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Assembly of a calix[4]arene-supported $Mn^{III}Mn^{II}$ cluster mediated by halogen interactions†

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A new calix[4]arene-supported $Mn^{III}Mn^{II}$ cluster, formed by the introduction of 3,5-dichlorobenzoate to a system known to afford $Mn^{III}_2Mn^{II}_2$ Single-Molecule Magnets (SMMs), assembles in a layered manner through halogen interactions; structural and magnetic properties of this new cluster are presented.

Calix[4]arenes (C[4]s) have been used extensively in the formation of supramolecular structures, as well as in various aspects of coordination chemistry due to their polyphenolic nature.[1] *p*-^{t}Bu-calix[4]arene (TBC[4], Fig. 1A) is readily accessible[2a] and is a typical starting point for the alteration of the general C[4] framework.[2b] The C[4] polyphenolic pocket (at what is termed the lower-rim) is an attractive feature for metal complexation,[3] and in this regard we (amongst others) have used TBC4 and related C[4]s for the construction of polynuclear transition metal (TM), lanthanide metal (LnM) and 3*d*–4*f* clusters that possess interesting magnetic properties.[4] In our studies we have discovered a range of structural/cluster motifs, and those most frequently encountered include a) $[Mn^{III}_2Mn^{II}_2(TBC[4])_2]$ Single-Molecule Magnets (SMMs),[4b,c] b) $[Mn^{III}_4Ln^{III}_4(C[4])_4]$ clusters that are magnetic refrigerants or SMMs depending on the lanthanide employed[4f,g] and $[Cu^{II}_9(TBC[4])_3]$ clusters[4d] that are versatile anion binding materials.

The synthesis of the TBC[4]-supported $Mn^{III}_2Mn^{II}_2$ cluster shown in Fig. 1B is high yielding and we recently began to investigate the role of ancillary ligands in hybrid TBC[4]-supported cluster formation with a view to disrupting formation of this favourable structural motif. Addition of either sodium phenylphosphinate or 2-(hydroxymethyl)pyridine (hmpH) to the reaction used to form the $[Mn^{III}_2Mn^{II}_2(TBC[4])_2]$ SMM affords very different results.[4e,j] The former results in a modulated TBC[4]-supported $Mn^{III}_2Mn^{II}_2$ cluster in which two $Mn^{III}Mn^{II}$ dimers are linked by two bridging phenylphosphinates (Fig. 1C).[4e] The latter results in a $Mn^{III}_3Mn^{II}_2$ cluster in which both ligands display characteristic metal complexation properties (Fig. 1D).[4j] In both examples the TBC[4]s house Mn^{III} ions within the cavity formed by the four lower-rim oxygen atoms, which also bridge to Mn^{II} ions located at the centre of the cage; behaviour entirely

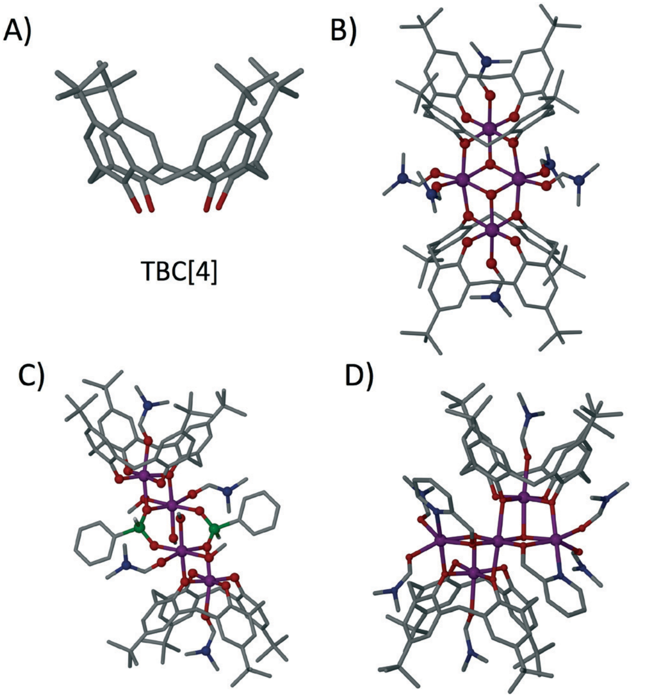

Fig. 1 A) *p*-^{t}Bu-calix[4]arene, TBC[4]. B) TBC[4]-supported $[Mn^{III}_2Mn^{II}_2]$ SMM motif.[4b,c] C) Phenylphosphinate-bridged dimer of TBC[4]-supported $[Mn^{III}Mn^{II}]$ dimers.[4e] D) TBC[4]-supported $Mn^{III}_3Mn^{II}_2$ cluster formed with hmp as an ancillary ligand.[4j] Colour code: C – grey, O – red, N – royal blue, Mn – purple, P – green. H atoms are omitted for clarity. Figures not to scale.

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consistent with other systems involving additional metal ions such as lanthanides.[4f,g]

Thia-, sulfinyl- and sulfonyl-bridged C[4]s have also been used in polynuclear metal cluster formation,[5,6] but the resulting materials differ markedly to those formed with methylene-bridged C[4]s due to the influence of the bridging atoms on the resulting coordination chemistry. The Liao[6a–c] and Hong[6d,e] groups recently used these alternative thia-C[4]-supported TM_4 sub-units as building blocks in a series of studies, where they showed that polybenzoates can been used as ancillary ligands to sequentially direct the formation/assembly of novel metal–organic nanocapsules. Given this, as well as our successful use of ancillary ligands in hybrid TBC[4]-supported cluster formation, we began to investigate the effect of aryl monocarboxylates on the structure of the $[Mn^{III}_2Mn^{II}_2(TBC[4])_2]$ SMM motif, prior to investigating topologically directing analogues. Here we report the first result of these studies, obtained by the introduction of sodium 3,5-dichlorobenzoate (Nadcb) to the reaction used to form the $[Mn^{III}_2Mn^{II}_2(TBC[4])_2]$ SMM. The benzoate was found to have a marked effect on cluster formation, affording a new $[Mn^{III}Mn^{II}(TBC[4])(dcb)(\mu\text{-dmso})(dmso)_3(H_2O)]$ species (**1**)[7] that assembles though halogen⋯halogen interactions into bi-layers that are reminiscent of the packing observed in TBC4 solvates.

Reaction of $MnCl_2{\cdot}4H_2O$ with TBC[4] and Nadcb in a basic dmso solution afforded single crystals of **1** that were suitable for X-ray diffraction studies.‡ The crystals were found to be in a monoclinic cell and structure solution was performed in the space group *C*2/*c*. The structure of **1** (Fig. 2) is best described as a mixed valence $Mn^{III}Mn^{II}$ dimer in which Mn1 is in the third oxidation state and bonded centrally within the plane of all four phenoxide oxygens of a tetraanionic TBC[4] (Mn–O range 1.910(7)–1.958(6) Å). The formation of this $[Mn^{III}\text{–}TBC[4]]^-$ moiety is expected, and is an extraordinarily common motif observed in our coordination chemistry experiments performed with the C[4] framework. The Jahn–Teller axis deviates from linearity (∠O5–Mn1–O12 = 172.19°) and along this vector Mn1 is bonded to a bridging dmso (Mn1–O5 2.282(6) Å) as well as the oxygen of a disordered ligated solvent (Mn1–O12 2.312(6) Å).[7] Distorted octahedral Mn2 is in the second oxidation state and is connected to Mn1 by a μ-phenoxide and a μ-dmso (Mn2–O2 2.200(7) Å and Mn2–O5 2.266(6) Å respectively). One aqua ligand (Mn2–O28 2.204(8) Å), two ligated dmso molecules (one of which is disordered over two positions, Mn–O range of 2.12(1)–2.24(1) Å) and a monodentate dcb ligand (Mn2–O10 2.169(8) Å) complete the coordination sphere of Mn2, as shown in Fig. 2. A hydrogen-bonding interaction is observed between the aqua ligand and the non-bonded C=O of the appended dcb, occurring with an O28⋯O11 distance of 2.650 Å.

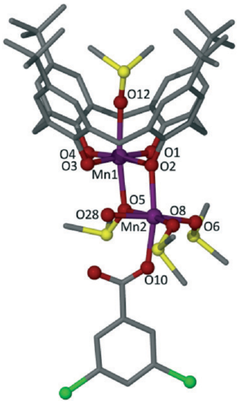

Fig. 2 Partially labelled structure of **1** showing the 3,5-dichlorobenzoate appended to the $Mn^{III}Mn^{II}$ cluster core, ligation of DMSO in the TBC[4] cavity and both bridging and terminal ligated solvent. Colour code: C – grey, O – red, S – yellow, Mn – purple, Cl – green. H atoms omitted for clarity.

By comparing Figures 1B and 2 it is clear that **1** resembles one half of the $Mn^{III}_2Mn^{II}_2$ butterfly. Thus, incorporation of 3,5-dichlorobenzoate has a profound impact on cluster formation. We recently reported cases of ancillary ligands "interrupting" the assembly process of the $[Mn^{III}_2Mn^{II}_2(TBC[4])_2]$ SMM; for example addition of sodium phenylphosphinate resulted in an 'elongated' or 'expanded' form of the archetypal $[Mn^{III}_2Mn^{II}_2(TBC[4])_2]$ SMM.[4e] This dimer of dimers (Fig. 1C) is important in the context of the present study as each (ferromagnetically coupled) $Mn^{III}Mn^{II}$ subunit resembles the metallic skeleton in **1**. The μ-O atom of dmso in **1** is replaced with a μ-O atom from a μ_3-phosphinate that in turn connects to the symmetry equivalent (s.e.) dimer. The use of 2-(hydroxymethyl)pyridine (hmpH) afforded a ferromagnetic $Mn^{III}_3Mn^{II}_2$ cluster (Fig. 1D) in which the present motif is also found, with hmp occupying the equivalent positions of coordinated water molecule and benzoate anion in **1**.[4j] These closely related structures all show the versatility of TBC[4] towards cluster formation with ancillary ligands, and demonstrate the retention of common coordination motifs for individual ligand types.

Analysis of the extended structure of **1** reveals that molecules assemble in a head-to-head bilayer that is akin to the packing found in TBC[4] solvates (Fig. 3A and B).[4b,8] Each appended benzoate moiety interdigitates between the cavities of TBC[4] moieties of s.e. molecules of **1** within each layer, thus forming alternating up–down chain type assemblies along the *c* axis (Fig. 3B). Closer inspection reveals that individual layers are bridged by halogen⋯halogen interactions between s.e. molecules of **1**, with two crystallographically unique Cl⋯Cl distances of 3.278(6) and 4.224(7) Å (Fig. 3C); these s.e. molecules are related by a twofold axis such that x, y, z becomes $1 - x, y, 1/2 - z$. The halogen bonding is type I and a survey of the literature shows that these distances are similar to those previously reported for aryl chlorides.[9] The individual layers in **1** are well separated and accordingly display a closest interlayer Mn⋯Mn contact of 14.636 Å. Within the layers adjacent clusters are less well isolated and display closest Mn⋯Mn contacts of 7.669 Å.

Dc magnetic susceptibility studies on powdered microcrystalline samples of **1** were performed in the 275–5 K temperature range in an applied field of 0.1 T, and are plotted as

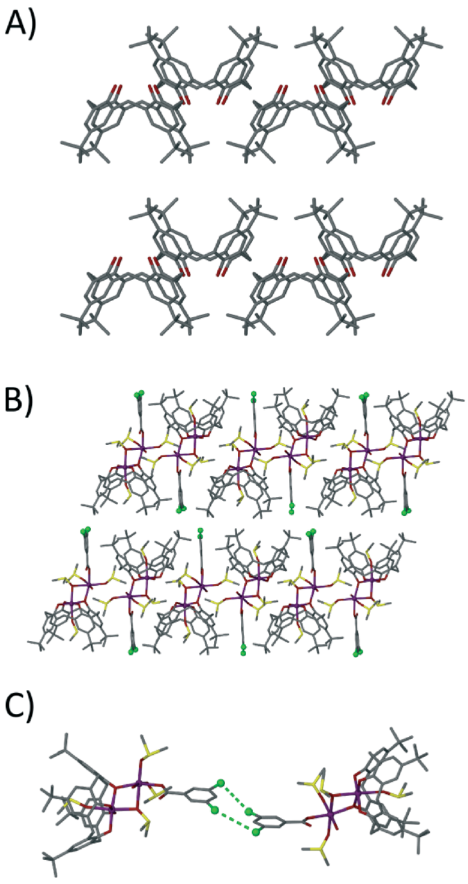

Fig. 3 A) Common anti-parallel bi-layer arrangement found for TBC[4] in the solid state.[4b,8] B) Extended structure in **1** showing modulated anti-parallel bilayer packing and intercalation of appended dcb. C) Type I halogen interactions[9] between symmetry equivalents of **1** across the bi-layer arrangement.

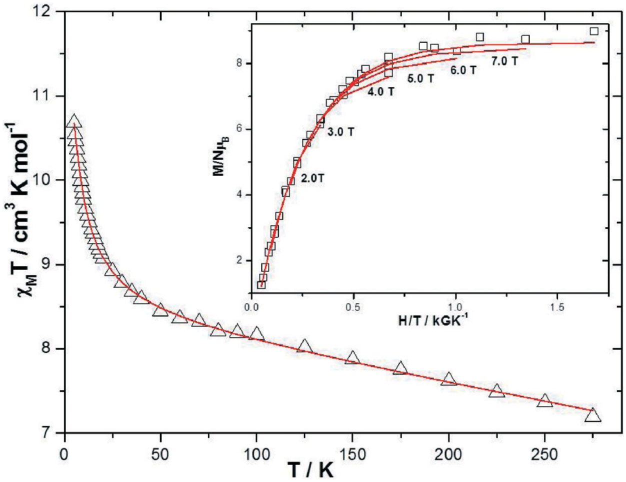

Fig. 4 Plot of $\chi_M T$ *vs.* T for complex **1** in an applied field of 0.1 T. Inset: magnetisation *versus* field in the 2–7 K and 2–7 T temperature and field ranges. The solid red lines are a fit of the experimental data to spin-Hamiltonian (1). See text for details.

the $\chi_M T$ product *versus* T in Fig. 4. The room temperature value of 7.195 cm^3 K mol^{-1} is close to the expected 7.375 cm^3 K mol^{-1} for non-interacting Mn^{III} and Mn^{II} ions with g = 2.00. As the temperature is decreased the $\chi_M T$ product increases, reaching a maximum value of ~10.7 cm^3 K mol^{-1} at 5 K. This behaviour is suggestive of weak ferromagnetic exchange between the metal ions. For the interpretation of the magnetic properties of **1** we employed the following spin-Hamiltonian:

$$\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2 + \mu_B Bg\sum_{1,2}\hat{S}_i + D\sum_{1,2}\hat{S}_{i,z}^2 - S(S+1)/3 \qquad (1)$$

where J is the isotropic exchange interaction parameter, $\hat{S}$ is a spin-operator, i runs from 1 to 2, μ_B is the Bohr magneton, B is the applied magnetic field, g = 2 is the g-factor of the Mn ions, D is the uniaxial anisotropy parameter of Mn^{III} and S = 2 and S = 5/2 are the electronic spins of Mn^{III} and Mn^{II}, respectively. The $\chi_M T$ product and the magnetisation *versus* field data at temperatures between 2 and 7 K in magnetic fields ranging from 2 to 7 T (inset of Fig. 4), were simultaneously fitted to spin-Hamiltonian (1) by use of a simplex algorithm,[10] affording the best-fit parameters J = +0.38 cm^{-1} and $D_{Mn(III)}$ = −3.34 cm^{-1}. These values are entirely consistent with other Mn–TBC[4] cages.[4b,c,e] Alternating current magnetic susceptibility measurements were performed on a polycrystalline sample of **1** in the 1.8–10 K range in zero applied dc field and a 3.5 G ac field oscillating in the 50–1000 Hz frequency range (Fig. S1†). **1** does display frequency-dependent out-of-phase (χ_M'') signals suggestive of SMM behaviour but no peaks are observed down to 2 K, precluding a more detailed analysis.

Conclusions

We have synthesised and characterised a [Mn^{III}Mn^{II}] cluster that results from addition of sodium 3,5-dichlorobenzoate to the reaction used to form C[4]-supported [Mn$^{III}_2$Mn$^{II}_2$] SMMs. The appended benzoate has disrupted formation of the SMM motif and the resulting cluster can be regarded as a half of this common structural type. The new [Mn^{III}Mn^{II}] cluster reported here, despite having an unusual shape, packs so as to mimic the solid state behaviour of both TBC[4] and the [Mn$^{III}_2$Mn$^{II}_2$] SMMs, with assembly occurring through halogen bonding interactions which bridge bi-layers. The magnetic behaviour of the dimer is also analogous to the parent butterfly structures, the exchange between the Mn^{III} and Mn^{II} ions being weakly ferromagnetic. This study has used ancillary ligands containing one carboxylate on the aromatic ring with a view to establishing structure/cluster altering viability of this ligand type. We will now focus on using polytopic benzoates in order to form a new family of molecules with tailored geometries and magnetic properties. Given the importance of halogen bonding in driving assembly[11] we will also investigate the structurally directing role of halogens placed at the C[4] upper-rim; this will be undertaken with a view to controlling the arrangement of [Mn$^{III}_2$Mn$^{II}_2$] SMMs in the solid state relative to TBC[4]-supported analogues. The results of these new avenues of investigation will be reported in due course.

Acknowledgements

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Notes and references

‡ TBC[4] was synthesised according to literature procedure,[2a] while 3,5-dichlorobenzoic acid was purchased from Sigma-Aldrich. Synthesis of 1: $MnCl_2 \cdot 4H_2O$ (0.15 g, 0.75 mmol), TBC[4] (0.1 g, 0.15 mmol), Nadcb (0.213 g, 1.0 mmol) and NEt_3 (0.1 g, 1.0 mmol) were dissolved in a mixture of DMSO (10 ml) and EtOH (10 ml). After 2 hours of stirring the solution was filtered an allowed to stand; crystals grew upon evaporation of the mother liquor over several days (23 mg, 12%). Elemental analysis (%) calculated for **1**, $C_{60}H_{84.6}Cl_2O_{12.3}S_{3.3}Mn_2$: C, 55.89%; H, 6.61%. Found: C, 55.97%; H, 6.52%. General crystallographic details: data were collected on a Bruker X8 Apex II CCD Diffractometer operating at 100(2) K with Mo-Kα radiation (λ = 0.71073 Å). Crystal data (CCDC 995697): $C_{60}H_{84.60}Cl_2O_{12.30}S_{3.30}Mn_2$, M = 1289.25, black block, 0.20 × 0.15 × 0.15 mm^3, monoclinic, space group $C2/c$, a = 38.315(3), b = 12.5251(10), c = 29.193(2) Å, β = 109.401(2)°, V = 13214.2(18) $Å^3$, Z = 8, $2\theta_{max}$ = 41.74°, 22 773 reflections collected, 6899 unique (R_{int} = 0.0679). Final GooF = 1.575, R_1 = 0.0930, wR_2 = 0.2546, R indices based on 4417 reflections with $I > 2\text{sigma}(I)$ (refinement on F^2). Unit cells of several single crystals and further analysis by powder X-ray diffraction (Fig. S2†) confirmed the bulk composition to be **1**.

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