-(μ -OEt)₂-Mn} core is retained, with a Mn1-O1-Mn1' angle of 102.85° and a Mn \cdots Mn distance of 3.039 Å (Mn-O-Mn-O torsion angle: 0 °). Indeed the only major structural difference between **5** and its siblings lies in the nature of the bonding of the 2-hydroxypyridine ligands; the ligand bonds to the metal centre via the deprotonated phenolic O-atom (Mn1-O4, 2.306 Å), with the pyridyl N atom now protonated and H-bonding to an O-atom of the chelating biphenoxide (N1(H1) \cdots O3 = 1.913 Å). A second intra-molecular H-bond is observed between the terminal EtOH ligands, that complete the octahedral coordination spheres at each Mn(III) centre, and O4 (O5(H5) \cdots O4', 1.907 Å). Much akin to the other family members, the {Mn₂} units in **5** connect into chains (dissecting the *ab* plane of the cell) via two symmetry equivalent C-H \cdots π close contacts ((C17-C21) \cdots H16(C16) = 3.293 Å), derived from interactions between aromatic pyridyl ring and ethyl protons of a close by terminal EtOH molecule (Figure S3). Furthermore these 1-D rows further connect in the remaining directions via further C-H \cdots π interactions comprising aromatic rings

and aromatic protons of juxtaposed biphenolate ligands of neighbouring $[\text{Mn}_2]$ complexes ([C9-C14]...H7(C7) = 2.583 Å).

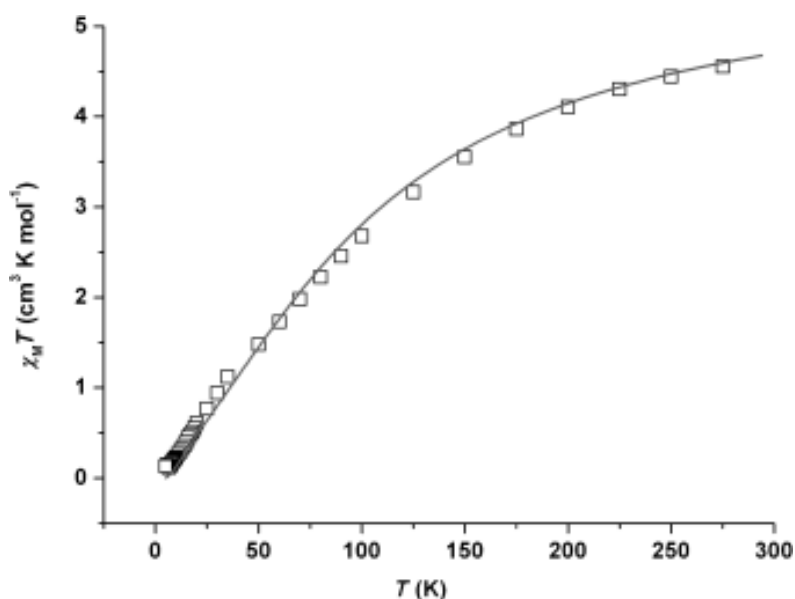


Figure 3. Plot of magnetic susceptibility ($\chi_m T$) vs. T for complex **4**. Solid red line represents the best-fit using the parameters provided in Table 2. See ESI for the magnetic susceptibility plots of **1-3** & **5**.

Magnetic Susceptibility Measurements

Magnetic susceptibility measurements on complexes **1-5** were carried out in the 300-5 K temperature range in an applied field of 0.1 T (Figure 3). The room temperature $\chi_m T$ products for **1-5** lie in the 4.03–4.55 $\text{cm}^3 \text{mol}^{-1} \text{K}$ range and are significantly lower than the expected value for two non-interacting Mn(III) ions of 6.00 $\text{cm}^3 \text{mol}^{-1} \text{K}$, assuming $g = 2.00$. This is an indication of antiferromagnetic exchange between the metal centres, as supported by the uniform drop in $\chi_m T$ on decreasing temperature. In each case the $T = 5 \text{ K}$ value is close to zero. Fitting of these data with a simple 1- J isotropic Hamiltonian ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_1$) affords the best fit parameters documented in Table 2 and represented by the solid red lines in Figures 3 and S4. The J -values span the small range of -10.5 cm^{-1} (in **4**) to -14.3 cm^{-1} (in **3**).

Formula	g	<i>J</i> -value (cm ⁻¹) Expt	<i>J</i> -value (cm ⁻¹) DFT	Mn ^{III} –Mn (Å)	Av. Mn–O– Mn angle (Å)	Mn–O– Mn–O torsion	Jahn- Teller Dihedral (Å)	Av. Mn–O (Å)	Ref
[Mn ₂ (OMe) ₂ (L) ₂ (MeOH) ₄] (1)	1.98	-12.2	-10.5	3.071	103.66	0	5.4	1.953	This work
[Mn ₂ (OMe) ₂ (L) ₂ (py) ₃] (2)	1.98	-12.5	-	3.007	100.93	15.37	-	1.950	This work
[Mn ₂ (OMe) ₂ (L) ₂ (3-pic) ₂] (3)	1.98	-14.3	-	3.054	104.04	0	-	1.936	This work
[Mn ₂ (OEt) ₂ (L) ₂ (3-pic) ₂] (4)	1.98	-10.5	-12.4	3.042	103.03	0	0	1.944	This work
[Mn ₂ (OEt) ₂ (L) ₂ (hpy) ₂ (EtOH) ₂] (5)	1.98	-13.5	-11.6	3.039	102.85	0	0	1.944	This work
[Mn ₂ (L)(OMe)(OAc)(MeOH) ₂]Br	1.90	-13.1	-	2.942	97.86	14.85	0.6	1.952	25
[Mn ₂ (3-OMe-salpentO)(OMe)(OAc)(MeOH) ₂]Br	1.98	-13.7	-	2.928	98.11	15.10	3.3	1.938	26
[Mn ₂ (5-NO ₂ -salpentO)(OMe)(OAc)(MeOH) ₂]I ₃	1.98	-12.4	-	2.911	97.95	15.75	4.5	1.930	27
[Mn ₂ (L ^{Se}) ₂ (OMe) ₂ (MeOH) ₂]	2.00	-11.8	-	3.038	102.57	7.06	6.5	1.947	28
[Mn ₂ (L ^S) ₂ (OMe) ₂ (MeOH) ₂]	2.00	-8.2	-	n.c.a	n.c.a	n.c.a	-	n.c.a	28
[Mn ₂ (3-Me-salpentO)(OMe)(OAc)(MeOH) ₂]Br	2.02	-15.1	-	2.929	98.22	16	0	1.937	29
[Mn ₂ (L)(OMe)Cl ₂ (MeOH) ₂]	2.00	-15.5	-	3.006	101.50	n.c.a	-	1.941	30
[Mn ₂ (OMe) ₂ (sal) ₂ (MeOH) ₄]	2.00	-10.33	-	3.025	102.97	0	5.2	1.934	31

Table 2. Selected magneto-structural parameters for *type I* Mn(III) dinuclear complexes discussed in this work and elsewhere. Magnetic data is reported in the $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_1$ formalism.

In order to put these results into context we have compared the structural and magnetic properties of **1-5** to those of all known μ -OR bridged [Mn(III)₂] clusters reported in the literature. Each compound may be grouped into one of three distinct categories (*Type I-III*) based on the orientation of the Jahn-Teller axes (references [25-50]), using an approach proposed by Tuchagues *et al* in 1995.^[43] Each of these three families can be categorized by noting the relative orientation of their associated Jahn-Teller axes with respect to one another as well as their orientation with respect to the μ -OR bridging plane (Figure 4). These classifications are reported in Tables 2-4 along with their associated magnetic spin Hamiltonian parameters (*J*- and *g*-values; ground spin state *S*), and all structural parameters which may have a significant bearing on their resultant magnetic properties. These parameters were then utilised in our subsequent magneto-correlation studies (*vide supra*).

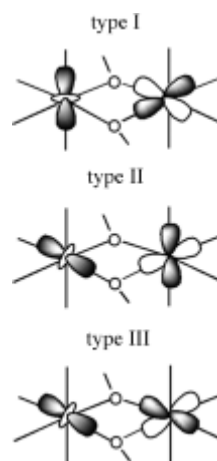


Figure 4. Schematic illustrating the three types of magnetic orbital spatial orientations observed within recognised μ -OR bridged $[\text{Mn}(\text{III})_2]$ complexes. Complexes **1-5** are classified as *type I* as described in this work.

Type I: Complexes belonging to the first category exhibit a co-linear orientation of their Jahn-Teller axes, each of which are perpendicular to the bridging plane of the dimer as observed here and elsewhere in the literature (Figure 4). Indeed the introduction of complexes **1-5** almost doubles the literature basis set for this type of dinuclear species. Magnetic exchange parameters (J) for these compounds are all weakly antiferromagnetic with values ranging from -8.2 cm^{-1} to -15.5 cm^{-1} .^{[28],[30]} Interestingly a group of O^{2-} bridged $[\text{Mn}(\text{III})_2\text{O}_2]$ complexes exhibiting *type I* conformations are known. As these compounds possess $\mu\text{-O}^{2-}$ bridging anions rather than $\mu\text{-OR}^-$ species they are exempt from our comparative study. The $\mu\text{-O}^{2-}$ bridging angles of these dimers are significantly more acute than the $\mu\text{-OR}$ analogues ($\sim 93 - 95^\circ$), leading to much shorter Mn \cdots Mn distances ($\sim 2.65\text{-}2.7 \text{ \AA}$) and as a result these compounds exhibit strong antiferromagnetic interactions with J values of $\sim -100 \text{ cm}^{-1}$.^[51]

Type II: This is the most common conformation exhibited by alkoxide bridged dinuclear Mn(III) complexes. Here the Jahn-Teller axes of the Mn(III) ions are parallel to one another as well as being parallel to the bridging $\mu\text{-OR}$ plane (Figure 4). The Mn–OR bonds in these types of complexes are thus elongated and as a result the extent of orbital overlaps amongst d -based orbitals appears to be altered. Indeed this may explain the magnetic coupling observed within these species as they exhibit magnetic exchange parameters which lie on the ferro- \leftrightarrow antiferromagnetic interface. For instance J -values ranging from the weakly antiferromagnetic (-1.68 cm^{-1}) in $[\text{Mn}_2(\text{L})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$; where L = N-(acetylacetylidene)-N'- α -methylsalicylidene,^[43] to weakly ferromagnetic ($J = +6.3 \text{ cm}^{-1}$) in the complex $[\text{Mn}_2(\text{salen})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (where $\text{H}_2\text{salen} = \text{N,N}'\text{-bis}(\text{salicylideneaminoato})\text{ethylene}$)^[34] have been observed (Table 3).

Formula	g	<i>J</i> -value (cm ⁻¹) Expt	<i>J</i> -value (cm ⁻¹) DFT	Mn...Mn (Å)	Av. Mn-O-Mn angle (Å)	Mn-O- Mn-O torsion	Jahn- Teller Dihedral (Å)	Av. Mn-O (Å)	Ref
[Mn ₂ (bbml) ₂ (acac) ₂](BF ₄) ₂	1.97	-0.18	-	3.178	105.27	n.c.a	-	1.99	32
[Mn ₂ (saltmen) ₂ (ReO ₄) ₂]	2.00	+2.65K	-	3.330	98.00	0	-	2.193	33
[Mn ₂ (salen) ₂ (H ₂ O) ₂](ClO ₄) ₂	2.00	+6.30	-	3.334	100.59	0	180	2.156	34
[Mn ₂ (saltmen) ₂ (O ₂ CMe) ₂]	1.98	+1.35	0.73	3.641	99.57	0	152.5	2.352	35(a)
[Mn ₂ (saltmen) ₂ (N ₃) ₂]	1.98	+0.60	-	3.922	98.39	0	180	2.527	35(b)
[Mn ₂ (salen) ₂ (NCO) ₂]	2.03	+0.73	-	3.584	97.82	0	180	2.346	35(c)
[Mn(3,5-Br-salen)(3,5-Br-salicylal)] ₂	2.00	+0.55	-	3.597	100.00	0	180	2.323	35(d)
[Mn ₂ (5-Br-salen) ₂ (MeOH) ₂](ClO ₄) ₂	1.96	-0.45	-0.62	3.307	99.85	0	180	2.152	35(e)
[Mn ₂ (L) ₂ (H ₂ O) ₂](ClO ₄) ₂	2.01	-1.68	-	3.318	103.38	0	180	2.109	36
[Mn ₂ (Hthme) ₂ (bpy) ₂](ClO ₄) ₂	1.71	+2.13	-	3.096	101.56	0	180	1.996	37
[Mn ₂ (L ₁) ₂ (N ₃) ₂]	2.04	-0.55	-	3.341	101.84	0	180	2.144	38a
[Mn ₂ (L ₂) ₂ (N ₃) ₂]	1.99	+1.32	-	3.361	96.76	0	180	2.375	38b
[Mn ₂ (OMe) ₂ (dbm) ₄]	1.98	+0.28	-	3.104	101.21	0	180	2.005	39
[Mn ₂ (2-OH(5-NO ₂ -sal)pn) ₂]	1.95	-5.0	-	3.247	99.07	0	180	2.127	40
[Mn ₂ (bbml) ₂ (tol) ₂](ClO ₄) ₂	1.97	-1.19	-	3.209	106.29	0	177.9	2.004	41
[Mn ₂ (saltmen) ₂ (H ₂ O) ₂](ClO ₄) ₂	1.93	+1.79	-	3.381	101.58	0	180	2.172	42(a)
[Mn ₂ (naphtmen) ₂ (H ₂ O) ₂](ClO ₄) ₂	1.96	+1.20	-	3.541	100.59	0	180	2.279	42(b)
[Mn ₂ (saltmen) ₂ (NCS) ₂](ClO ₄) ₂	1.99	+0.55	-	4.092	96.24	0	180	2.657	42(c)
[Mn ₂ (naphmen) ₂ (NCS) ₂](ClO ₄) ₂	2.03	+0.12	-	4.388	96.57	0	180	2.818	42(d)
[Mn ₂ (naphmen) ₂ (Cl) ₂](ClO ₄) ₂	2.04	+0.38	-	4.102	94.20	0	180	2.699	42(e)
[Mn ₂ (3-NO ₂ -salpro) ₂ (H ₂ O)].H ₂ O	2.04	-1.62	-	3.223	100.52	0	180	2.095	43
[Mn ₂ (salpn) ₂ (NCO) ₂]	2.02	0.42	-	3.429	100.58	0	180	2.241	44a
[Mn ₂ (salmen) ₂ (N ₃) ₂]	2.00	0.58	-	3.433	98.54	0	180	2.246	44b
[Mn ₂ (acphpn) ₂ (N ₃) ₂]	2.00	-0.20	-	3.425	101.23	0	180	2.202	44c

[Mn ₂ (L) ₂ (N ₃) ₂]	2.03	0.59	-	3.368	98.06	0	180	2.215	45
[Mn ₂ (salpn) ₂ (N ₃) ₂]	2.00	0.90	-	3.388	98.42	0	180	2.221	46a
[Mn ₂ (salpn) ₂ (NCS) ₂]	2.01	0.14	-	3.369	99.39	0	180	2.192	46b
[Mn ₂ (sapln) ₂ (H ₂ O) ₂]	2.00	1.10	-	3.315	99.50	0	180	2.158	46c
[Mn ₂ (5-Cl-sapln) ₂ (N ₃) ₂]	1.95	1.79	-	3.440	101.42	0	180	2.210	47
[Mn ₂ (acphen) ₂ (NCS) ₂]	2.00	-0.79	-	3.374	102.14	0	180	2.159	48

Table 3. Selected magneto-structural parameters for *type II* Mn(III) dinuclear complexes discussed in this work and elsewhere. Magnetic data is reported in the $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_1'$ formalism.

Type III: Here the Jahn-Teller axes of the metal ions are perpendicular to one another: one lying parallel to the bridging plane, the other perpendicular to it (Figure 4). Just two alkoxide bridged [Mn(III)₂] complexes exhibiting this conformation exist to date. Furthermore both complexes exhibit relatively strong ferromagnetic coupling, proposed due to the non-colinearity of their respective elongated axes.^{[49],[50]} The rarity of these compounds is perhaps due to the low level of symmetry this conformation requires, with the complexes possessing different ligands at each of their two Mn(III) centres (Table 4).

Formula	g	J-value (cm ⁻¹) Expt	J-value (cm ⁻¹) DFT	Mn...Mn (Å)	Av. Mn-O- Mn angle (Å)	Mn-O- Mn-O torsion	Jahn- Teller Dihedral (Å)	Av. Mn- O (Å)	Ref
[Mn ₂ (OMe) ₂ (L)(MeOH)](ClO ₄)	2.00	+6.25	+9.45	3.122	101.10	7.32	81.9	2.022	49
[Mn ₂ (OMe) ₂ (HL) ₄]	1.90	+9.85	+9.8	3.084	102.51	2.20	117.1	1.976	50

Table 4. Selected magneto- and structural parameters for *type III* Mn(III) dinuclear complexes discussed in this work and elsewhere. Magnetic data is reported in the $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_1'$ formalism.

Since only the orientation between the two planes differs in the three types, we have defined a dihedral plane between the two Jahn-Teller axes which emerges as the key structural factor governing the differences in magnetic behaviour between *types I-III* and this parameter clearly defines the three categories of structures noted above. The collected experimental structures are plotted in Figure 5 as *J* versus dihedral plane. The way the dihedral angle has been measured within the dihedral plane is

shown in Figure 5 (the solid blue lines). As per our classification, all three types can be clearly distinguished. This is not true for any other structural parameters such as short/long Mn-O distances (where a scattered picture emerges). Accordingly, *type I* structures have dihedral planes $< 10^\circ$, *type II* structures fall into the $152\text{-}180^\circ$ range and *type III* structures (where a strong ferromagnetic exchange has been observed) fall in the middle ground with the dihedral angles of 81.9 and 117.1° for the two structures reported (Figure 5).

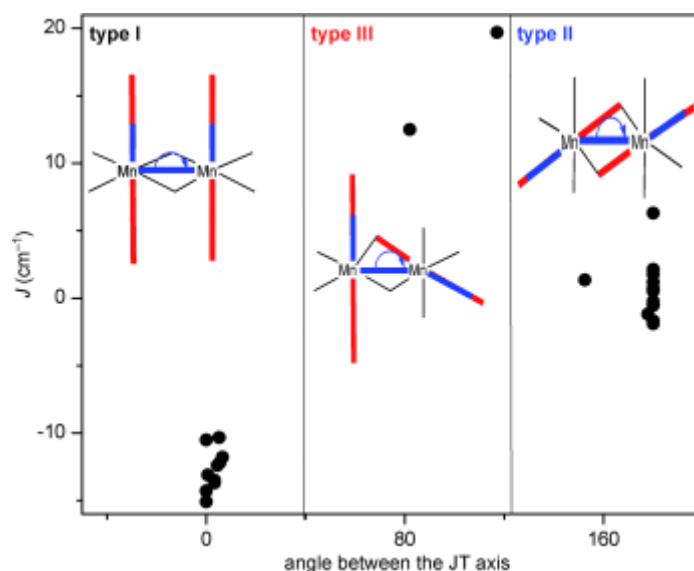


Figure 5. Plot of J (cm^{-1}) versus the angle forged between the two JT axes in Mn dimers of *Types I-III*.

As is apparent from Tables 2-4 and Figure 5 the magnitude of the exchange interaction J varies across the three *types I-III*. To understand in detail the difference in sign and magnitude of J observed among these structures and also to develop magneto-structural correlations based on other structural parameters, an extensive theoretical study based on density functional methods has been undertaken.

Theoretical Studies

In order to explain the variation in magnetic behaviour between the three types of complexes presented here, we have carried out DFT calculations on selected structures from *type I* [**1**, **4** and **5**], *type II* [**II-1**, **II-2**] and *type III* [**III-1**, **III-2**]. The computed J values are given in Tables 2-4. As is evident from the presented data the J values calculated are in good agreement with the experimentally reported values for these complexes. In fact apart from complex **III-2**, excellent agreement in terms of the sign and magnitude of J has been observed in all the computed cases. The chosen methodology and the theoretical level are also able to effectively reproduce the magnitude and values of J even in borderline cases where the J values are less than 1 cm^{-1} .

To probe the electronic origin of the differences between the three types, a spin density plot has been computed for one structure from each type (**1**, **II-2** and **III-2**), as shown in Figure 6. The computed spin density of the metal atoms and the atoms which are coordinated to Mn(III) for complexes **1**, **II-2** and **III-2** are listed in Table 5. The modulus of the spin densities on each manganese atom is calculated to be > 3.7 in all three types, indicating that the magnetic orbitals are centred on the metals and that there is some unpaired spin density on the ligands. Generally, when the unpaired electrons are located in a metal π -type orbital (e.g. t_{2g}) spin polarization is expected to dominate, while if it is in a σ -type orbital a spin delocalization mechanism is expected to predominate. However this also then depends on the nature of the donor atoms.^[15d] For Mn(III) ions, since the unpaired electrons are located in three t_{2g} like orbitals and in the d_z^2 orbital of the e_g set, a mechanism encompassing a mixture of spin delocalization and spin polarization is expected. As the Jahn-Teller axis coincides with the d_z^2 orbital direction, the ligand atoms which are coordinated via the Jahn-Teller axis are expected to have the positive spin density as here the spin delocalization will be predominant. In other directions, a mechanism comprising a mixture of spin delocalization and spin polarization is found, leading to either positive or negative spin densities on the donor atoms. In all three cases (**1**, **II-2** and **III-2**) the super-exchange propagates through the two bridging μ -alkoxo groups and the spin density on these bridging oxygen atoms is expected to influence the sign and magnitude of the J values.

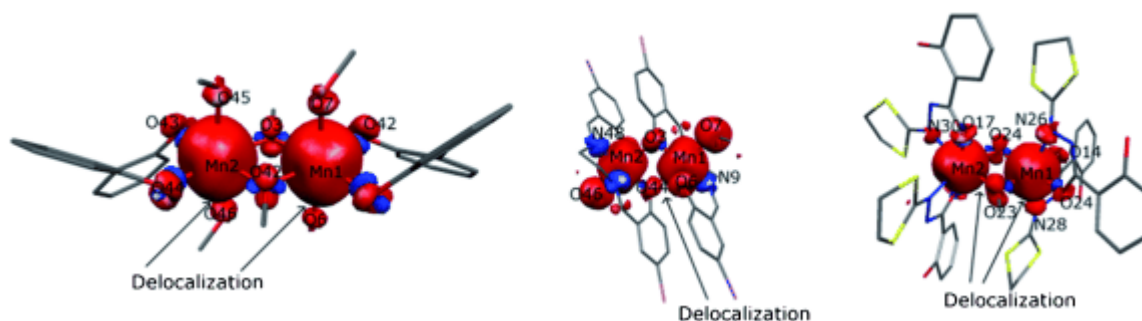


Figure 6. B3LYP computed spin density plot for *type I-III* with a cut-off value of 0.005 au.

(turn to next page →)

Complex (I)		Complex (II-2)		Complex (III-2)	
Atom specification	Spin densities	Atom specification	Spin densities	Atom specification	Spin densities
Mn1	3.9414	Mn1	3.7468	Mn1	3.8862
Mn2	3.9414	Mn2	3.7468	Mn2	3.8738
O3	0.0026	O3	0.0278	O11	-0.0028
O4	-0.0023	O6	0.0220	O14	-0.0045
O5	0.0114	O7	0.2793	O17	-0.0141
O6	0.0082	N8	-0.0833	O20	-0.0297
O7	0.0166	N9	-0.0561	O23	0.0379
O42	0.0026	O44	0.0278	O24	0.0069
O43	-0.0023	O45	0.0220	N26	0.0258
O44	0.0114	O46	0.2793	N28	0.0205
O45	0.0082	N47	-0.0803	N30	0.0040
O46	0.0166	N48	-0.0561	N32	-0.0283

Table 5. DFT computed spin densities of selected atoms of complex **1**, **II-2** and **III-2**.

For *type I* structures, both μ -oxygen atoms have a very small positive spin density indicating that both the spin polarization and delocalization mechanisms compete, leading to very small spin densities on both oxygen atoms. In *type II* structures, since the Jahn-Teller axis is along the μ -O-atoms, a predominant spin delocalization from one of the Mn atoms and a mixture from the second Mn atom is expected, leading to a significant increase in the spin density compared to *type I* structures. In *type III* structures, since the Jahn-Teller axes are perpendicular, behaviour lying in-between that of *type I* and *type II* is observed, where one of the oxygen atoms (O23) has significant spin density, while the other (O24) has negligible spin density. These differences in the mechanism and differing magnitude of spin densities on the μ -alkoxo group is expected to be exemplified in the computed exchange interaction (Figure 6).^[15d]

Orbital analysis

To probe the electronic origin further, MO analysis has been performed on complexes **1**, **II-2** and **III-2**. The DFT Kohn-Sham orbitals are very useful for qualitatively analysing the J values, and for providing some insight into the coupling mechanism. The qualitative model of Kahn-Briat^[52] takes into consideration the overlap between the non-orthogonal magnetic orbitals and relates it to the J values. Even though *types I-III* differ in their net J values, the net exchange interactions have contributions from both the antiferromagnetic (J_{AF}) and ferromagnetic (J_F) parts. The computed overlap integral between the singly occupied orbitals is directly proportional to J_{AF} . It has been noted in several instances that the so-called cross-interaction between the empty $d_x^2-y^2$ orbitals and the singly occupied orbitals leads to ferromagnetic interactions and this has been qualitatively studied to rationalize the weak interactions observed in Mn(III) dimers in general.^[53] We have decided to compute the overlap integral for this pair, since its magnitude is expected to reveal the strength of the “cross-interaction” that exists in this molecule and thus can be translated as the contribution to J_F . The d -based orbitals of the alpha set for *types I-III* are shown in Figure 7. The results of the overlap integral calculation are summarized in the computed energy level diagram of Figure 8. A double-headed arrow connecting the alpha and beta sets indicates a significant overlap between the two orbitals (*note*: a red arrow indicates significant cross-interaction). As is evident from the graph, *type I* structures have significant overlap with SOMOs but do not have any significant interaction with the $d_x^2-y^2$ orbitals leading to a decrease in the J_F contribution (See Tables S3 -7 for the complete list of computed overlap integrals). Among others, the $d_{yz}-d_{yz}$, $d_z^2-d_{yz}$, $d_{yz}-d_z^2$, $d_{yz}-d_{xy}$, $d_z^2-d_{yz}$, $d_{xy}-d_z^2$ interactions are notable. A larger J_{AF} contribution and a negligible J_F contribution lead to a large antiferromagnetic net J for this type of complex. For *type II* structures, both the J_F and J_{AF} contributions exist, with the significant exchanges being $d_{yz}-d_{yz}$, $d_{xz}-d_{yz}$, $d_{yz}-d_{xz}$, $d_{xz}-d_{xz}$ and $d_{xy}-d_{xy}$ along with some significant cross-interactions. Here the J_{AF} and J_F contributions essentially cancel each other out, leading to a very weak net exchange. The sign of the exchange (ferro or antiferro) in this type of complex is determined by the predominant factor. For *type III* structures on the other hand, fewer J_{AF} interactions are observed and the cross-interactions play a vital role. A large cross-interaction is evident from the broken symmetry $d_x^2-y^2$ orbital plotted in Figure 7. A stronger J_F and weaker J_{AF} leads to relatively strong net ferromagnetic exchange.

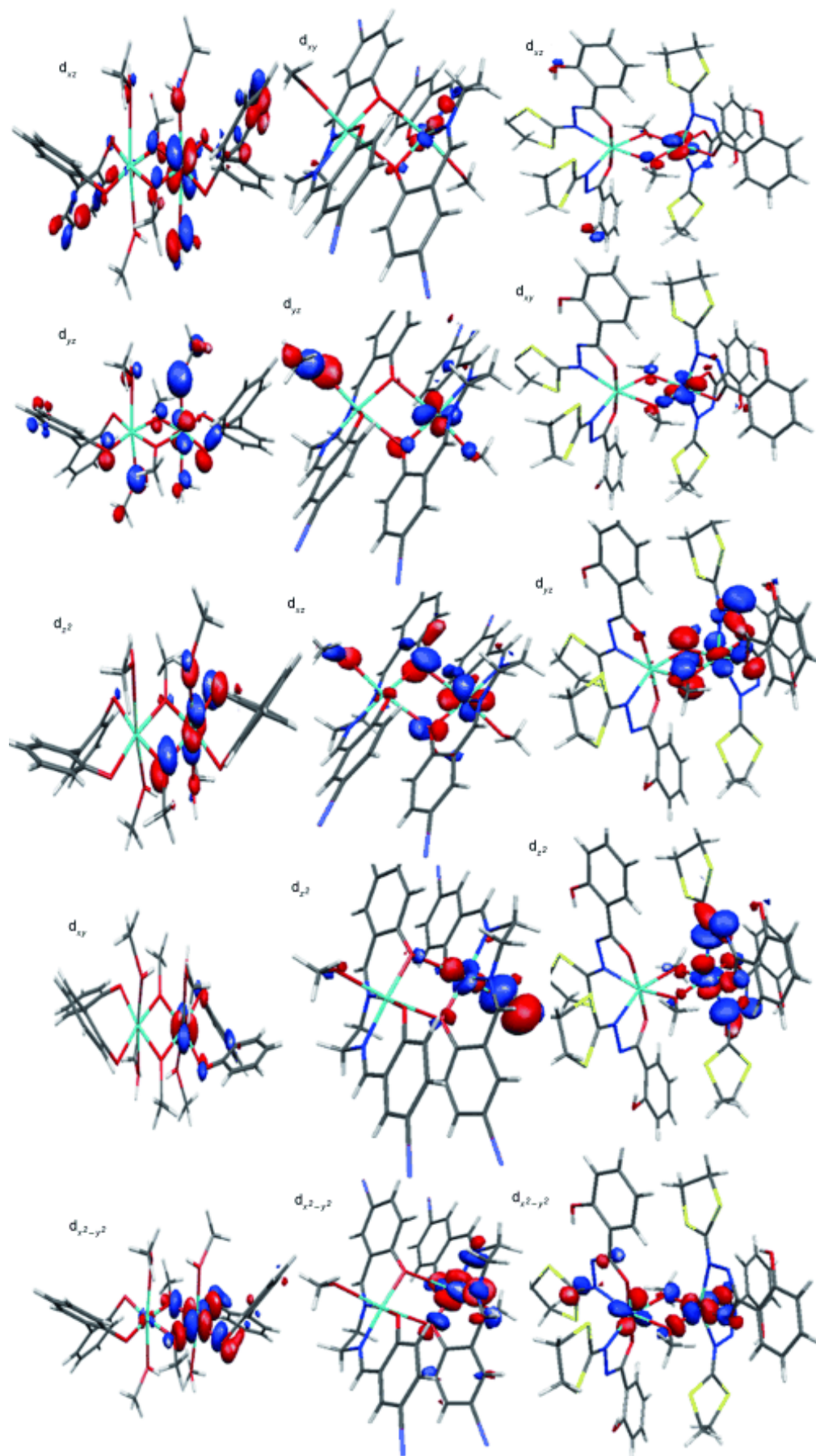


Figure 7. Alpha magnetic orbitals of types *I*, *II* and *III* in order of decreasing energy (top to bottom).

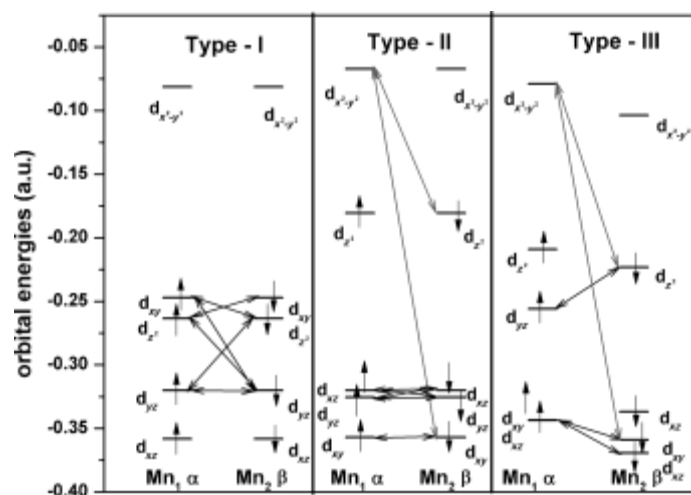


Figure 8. Dominant interactions between the magnetic orbitals in *Type I-III* structures. Anti-ferromagnetic interactions are shown as black lines and ferromagnetic interactions as red lines.

As mentioned before, the differences in the magnitude and the sign of J arise due to the difference in the orientation of the d_z^2 orbital - which coincides with the Jahn-Teller axis. On several occasions the Jahn-Teller orientation has been evoked to explain the reduction in the cluster anisotropy and here for the first time with quantitative calculations and qualitative analysis, we provide direct evidence that the JT orientation is important in determining the sign as well as magnitude of the coupling in Mn(III) dimers. A perpendicular alignment of the JT axes for the dinuclear unit is expected to exhibit a relatively strong ferromagnetic interaction. However we point out that this orientation is also likely to lead to a decrease in the cluster anisotropy, an important parameter to consider when designing molecular nanomagnets.

Since all of the complexes in this study possess different terminal ligands we then sought to determine the effect of a change in the nature of the terminal ligands on the J values. Thus we have modelled two complexes (labelled *a* and *b*), where the terminal ligands of complexes **1** and **III-2** were interchanged. This gives $J = -8.4 \text{ cm}^{-1}$ and $+21.6 \text{ cm}^{-1}$ compared to -10.2 cm^{-1} and $+9.8 \text{ cm}^{-1}$ for their original complexes, respectively. This clearly indicates that the terminal ligands have negligible contribution to the exchange coupling constant.

Magneto-structural correlations

Although the experimental studies and the theoretical analysis presented in this work strongly suggest that the orientation of the Jahn-Teller axis is the most important parameter in controlling J across the three types presented, within a particular type other structural parameters are expected to influence the final observed J value. Indeed to our knowledge, no theoretical correlations have been developed for

this topology in order to understand the unique structural features that are expected to affect the resultant J values. Here we have thus decided to develop correlations for a *type I* structure in the shape of our own complex **1** (Figure 1). There are four structural parameters deemed vital in influencing and determining the J value: Mn-O-Mn angle, Mn-O distance, Mn-O-Mn-O dihedral angle and the out-of-plane shift of the alkyl group (μ -OR) of the compound in question (described by τ). The developed correlations for these four parameters are given in Figure 9. The experimental parameters listed in Table 2 along with the experimental J have also been plotted along with the computed points (solid squares). For the data obtained from the experimental structure, the three *types I-III* are distinguished in different colours.

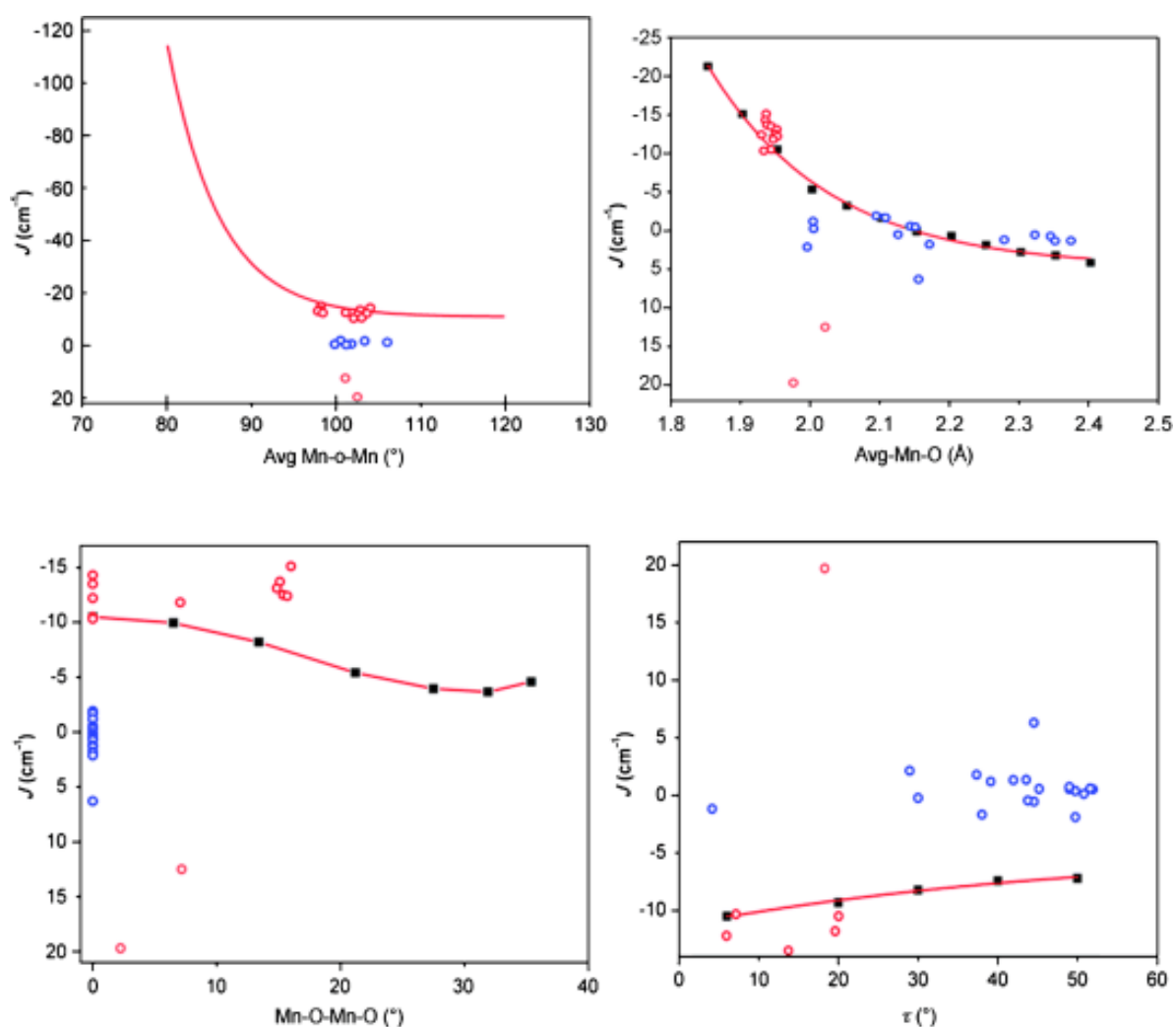


Figure 9. Magneto-structural correlations developed by varying structural parameters Mn-O-Mn and Mn-O-Mn-O angles, Mn-O distance and τ using DFT calculations. Experimental values are represented in coloured circles, Red-(*type I*); Blue-(*type II*) and Orange-(*type III*).

Bond Angle: By varying the average Mn-O-Mn angle from 80.1 to 119.8°, a correlation has been developed for J and its value varies exponentially, as represented in Figure 9. The J parameter decreases and become less antiferromagnetic upon increasing Mn-O-Mn angle. At an acute angle, relatively strong antiferromagnetic exchange has been encountered with the steep increase in negative J due to significant overlap of the d_{xy} orbital with other orbitals, as evidenced from the overlap integral values (Table S3). Since the Mn-O-Mn angle decreases with a decrease in the Mn^{III}Mn distance, this effect is somewhat expected. However at large angles, an overall drop in the overlap values is detected and this leads to smaller negative J values. There is no switch from antiferromagnetic to ferromagnetic and this is essentially due to negligibly small cross-interactions at all the computed angles. The experimental *type I* data points lie within the computed points, revealing that this is a rather reliable parameter. As expected, *type II* and *III* structures deviate from the computed data and this once again suggests that the JT orientation is more important than any other structural parameter.

Bond Distance: The second correlation is carried out by varying the average Mn-O distances from 1.853 to 2.403 Å. This parameter also exhibits an exponential relationship (Figure 9) whereby the J value steadily decreases (becomes less antiferromagnetic) with increasing average distance. Moreover as the Mn-O distance passes a value of 2.103 Å, the interaction becomes ferromagnetic. This is because as the Mn-O distance increases, the *type I* structure will be converted into other types (*II* and *III* for example) and this leads to significant increase in cross interaction and a predominant ferromagnetic exchange. The experimental data points fit with the *type I* structures at shorter Mn-O distances and *type II* structures at longer Mn-O distances.

Dihedral Angle: The Mn-O-Mn-O dihedral angle in **1** is varied from 0 to 35.4° to obtain the third correlation. The plot of dihedral angle versus J is shown in Figure 9. Only a small variation in J is detected and the complex becomes less ferromagnetic as the dihedral angle increases. This is as a result of the reduction in the d_z^2 - d_z^2 overlap. Here the experimental data points are rather scattered, suggesting that this parameter may not be particularly significant.

Out-of-plane displacement of methyl groups (τ): The fourth correlation analysis involved monitoring J when the out-of-plane displacement parameter (τ) of the bridging methyl O atoms was manipulated in the 6 to 50° range. The τ versus J plot (Figure 9) shows a linear relationship. As in the case of the dihedral correlation, an increase in the out-of plane displacement of the methyl group also leads to less antiferromagnetic J values, due to a reduction in overlap between the singly occupied orbitals of the Mn(III) ions (Table S7).

Concluding Remarks

Based on the structural variation observed among the reported Mn(III) dimeric structures having two alkoxide-bridges, a unique structural feature which distinguishes the type of magnetic interaction observed is proposed. This parameter, based on the orientation of the Jahn-Teller axes of the two Mn(III) atoms, sharply categories three different types of dimers where *type I* represent moderately strong antiferromagnetic exchange, *type III* structures exhibit moderately strong ferromagnetic interactions and *type II* structures are classified as borderline where a weak ferro- or antiferromagnetic interaction is detected. These three types of classification are supplemented with the synthesis and characterisation of a new family of alkoxide-bridged Mn(III) dimers of general formula $[\text{Mn(III)}(\mu\text{-OR})_2(\text{biphen})_2(\text{ROH})_x(\text{L})_y]$ (where R = Me, Et; H₂biphen = 2,2-biphenol and L = terminally bonded N-donor ligand). All five structures reported here belong to *type I* and help us to extended the database to validate the proposed correlations. Additionally a detailed computational study on all three types was undertaken to probe the electronic origin of the differences in the magnetic behaviour observed. Our computations reveal that the magnetic exchange interaction has two contributions, J_{AF} and J_{F} , with the J_{F} contribution arising due to the cross interaction between the SOMOs and the unoccupied d -orbitals. The strength of J_{F} is vital as it determines the sign and magnitude of the J observed in all three types. However the strength of J_{F} is related to the orientation of the d_z^2 orbitals in a particular structure. Since the orientation of the d_z^2 orbital is related to the Jahn-Teller elongation, our study reveals that a perpendicular orientation of the d_z^2 orbitals enhances J_{F} significantly, leading to a strong ferromagnetic interaction (*type III*). A parallel orientation of the two Jahn-Teller axes which lie in the bridging plane is found to be a border line case (*type II*). If these axes do not form the μ -alkoxide bridges, then a moderately strong antiferromagnetic interaction is encountered (*type I*). The electronic origins of these differences were traced back to the orbital overlaps and this has been quantitatively analysed using overlap integral computation.

In the field of molecular magnetism a strong ferromagnetic interaction is a highly sought-after parameter as the ferromagnetic interaction maximizes the ground state S value and its strength helps to promote an isolated ground state. Although a plethora of SMMs comprising Mn(III) ions have been reported there have been no extensive studies undertaken to pinpoint the unique structural features which would yield this highly sought-after parameter. The combined experimental and theoretical study undertaken here reveals that the orientation of Jahn-Teller axes plays an important role in the magnetic coupling, with a perpendicular orientation leading to a strong ferromagnetic exchange. However it is well known that a perpendicular orientation of Jahn-Teller axes leads to a decrease in the anisotropy of the cluster, which is an important parameter in designing molecular nanomagnets. Our study therefore suggests that large anisotropy and a strong ferromagnetic interaction are unlikely to coexist in Mn(III) clusters containing only $[\text{Mn}(\mu\text{-OR})_2]$ building blocks.

Experimental Section

Physical Measurements

Infra-red spectra were recorded on a Perkin Elmer FT-IR Spectrum One spectrometer equipped with a Universal ATR Sampling accessory (NUI Galway). Elemental analysis detailed was carried out by Marion Vignoles of the School of Chemistry microanalysis service at NUI Galway. Variable-temperature, solid-state direct current (dc) magnetic susceptibility data down to 1.8 K were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T dc magnet (University of Edinburgh). Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants.

X-Ray crystallography

The structures of 1-5 were collected on an Xcalibur S single crystal diffractometer (Oxford Diffraction) using an enhanced Mo source. Each data reduction was carried out on the CrysAlisPro software package. For more detailed refinement information please consult the ESI. Full details can also be found in the CIF files: CCDC 843730-843733 (1-4) and 843849 (5).

Computational Details

All calculations were performed using the hybrid B3LYP54 functional with Alrich^[54] triple- ζ basis set as implemented in the Gaussian 09^[55] suite of programs. The J values were computed from the energy differences between the high spin (EHS) state calculated using single determinant wave functions, and the low spin (EBS) state determined using the Broken Symmetry (BS) approach developed by Noodleman.^[56] Negative and positive values for J correspond to antiferromagnetic and ferromagnetic interactions, respectively. Details of the computational method employed to compute the exchange interaction is discussed elsewhere.^[57]

Syntheses

All reactions were performed under aerobic conditions at room temperature and all reagents and solvents were used as purchased. Caution: Due care and attention should be given when working with the potentially explosive perchlorate and nitrate salts.

Preparation of [Mn(III)₂(μ-OMe)₂(biphen)₂(MeOH)₄] (1): A 1.456 M aqueous solution of Mn(NO₃)₂·6H₂O (2 cm³, 2.9 mmol) and 2,2'-biphenol (0.54 g, 2.9 mmol) were dissolved in 30 cm³ of MeOH. NaOH (0.115 g, 2.9 mmol) was then added and the solution was left stirring for 10 minutes. The resultant deep brown solution was then filtered and allowed to stand. X-ray quality crystals of **1** were obtained upon slow evaporation of the mother liquor overnight. Elemental analysis calc. (%) for C₃₀H₃₈O₁₀Mn₂: C 53.90, H 5.73, Found: C 53.82, H 5.93. FT-IR (cm⁻¹): 3056.0(w), 1587.6(w), 1488.8(m), 1469.2(m), 1430.8(s), 1250.6(s), 1220.9(s), 1154.1(w), 1118.1(w), 1096.2(w), 1046.8(w), 1007.6(w), 934.0(w), 857.8(s), 836.6(m), 753.1(vs), 728.0(s), 710.0(m).

Preparation of [Mn(III)₂(μ-OMe)₂(biphen)₂(py)₃] (2): MnBr₂·4H₂O (0.5 g, 1.74 mmol) and 2,2'-biphenol (0.32 g, 1.74 mmol) were dissolved in 40 cm³ of MeOH. NaOPh·3H₂O (0.15 g, 0.87 mmol) and NaOH (0.035 g, 0.87 mmol) were then added and the resultant deep brown solution was stirred for 15 minutes. After this time an excess of pyridine was added (12 cm³, 149 mmol) and the mixture was left stirring for a further 10 minutes. The solution was then filtered and left to stand in a fume-cupboard covered by a perforated lid. X-ray quality crystals of **2** were obtained upon slow evaporation of the mother liquor after 2 days. Elemental analysis calc. (%) for C₄₁H₃₇O₆N₃Mn₂: C 63.33, H 4.80, N 5.40; Found: C 63.28, H 4.76, N 5.48. FT-IR (cm⁻¹): 3060.7(w), 3003.3(w), 2920.9(w), 2815.5(w), 1595.7(m), 1585.2(w), 1557.0(w), 1486.7(m), 1464.3(m), 1443.2(m), 1431.3(s), 1357.5(w), 1292.4(w), 1256.9(s), 1212.0(s), 1152.2(w), 1113.3(w), 1096.5(w), 1053.4(s), 1035.6(m), 1003.4(m), 932.8(w), 857.4(s), 832.7(m), 768.1(s), 755.0(m), 731.8(m), 698.6(s).

Preparation of [Mn(III)₂(μ-OMe)₂(biphen)₂(3-pic)₂].2H₂O (3): MnBr₂·4H₂O (0.167 g, 0.58 mmol) and 2,2'-biphenol (0.11 g, 0.59 mmol) were dissolved in 20 cm³ of MeOH. NaOPh·3H₂O (0.05 g, 0.43 mmol) and NaOH (0.012 g, 0.3 mmol) were then added in sequence, and the solution was left stirring for 5 minutes. After this time an excess of 3-picoline (2 cm³, 20.55 mmol) was added and the reactant mixture was allowed to stir for a further 15 minutes. The resultant deep brown solution was then filtered, covered with a perforated lid and allowed to stand in the fume-cupboard. X-ray quality crystals of **3** were obtained upon slow evaporation of the mother liquor after 24 h. Elemental analysis calc. (%) for C₃₈H₃₆O₆N₂Mn₂: C 62.82, H 4.99, N 3.83; Found: C 62.77, H 5.02, N 3.83. FT-IR (cm⁻¹): 3050.9(w), 2922.7(w), 2819.7(w), 1738.3(w), 1581.9(w), 1485.0(m), 1461.6(m), 1428.0(s), 1272.1(m), 1255.8(s), 1221.8(s), 1193.0(m), 1096.6(w), 1053.0(m), 1003.7(m), 935.9(w), 866.8(m), 832.7(m), 798.2(m), 761.4(vs), 726.3(s), 703.5(s).

Preparation of $[Mn(III)_2(\mu-OEt)_2(biphen)_2(3-pic)_2]$ (4**):** $MnBr_2 \cdot 4H_2O$ (0.5 g, 1.74 mmol) and 2,2'-biphenol (0.32 g, 1.72 mmol) were dissolved in 40 cm³ EtOH. Sequentially, NaOMe (0.28 g, 5.2 mmol) and 3-picoline (2 cm³, 20.55 mmol) were added and the solution was left stirring for 10 minutes. The resultant deep brown solution was then filtered, covered with a perforated lid and allowed to stand in the fume-cupboard. X-ray quality crystals of **4** were obtained upon slow evaporation of the mother liquor after 24 h. Elemental analysis calc. (%) for $C_{40}H_{40}O_6N_2Mn_2$: C 63.66, H 5.34, N 3.71; Found: C 63.82, H 5.28, N 4.04. FT-IR (cm⁻¹): 3052.2(w), 2969.6(w), 2927.7(w), 1625.2(w), 1581.9(m), 1486.6(m), 1464.6(m), 1427.4(s), 1382.7(m), 1273.5(m), 1258.4(s), 1225.5(s), 1194.0(m), 1152.5(w), 1127.4(w), 1087.8(m), 1037.5(s), 1003.5(m), 935.4(w), 889.1(m), 869.2(s), 858.9(m), 835.3(m), 797.1(m), 763.7(vs), 728.7(m), 712.9(m), 703.6(s), 653.1(m).

Preparation of $[Mn(III)_2(\mu-OEt)_2(biphen)_2(1-OH-py)_2(EtOH)_2]$ (5**):** $Mn(ClO_4)_2 \cdot 6H_2O$ (0.35 g, 0.96 mmol) and 2,2'-biphenol (0.26 g, 1.4 mmol) were dissolved in 40 cm³ EtOH. The ligand 2-hydroxypyridine (0.26 g, 2.74 mmol) and $NMe_4(OH)$ (0.25 g, 2.75 mmol) were then added in sequence and the resultant deep brown solution was left to stir for 10 minutes. After this time the solution was filtered, covered with a perforated lid and allowed to stand in the fume hood for several days. X-ray quality crystals of **5** were obtained upon slow evaporation of the mother liquor after 2 days. Elemental analysis calc. (%) for $C_{42}H_{48}O_{10}N_2Mn_2$: C 59.30, H 5.69, N 3.29; Found: C 59.35, H 5.67, N 3.16. FT-IR (cm⁻¹): 3254.6(w), 3047.6(w), 2920.5(w), 1695.8(w), 1642.8(vs), 1606.9(s), 1537.4(m), 1487.1(m), 1470.0(m), 1430.7(s), 1406.1(m), 1376.1(m), 1274.6(s), 1261.4(m), 1233.2(s), 1154.3(m), 1093.0(m), 1044.4(s), 992.2(m), 963.4(w), 933.1(w), 895.0(m), 866.6(m), 841.3(m), 762.6(vs), 727.8(s), 711.6(m), 669.0(w).

References

- [1] O. Kahn, *Angew. Chem. Int. Ed.*, **1985**, 24, 834.
- [2] (a) L. Bogani, W. Wernsdorfer, *Nature Mater.*; **2008**, 7, 179-186. (b) M. N. Leuenberger, D. Loss, *Nature*, **2001**, 410, 789-793. (c) R. E. P. Winpenny, *Angew. Chem. Int. Ed.*, **2008**, 47, 7992-7994. (d) M. Evangelisti, E. K. Brechin, *Dalton Trans.*, **2010**, 39, 4672-4676.
- [3] B. Guba, *Proc. Roy. Soc. London Ser.* **1951**, 206, 353-373.
- [4] B. Bleaney, K. D. Bowers, *Proc. Roy. Soc. London Ser.* **1952**, 214, 451-465.
- [5] J. N. Van Niekerek, F. K. L. Schoening, *Acta Crystallogr.* **1953**, 6, 227-232.
- [6] (a) W. E. Hatfield. *ACS Symp. Ser.* **1975**, 5, 108. (b) D. J. Hodgson. *Prog. Inorg. Chem.*, **1975**, 19, 173. (c) K. T. McGregor, N. T. Watkins D. L. Lewis, R. F. Drake, D. J. Hodgson, W. E. Hatfield. *Inorg. Nucl. Chem. Lett.* **1973**, 9, 423. (d) D. L. Lewis K. T.; McGregor, W. E. Hatfield, D. J. Hodgson. *Inorg. Chem.* **1974**, 13, 1013. (e) E. D. Estes, W. E. Hatfield, D. J. Hodgson. *Inorg. Chem.*, **1974**, 13, 1954.
- [7] (a) W. E. Marsh, K. C. Patel, W. E. Hatfield, D. J. Hodgson. *Inorg. Chem.* **1983**, 22, 511-515. (b) C. P. Landee, R. E. Greeney. *Inorg. Chem.* **1986**, 25, 3771-3775.
- [8] R. Costa, I. de. P. H. Moriera, S. Youngme, K. Siriwong, N. Wannarit, F. Ilias, *Inorg. Chem.*, **2010**, 49, 285-294.
- [9] S. S. Tandon, L. K. Thompson, M. E. Manuel, J. N. Bridson, *Inorg. Chem.*, **1994**, 33, 5555-5570.
- [10] (a) S. M. Gorun, S. J. Lippard, *Inorg. Chem.*, **1991**, 30, 1625-1630. (b) R. Werner, S. Ostrovsky, K. Griesar, W. Haase, *Inorg. Chim. Acta*, **2001**, 326, 78-88. (c) H. Weighe, H. U. Güdel., *J. Am. Chem. Soc.*, **1997**, 119, 6539-6543. (d) H. Weighe, H. U. Güdel., *J. Am. Chem. Soc.*, **1998**, 120, 2870-2879.
- [11] (a) W. E. Hatfield, J. J. MacDougall, R. E. Sheperd, *Inorg. Chem.* **1981**, 20, 4216-4219. (b) R. P. Scaringe, D. J. Hodgson, W. E. Hatfield., *Transition Met. Chem.* **1981**, 6, 340-344. (c) S. Cline, D. J. Hodgson, S. Kallesøe, S. Larsen, E. Pedersen., *Inorg. Chem.* **1983**, 22, 637-642. (d) D. J. Hodgson, *NATO ASI Series (C): Mathematical and Physical Sciences.* **1985**, 140, 497-522.
- [12] (a) T. K. Karmakar, B. K. Ghosh, A. Usman, H.-K. Fun, E. Riviere, T. Mallah, G. Aromi, S. K. Chandra, *Inorg. Chem.* **2005**, 44, 2391-2399.
- [13] D. A. Pantazis, V. Krewald, M. Orto, F. Neese., *Dalton Trans.*, **2010**, 39, 4959-4967.

- [14] (a) R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature*, **1993**, 365, 141. (b) R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson. *J. Am. Chem. Soc.*, **1993**, 115, 1804.
- [15] (a) T. Cauchy, E. Ruiz, S. Alvarez, *J. Am. Chem. Soc.*, **2006**, 128, 15722. (b) E. Ruiz, *Struct. Bonding*, **2004**, 113, 71. (c) P. J. Hay, J. C. Thibeault, R. Hoffmann, *J. Am. Chem. Soc.*, **1975**, 97, 4884. (d) O. Kahn, B. Briat., *J. Chem. Soc., Faraday Trans. 2*, **1976**, 72, 268.
- [16] (a) S. Gehring, P. Fleischhauer, H. Paulus, W. Haase, *Inorg. Chem.* **1993**, 32, 54-60. (b) Zhang, Y.-Q.; Luo, C.-L. *Dalton Trans.*, **2009**, 5627-5636.
- [17] (a) J. Tercoro, E. Ruiz, S. Alvarez, A. Rodriguez-Forteza, P. Alemany, *J. Mater. Chem.*, **2006**, 16, 2729-2735. (b) L. Gregoli, C. Danieli, A. Laure-Barre, P. Neugebauer, G. Pellegrino, G. Poneti, R. Sessoli, A. Cornia, *Chem. Eur. J.*; **2009**, 15, 6456-6467. (c) M. A. Palacios, A. J. Mota, J. E. Perea-Buceta, F. E. White, E. K. Brechin, E. Colacio., *Inorg. Chem.*, **2010**, 49, 10156-10165. (d) S. Sasmal, S. Hazra, P. Kundu, S. Majumder, N. Aliaga-Alcalde, E. Ruiz, S. Mohanta., *Inorg. Chem.* **2010**, 49, 9517-9526.
- [18] (a) C. J. Milios, R. Inglis, A. Vinslava, R. Bagai, W. Wernsdorfer, S. Parsons, S. P. Perlepes, E. K. Brechin, *J. Am. Chem. Soc.*, **2007**, 129, 12505-12511. (b) A. Prescimone, C. J. Milios, J. Sanchez-Benitez, K. V. Kamenev, C. Loose, J. Kortus, S. Moggach, M. Murrie, J. E. Warren, E. K. Brechin, *Dalton Trans.*, **2009**, 4858-4867. (b) R. Inglis, L. F. Jones, C. J. Milios, S. Datta, A. Collins, S. Parsons, W. Wernsdorfer, S. Hill, S. P. Perlepes, S. Piligkos, E. K. Brechin, *Dalton Trans.*, **2009**, 3403-3412.
- [19] O. Waldmann, R. Koch, S. Schromm, J. Schulein, P. Muller, I. Bernt, R. W. Saalfrank, F. Hampel, E. Balthes, *Inorg. Chem.* **2001**, 40 2986-2995
- [20] (a) J. Bartolome, G. Filoti, V. Kunschcr, G. Schinteie, V. Mereacre, C. E. Anson, A. K. Powell, D. Prodius, C. Turta, *Phys. Rev. B.* **2009**, 80, 014430. (b) G. Rajaraman, F. Totti, A. Bencini, A. Caneschi, R. Sessoli, D. Gatteschi, *Dalton Trans.*, **2009**, 3153-3161.
- [21] E. Ruiz, S. Alvarez, A. Rodriguez-Forteza, P. Alemany, Y. Pouillon and C. Massobrio. *From Magnetism: Molecules to Materials II*, eds. J. S. Miller and M. Drillon, Wiley-VCH Verlag GmbH, Weinheim, Germany, 2001, vol. II, pp. 227-279.
- [22] G. Aromi, E. K. Brechin, *Struct. Bond. (Springer)*, **2006**, 122, 1-67.
- [23] For examples of the 1st row coordination chemistry of the 2,2'-biphenolate ligand see: (a) N. Berg, L. F. Jones., *CrystEngComm.*, **2010**, 12, 3518-3521. (b) N. Berg, L. F. Jones.,

- CrystEngComm.*, **2011**, 13, 5510-5518. (c) D. P. Goldberg, A. Caneschi, S. J. Lippard. *J. Am. Chem. Soc.*, **1993**, 115, 9299-9300. (d) D. P. Goldberg, A. Caneschi, C. D. Delfs R. Sessoli, S. J. Lippard. *J. Am. Chem. Soc.*, **1995**, 117, 5789-5800. (e) A. R. Schake, E. A. Schmitt, A. J. Conti, W. E. Strieb, J. C. Huffman, D. N. Hendrickson, G. Christou. *Inorg. Chem.*, **1991**, 30, 3192-3199. (f) E. W. Ainscough, A. M. Brodie, S. J. McLachlan, K. L. Brown. *J. Chem. Soc. Dalton Trans.*, **1983**, 1385-1389. (g) J. S. Bashkin, A. N. Schake, J. B. Vincent, H.-R. Chang, Q. Li, J. C. Huffmann, G. Christou, D. N. Hendrickson. *J. Chem. Soc. Chem. Commun.*, **1988**, 700-702.
- [24] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor. *J. Chem. Soc., Dalton Trans.*, **1984**, 7, 1349-1356.
- [25] H. Biava, C. Palopoli. S. Shova. M. De Gaudio. V. Daier, M. González-Sierra. J. P. Tuchagues. S. Signorella. *J. Inorg. Biochem.* **2006**, 100, 1660–1671.
- [26] C. Palopoli. M. González-Sierra, G. Robles, F. Dahan, J. P. Tuchagues, S. Signorella. *Dalton Trans.* **2002**, 3813-3819.
- [27] V. Daier. H. Biava, C. Palopoli. S. Shova. J. P. Tuchagues. S. Signorella. *Jour. Inorg. Biochem.* **2004**, 98, 1806–1817.
- [28] T. K. Paine, T. Weyhermüller. E. Bothe, K. Wieghardt, P. Chaudhuri. *Dalton Trans.* **2003**, 3136-3144.
- [29] D. Moreno, C. Palopoli, V. Daier, S. Shova, L. Vendier. M. González-Sierra, J. P. Tuchagues. S. Signorella. *Dalton Trans.*, **2006**, 5156-5166.
- [30] M. Mikuriya, Y. Yamoto. *Inorg. Chim. Acta.* **1991**, 181, 1-2.
- [31] X. S. Tan, W. X. Tang. *Polyhedron.* **1996**, 15, 2671-2675.
- [32] J.-J. Zhang. Q.-H. Luo, C.-Y. Duan, Z.-L. Wang, Y.-H. Mei. *J. Inorg. Biochem.* **2001**, 86, 573-579.
- [33] H. Miyasaka, R. Clerac, W. Wernsdorfer, L. Lecren, C. Bonhomme. K.-I. Sugiura, M. Yamashita. *Angew. Chem. Int. Ed.* **2004**, 43, 2801-2805.
- [34] H.-L. Shyu, H.-H. Wei, Y. Wang. *Inorg. Chim. Acta.* **1999**, 290, 8-13.
- [35] Z. Lu, M. Yuan, F. Pan, S. Gao. D. Zhang, D. Zhu. *Inorg. Chem.* **2006**, 45, 3538-3548.
- [36] N. Matsumoto, Z.-J. Zhong, H. Okawa. S. Kida. *Inorg. Chim. Acta.* **1989**, 160, 153-157.

- [37] G. Rajaraman, E. Carolina Sanudo, M. Helliwell, S. Piligkos, W. Wernsdorfer, G. Christou, E. K. Brechin. *Polyhedron*. **2005**, 24, 2450-2454.
- [38] S. Saha, D. Mal, S. Koner, A. Bhattacharjee, P. Gütllich, S. Mondal, M. Mukherjee, K.-I. Okamoto. *Polyhedron*. **2004**, 23, 1811-1817.
- [39] G. L. Abbati, A. Cornia, A. C. Fabretti, A. Caneschi, D. Gatteschi. *Inorg. Chem.* **1998**, 37, 3759-3766.
- [40] A. Gelasco, M. L. Kirk, J. W. Kampf, V. L. Pecoraro. *Inorg. Chem.* **1997**, 36, 1829-1837.
- [41] J.-J. Zhang, Y.-Y. Tang, Q.-H. Luo, C.-Y. Duan, Z.-L. Wang, Y.-H. Mei. *Polyhedron*. **2001**, 20, 2285-2291.
- [42] H. Miyasaka, R. Clerac, T. Ishii, H.-C. Chang, S. Kitagawa, M. Yamashita. *Chem. Soc. Dalton Trans.* **2002**, 1528-1534.
- [43] Z.-Y. Zhang, C. Brouca-Cabarrecq, C. Hemmert, F. Dahan, J.-P. Tuchagues. *J. Chem. Soc. Dalton Trans.* **1995**, 1453-11460.
- [44] G. Bhargavi, M. V. Rajeskhara, J.-P. Costes, J.-P. Tuchagues. *Polyhedron*, **2009**, 28, 1253-1260.
- [45] S. Mandal, G. Rosair, J. Ribas, D. Bandyopadhyay. *Inorg. Chim. Acta.*, **2009**, 362, 2200-2204.
- [46] Y. Feng, C. Wang, Y. Zhao, J. Li, D. Liao, S. Yan, Q. Wang. *Inorg. Chim. Acta*, **2009**, 362, 3563-3568.
- [47] J. H. Yoon, D. W. Ryu, H. C. Kim, S. W. Yoon, B. J. Suh, C. S. Hong. *Angew. Chem. Int. Ed.*, **2009**, 15, 3661-3665.
- [48] G. Bhagravi, M. V. Rajasekharan, J.-P. Tuchagues. *Inorg. Chim. Acta.*, **2009**, 362, 3247-3252.
- [49] M. F. Anderlund, J. Zheng, M. Ghiladi, M. Kritikos, E. Rivière, L. Sun, J.-J. Girerd, B. Akermark. *Inorg. Chem. Commun.* **2006**, 9, 1195-1198.
- [50] C. Beghidja, G. Rogez, J. Kortus, M. Wesolek, R. Welter. *J. Am. Chem. Soc.* **2006**, 128, 3140-3141.
- [51] (a) R. Celenligil-Cetin, P. Paraskevopoulou, N. Lalioti, Y. Sanakis, R. J. Staples, N. P. Rath, P. Stavropoulos. *Inorg. Chem.*, **2008**, 47, 10998-11009. (b) L. Dubois, J. Pécaut, M.-F. Charlot, C. Baffert, C. Collomb, M. N. Deronzier, J. M. Latour. *Chem. Eur. J.*, **2008**, 14, 3013-3025. (c) Y.

- Mikata, H. So, A. Yamashita, A. Kawamura, M. Mikuriya, K. Fukui, A. Ichimura, S. Yano, *Dalton Trans.*, **2007**, 3300-3334. (d) J. Glerup, P. A. Goodson, A. Hazell, R. Hazell, D. J. Hodgson, C. J. McKenzie, K. Nichelsen, U. Rychlewska, H. Toftlund. *Inorg. Chem.* **1994**, 33(18), 4105-4111.
- [52] A. D. Becke. *J. Chem. Phys.*, **1993**, 98, 5648-5652.
- [53] R. Hotzelmann, K. Wieghardt, U. Florke, H.-J. Haupt, D. C. Weatherburn, J. Jacques Bonvoisin, G. Genevive Blondin, J.-J. Girerd. *J. Am. Chem. Soc.*, **1992**, 114, 1681-1696.
- [54] (a) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, 97, 2571-2577. (b) A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, 100, 5829-5835.
- [55] *Gaussian 09, Revision A.02*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- [56] L. Noodleman, *J. Chem. Phys.*, **1981**, 74, 5737-5743
- [57] E. Ruiz, S. Alvarez, J. Cano, P. Alemany. *J. Comput. Chem.*, **1999**, 20, 1391-1400. (b) E. Ruiz, A. Rodriguez-Forteza, J. Cano, S. Alvarez, P. Alemany, *J. Comput. Chem.*, **2003**, 24, 982-989. (c) G. Rajaraman, J. Cano, E. K. Brechin, E. J. L. McInnes, *Chem. Commun.*, **2004**, 1476-1477. (d) P. Christian, G. Rajaraman, A. Harrison, J. J. W. McDouall, J. Raftery, R. E. P. Winpenny. *Dalton. Trans.*, **2004**, 2550-2555. (e) G. Rajaraman, M. Murugesu, E. C. Sanudo, M. Soler, W. Wernsdorfer, M. Helliwell, C. Muryn, J. Raftery, S. J. Teat, G. Christou, E. K. Brechin, *J. Am. Chem. Soc.*, **2004**, 126, 15445-15457. (f) A. Bencini, F. Totti, *Int. J. Quantum Chem.*, **2005**, 101, 819-825. (g) K. Hegetschweiler, B. Morenster, J. Zubieta, P. J. Hagrman, N. Lima, R. Sessoli, F. Totti, *Angew. Chem., Int. Ed. Engl.*, **2004**, 43, 3436-3439.