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Influencing the orientation of Jahn-Teller axes in butterfly-like Mn^{III}_4 clusters

Ross McLellan,^[a] Maria A. Palacios,^[b] Euan K. Brechin^{*,[b]} and Scott J. Dalgarno^{*,[a]}

A bis-phenolate that has structural similarities to both calix[4]arene and the oxcalix[n]arenes provides access to a 'butterfly'-like Mn_4 cluster in which all metals are in the oxidation state +3. Specific properties of this ligand, in comparison to others in the literature, offer a route to influencing the orientation of the Jahn-Teller axes within this cluster motif, which possesses a rare oxidation state arrangement.

Methylene-bridged calix[n]arenes are cyclic polyphenols that have emerged as excellent platforms for the synthesis of new polynuclear transition and lanthanide metal clusters (TM and Ln respectively).^[1,2] We have explored this chemistry extensively with *p*-^tBu-calix[4]arene / calix[4]arene (TBC[4] / C[4]) in particular and have reported a range of novel cluster motifs including: a) $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{TBC}[4])_2]$ Single-Molecule Magnets (SMMs, Fig. 1);^[1b,c] b) $[\text{Cu}^{\text{II}}_9(\text{TBC}[4])_3]$ clusters^[1d] that are versatile anion binding materials; c) $[\text{Mn}^{\text{III}}_4\text{Ln}^{\text{III}}_4(\text{C}[4])_4]$ clusters that are magnetic refrigerants or SMMs depending on the lanthanide employed;^[1e,f] d) $[\text{Fe}^{\text{III}}_2\text{Ln}^{\text{III}}_2(\text{TBC}[4])_2]$ clusters^[1g] and e) octahedral $[\text{Ln}^{\text{III}}_6(\text{TBC}[4])_2]$ clusters.^[1h] This study has allowed us to establish a set of metal-ion binding rules for the general C[4] framework, and perhaps the most important feature of this is that the polyphenolic pocket shows strong affinity for Mn^{III} ions in competition experiments.

The metallic skeleton in the $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{TBC}[4])_2]$ SMMs mentioned above describes a planar diamond or butterfly-like topology in which the wing-tip manganese ions (within the C[4] cavity) are in the oxidation state +3, and the body manganese ions are in the oxidation state +2 (Fig. 1). These ions are linked via two $\mu_3\text{-OH}^-$ ions located in the center of the diamond forming a $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{OH})_2]^{8+}$ core. The four positions around the equatorial plane of each wing-tip Mn^{III} ion are occupied by the oxygen atoms of a TBC[4] support, and in each case two of these μ -bridge to the central Mn^{II} ions. The remaining positions around all of the $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$ ions are occupied by ligated DMF molecules and the Jahn-Teller axes of the cavity-bound (and distorted octahedral) Mn^{III} ions are defined by the $\text{O}(\text{DMF})\text{-Mn-O}(\mu_3\text{-OH})$ vector.

A search of the Cambridge Structural Database for clusters with a general Mn_4O_6 core (Fig. 2A) with no specific oxidation state distributions returns a total of 66 entries.^[3] Analysis revealed a number of interesting trends. The first is that the

vast majority of these have the opposite oxidation state distribution to that found in the $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{TBC}[4])_2]$ SMM, *i.e.* the wing-tip and body ions of the butterfly are Mn^{II} and Mn^{III} , respectively.^[4] Six clusters have an arrangement in which wing-tip and body Mn ions are all in the oxidation state +3, five of which are formed from reactions with ligands containing salicylideneamino moieties (see Figure 2B).^[5-7]

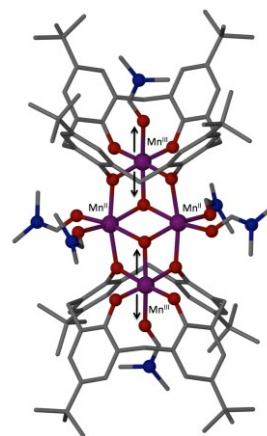


Figure 1. $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{TBC}[4])_2]$ Single-Molecule Magnet showing a) the butterfly-like cluster motif, b) bridging nature of the $\mu_3\text{-OH}$ (H atoms not shown) and TBC[4] anions, c) ligated DMF occupying the TBC[4] cavities and d) the Jahn-Teller axes defined by the $\text{O}(\text{DMF})\text{-Mn-O}(\mu_3\text{-OH})$ vector indicated with arrows.^[1b,c]

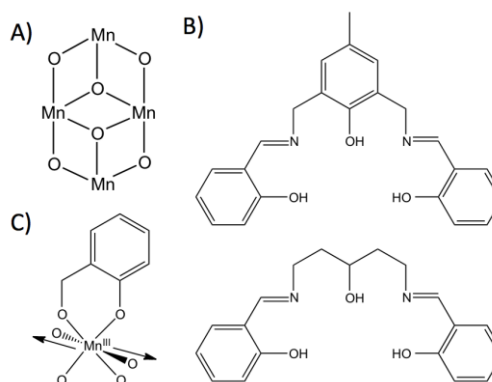


Figure 2. A) General Mn_4O_6 butterfly fragment used for the CSD analysis. B) Examples of salicylideneamino containing ligands that afford butterfly-like clusters in which all Mn ions are in oxidation state +3.^[5-7] Common orientation of Jahn-Teller axes in ligands containing adjacent phenol and methanol moieties.^[8]

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The final trend we observed is that, within our search for the general Mn_4O_6 fragment / core, ligands containing phenol and *ortho*-methanol moieties bind Mn^{III} ions with the Jahn-Teller axes oriented orthogonal to the near planar ligand fragment (Fig. 2C).⁸ We recently began to investigate TM and

Ln cluster formation with bis(5-tert-butyl-2-hydroxy-3-hydroxy-methylphenyl)methane (H_4L1 , Fig. 3A) as it bears a striking similarity to calix[n]arenes and oxacalix[n]arenes, and would thus provide useful data for structural comparison to related building blocks. We have reported the formation of a family of near-linear Ln^{III} trimers^[9] as well as a large Co_{15} cluster using this ligand as a support.^[10] The latter involved *in situ* generation of carbonate which was found to play a pivotal structural role in cluster formation. In both cases $L1$ displayed calixarene character and accommodated varying degrees of deprotonation. Given the results arising from our CSD search we anticipated that it would be possible to a) bind two Mn^{III} ions with this ligand, b) form a butterfly-like cluster and c) therefore influence the magnetic properties of the resulting assembly *via* the curvature associated with H_4L1 . The second assumption was based on the remaining Mn^{III}_4 butterfly-like cluster $[Mn^{III}_4(AcVn)_2(\mu_3-OMe)_2(\mu-OMe)_2(MeOH)_2]$ (**1**; AcVn = acetone-divanillin aldol) found in our CSD search (Fig. 3B).^[11] This cluster arises from an *in situ* Mn^{II+} -promoted double-aldol reaction between vanillin and acetone. Notably this di-vanillin ligand represents two halves of H_4L1 that are linked at the methanol functionality by an additional carbon atom bridge (compare Fig. 3A and 3C). Analysis of the cluster shows that the Jahn-Teller axes lie orthogonal to the phenol / methanol fragment planes in the acetone-di-vanillin ligand as one would predict.

Reaction of H_4L1 , manganese (II) nitrate and base in methanol afforded dark green single crystals that were found to be of formula $[Mn^{III}_4(L1)_2(\mu-OMe)_2(\mu_3-OMe)_3(MeOH)_4] \cdot 2MeOH$ (**2**·**2MeOH**, Fig. 4). The crystals were found to be of triclinic symmetry and the asymmetric unit comprises one half of the expected tetranuclear butterfly-like cluster and a methanol of crystallization. The two crystallographically unique Mn^{III} ions ($Mn1$ and $Mn2$, Fig. 4) are coordinated to a fully deprotonated $L1$ tetra-anion, one $\mu-OMe^-$ (O7) and one μ_3-OMe^- (O5).^[12] The coordination sphere of $Mn1$ is completed by a ligated MeOH (O6) and symmetry equivalent (s.e.) μ_3-OMe^- (O5^a). Similarly the coordination sphere of $Mn2$ is completed by a ligated MeOH (O8) and a s.e. methoxide arm of the $L1$ tetra-anion (O4^a). Given the orientation of the phenol / methanol fragments in H_4L1 , the orientation of the Jahn-Teller axes of $Mn1$ and $Mn2$ has been influenced and these lie perpendicular to each other as expected; as a result the two crystallographically unique axes are defined by the O6(MeOH)- $Mn1$ -O5(μ_3-OMe^-) and O8(MeOH)- $Mn2$ -O5(μ_3-OMe^-) vectors (Fig. 4).

Examination of the extended structure of **2** shows that the molecules assemble as H-bonded chains along the b axis within layers (Fig. S1), and this occurs with two crystallographically unique H-bonding interactions; one is found between the ligated MeOH on $Mn2$ and the MeOH of crystallization (O8...O9 distance of 2.578 Å), whilst the other is between the MeOH of crystallization and a s.e. methoxy arm of an $L1$ tetra-anion (O9...O2^a distance of 2.680 Å). The closest intermolecular metal-metal distance is found to be 6.715 Å along the b axis, with other distances being significantly greater, thereby indicating that the clusters are well separated by the bis-phenolate ligand supports. The extended packing mimics that found in the aforementioned $[Mn^{III}_2Mn^{II}_2(TBC[4])_2]$ SMMs (Figures S1-S3),^[1b,c] and also that of the di-vanillin ligand supported cluster **1**.^[11]

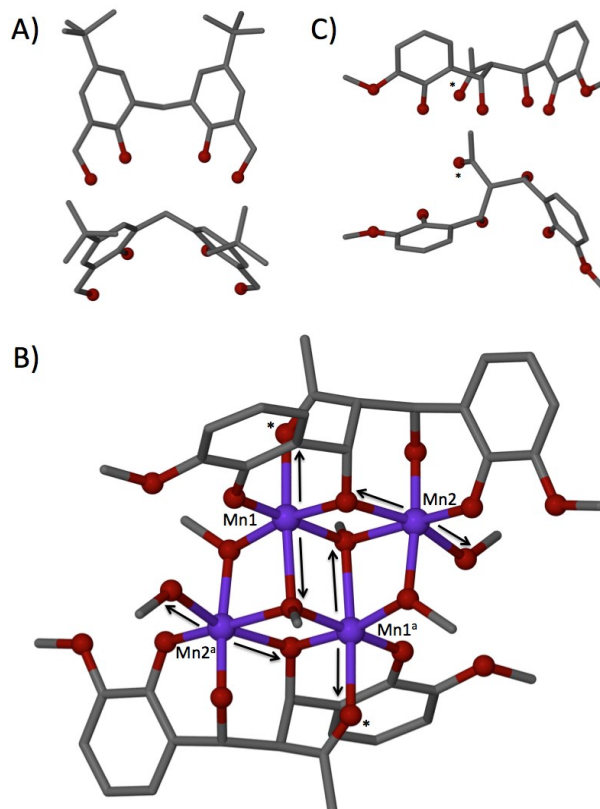


Figure 3. A) Two views of the bis-phenolate (H_4L1) used in this study showing calixarene like character / curvature induced by the methylene bridge. B) Partially labelled Mn^{III}_4 butterfly cluster (**1**) formed during Mn^{II+} promoted double-aldol addition reaction between acetone and vanillin, with Jahn-Teller axes indicated with arrows.^[11] C) Two views of the di-vanillin ligand from B) showing the shape caused by additional linking C atoms relative to those in H_4L1 . H atoms omitted for clarity in (A) – (C) and * denotes a carbonyl group in (B) and (C).

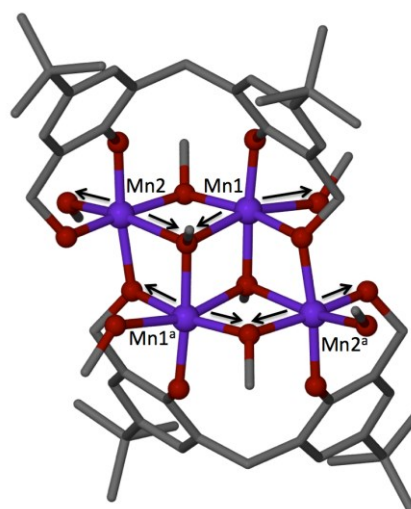


Figure 4. Partially labelled structure of **2**·**2MeOH** showing the Mn^{III}_4 butterfly cluster and orientation of Jahn-Teller axes (indicated with arrows). H atoms and MeOH molecules of crystallisation omitted for clarity.

Close examination of the cluster cores shows very close structural positioning of the Mn^{III} ions. Cluster **1** has $Mn1$ - $Mn1^a$, $Mn1$ - $Mn2$, $Mn2$ - $Mn1^a$ and $Mn2$ - $Mn2^a$ distances of 3.25, 3.12,

3.13 and 5.34 Å respectively (Fig. 3B). Similar analysis of the polymetallic core in **2** reveals Mn1-Mn1^a, Mn1-Mn2, Mn2-Mn1^a and Mn2-Mn2^a distances of 3.18, 3.16, 3.10 and 5.39 Å (Fig. 4). Comparison between Figures 3B and 4 shows a marked difference in Jahn-Teller orientation between **1** and **2**, a feature that is a direct result of the arrangement of the phenol / methanol fragments in the L1 ligands, and one that has important consequences for the resultant magnetic behaviour. Direct current magnetic susceptibility studies were performed on polycrystalline samples of **2** in the $T = 5\text{--}300$ K range in an applied field, $H = 0.1$ T. The results are plotted as the $\chi_M T$ product versus T in Figure 5. The $\chi_M T$ value of ~ 14 cm³ K mol⁻¹ at 300 K is above the spin-only ($g = 2.0$) value of 12 cm³ K mol⁻¹ expected for four non-interacting high-spin Mn^{III} ($3d^4$) ions. The value increases constantly with decreasing temperature reaching a maximum value of ~ 28 cm³ K mol⁻¹ at 20 K, below which it decreases to a value of ~ 16 cm³ K mol⁻¹ at 5 K. This behaviour is indicative of the presence of ferromagnetic exchange between neighbouring metal ions, with the low temperature decline being due to intermolecular AF interactions and/or zero-field splitting (zfs) effects. The experimental data can be fitted to the isotropic spin-Hamiltonian (1), by use of the Levenberg–Marquardt algorithm^[13]:

$$\hat{H}_{iso} = -2 \sum_{i,j>i} J \hat{S}_i \cdot \hat{S}_j + \mu_B H g \sum_i \hat{S}_i \quad (1)$$

where i, j are indices running through the constituent single ions, J is the isotropic exchange parameter, \hat{S} is a spin operator, μ_B is the Bohr magneton, $g = 2.0$ is the g -factor of Mn^{III} and H is the applied magnetic field. We have used the model in the inset of Figure 5, which includes two different exchange interactions. We have not included the $T < 20$ K data to avoid the use of additional [and correlated] intermolecular interactions and zfs parameters. This affords $J_1 = +8.64$ cm⁻¹ and $J_2 = +1.34$ cm⁻¹ with the resulting $S = 8$ ground state being separated by ~ 11 cm⁻¹ from the first ($S = 7$) excited state (Figure S4). A Curie-Weiss fit of the $1/\chi_M$ versus T data affords $\theta = +23$ K. The nature and magnitude of the nearest neighbour interactions are consistent with a recently published magnetostructural correlation (MSC) for alkoxide-bridged Mn^{III} dimers.^[14] Magnetisation data (Figure S5) collected in the $T = 2\text{--}6$ K and $H = 3\text{--}7$ T temperature and field ranges can be fitted by assuming only the ground spin-state is thermally populated under these experimental conditions. We employed anisotropic spin-Hamiltonian (2) that takes into account spin-variables relevant to the $S = 8$ ground spin-state **only**,

$$\hat{H}_{aniso} = D_S = 8 \left[\hat{S}_z^2 - (S+1)S/3 \right] + \mu_B H g S = 8 \hat{S} \quad (2)$$

where D and $g = 2$ are the uniaxial anisotropy parameter and g -value of the $S = 8$ ground spin-state. Spin-Hamiltonian (2) was fitted to the experimental data by use of the simplex algorithm,^[13] to give the best-fit parameter $D_{(S=8)} = -0.37$ cm⁻¹.

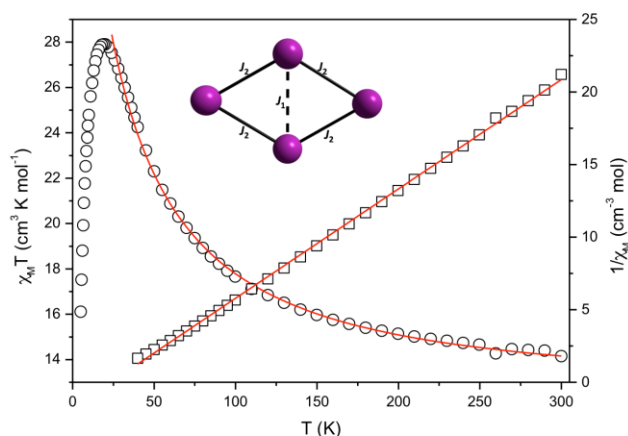


Figure 5. Plot of $\chi_M T$ and $1/\chi_M$ versus T for complex **2**. The solid red lines are a fit of the experimental data. See the main text for details.

In conclusion we have shown that it is possible to influence the orientation of Mn^{III} ion Jahn-Teller axes in target cluster formation by ligand design, through careful control over substituent positioning. Control over the relative positions of JT axes in neighbouring Mn^{III} ions has been shown recently to be crucial in determining the nature and magnitude of the magnetic exchange interaction. This will inform future ligand design and cluster formation with these and other calixarene analogue ligands. These results will be reported in due course.

Experimental Section

H₄L1 was prepared according to literature procedures.^[15]
Synthesis of 2·2MeOH: H₄L1 (1g, 2.69 mmol) and Mn(NO₃)₂·4H₂O (1.35g, 5.38 mmol) were stirred in a mixture of dmf (10 mL) and MeOH (40 mL) for 10 minutes. NaOH (0.64 g, 16.14 mmol) in MeOH (50mL) was added and the dark green solution stirred for a further two hours. A dark green precipitate was collected by filtration and recrystallized from hot methanol, affording **2·2MeOH** in modest yield (34%). Elemental analysis (%) calculated for 1, C₅₆H₉₂Mn₄O₁₈: C, 52.83 %; H, 7.28 %. Found: C, 52.53 %; H, 7.49 %. **Crystal Data (CCDC 980027):** C₅₆H₉₂Mn₄O₁₈, $M = 1273.06$, Dark Green Block, $0.40 \cdot 0.30 \cdot 0.25$ mm³, triclinic, space group $P-1$ (No. 2), $a = 11.4692(9)$, $b = 12.0182(11)$, $c = 13.2154(12)$ Å, $\alpha = 80.382(3)$, $\beta = 71.256(3)$, $\gamma = 66.732(3)^\circ$, $V = 1583.0(2)$ Å³, $Z = 1$, $D_c = 1.335$ g/cm³, $F_{000} = 672$, Bruker X8 Apex II CCD Diffractometer, MoK α radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{max} = 46.5^\circ$, 14532 reflections collected, 4342 unique ($R_{int} = 0.0418$). Final $Goof = 1.041$, $R1 = 0.0493$, $wR2 = 0.1199$, R indices based on 3268 reflections with $I > 2\sigma(I)$ (refinement on F^2).

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Keywords: Manganese • Coordination Chemistry • Magnetism • Jahn-Teller • Calixarenes

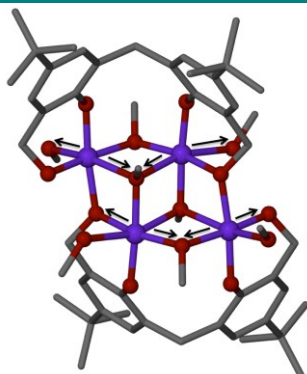
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COMMUNICATION

A bis-phenolate with calixarene character influences the orientation of Jahn-Teller axes in a tetranuclear Mn^{III} cluster. Structural changes and prevailing magnetic properties are presented.



Ross McLellan, Maria A. Palacios, Euan K. Brechin and Scott J. Dalgarno**

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Influencing the orientation of Jahn-Teller axes in butterfly-like Mn^{III}_4 clusters