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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

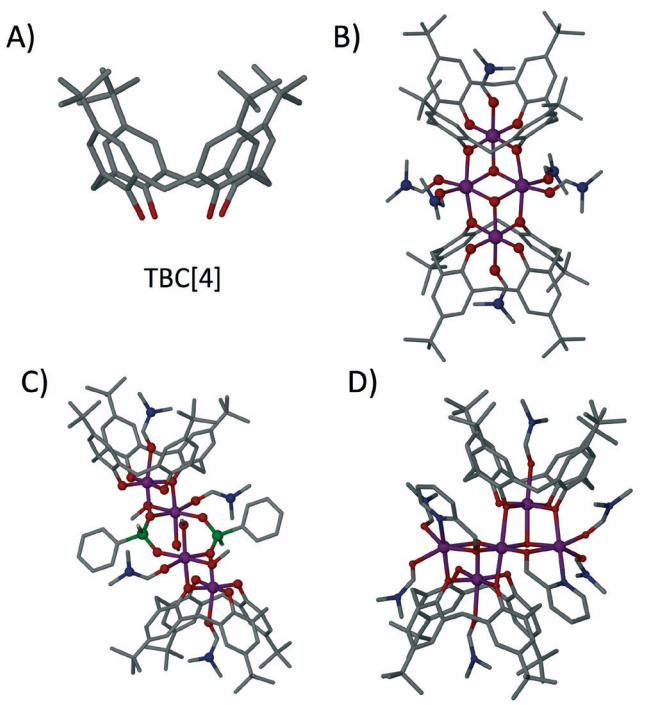

Fig. 1 A) *p*-^{t}Bu-calix[4]arene, TBC[4]. B) TBC[4]-supported $[Mn^{III}_2Mn^{II}_2]$ SMM motif.[4b,c] C) Phenylphosphinate-bridged dimer of TBC[4]-supported $[Mn^{III}Mn^{II}]$ dimers.[4e] D) TBC[4]-supported $Mn^{III}_3Mn^{II}_2$ cluster formed with hmp as an ancillary ligand.[4j] Colour code: C – 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 $C2/c$. 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.

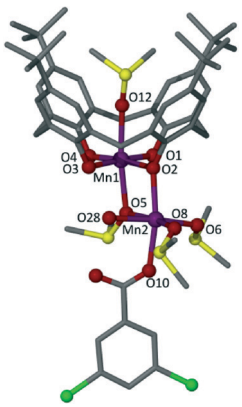

Fig. 2 Partially labelled structure of **1** showing the 3,5-dichlorobenzoate appended to the $Mn^{III}Mn^{II}$ cluster core, ligation of DMSO in the TBC[4] cavity and both bridging and terminal ligated solvent. Colour code: C – grey, O – red, S – yellow, Mn – purple, Cl – green. H atoms omitted for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

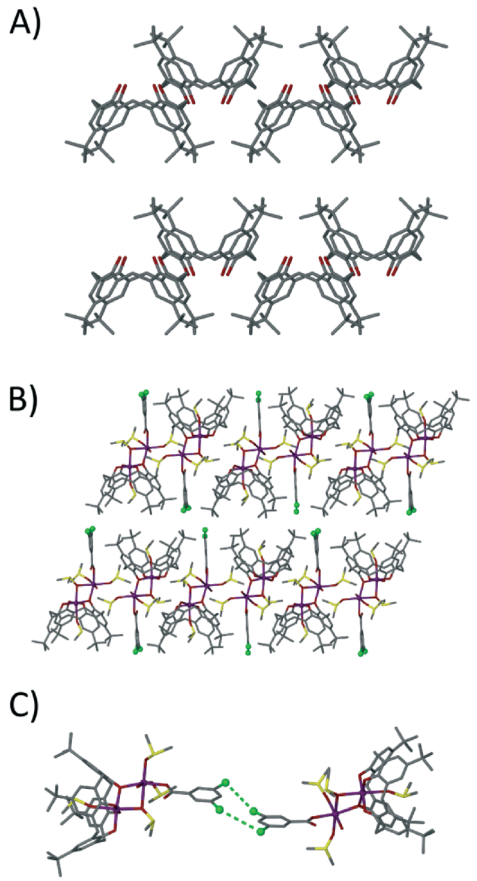

Fig. 3 A) Common anti-parallel bi-layer arrangement found for TBC [4] in the solid state.[4b,8] B) Extended structure in **1** showing modulated anti-parallel bilayer packing and intercalation of appended dcb. C) Type I halogen interactions[9] between symmetry equivalents of **1** across the bi-layer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

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:

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

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.

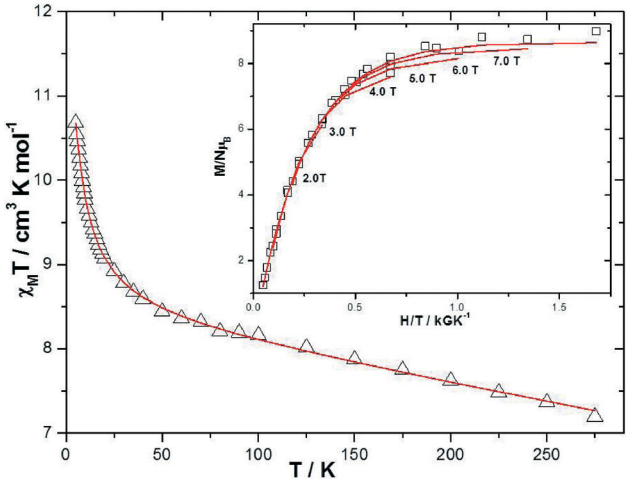

Fig. 4 Plot of $\chi_M T$ *vs.* T for complex **1** in an applied field of 0.1 T. Inset: magnetisation *versus* field in the 2–7 K and 2–7 T temperature and field ranges. The solid red lines are a fit of the experimental data to spin-Hamiltonian (1). See text for details.

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 $[Mn^{III}{}_2Mn^{II}{}_2]$ 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 $[Mn^{III}{}_2Mn^{II}{}_2]$ 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 $[Mn^{III}{}_2Mn^{II}{}_2]$ 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 $I > 2$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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