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## Dalton Transactions

# The remarkable influence of $N, O$-ligands in the assembly of a bis-calix[4]arene-supported [ $\mathrm{Mn}^{\mathrm{IV}}{ }_{2} \mathrm{Mn}^{\mathrm{III}}{ }_{10} \mathrm{Mn}^{\mathrm{II}}{ }_{8}$ ] cluster 

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The latter represents a topology often encountered in our research in which we have used methylene-bridged calix[4]arenes as ligands / cluster supports. These molecules (e.g. $\quad$-t$^{\text {t Bu-calix[4]arene }}$ and $p$ - H -calix[4]arene, hereafter collectively termed $\left.\mathrm{H}_{4} \mathrm{C}[4] \mathrm{s}\right)$ have emerged as versatile platforms for the synthesis of polymetallic clusters, capable of affording a wide variety of different structural topologies depending on the nature of the metal ions present; markedly different structures result from the incorporation of $3 d, 34,,^{4}$ or $3 d$ and $4 f$ metal ions. ${ }^{5}$ From our work we have established a vast library of C[4]-supported metal clusters in which a recurring structural theme is that [C[4]TM $\left.{ }^{\text {III }}\right]^{-}$, [C[4]TM" $]^{2-}$ or [C[4]Ln"II] moieties act as bridges to metal ions within the cluster through their phenolate groups, but also as polyhedral capping fragments. ${ }^{6}$ With respect to the present contribution, particularly noteworthy systems resulting from these studies include a family of $\left[\mathrm{Mn}^{\prime \prime{ }_{2}} \mathrm{Mn}^{2}{ }_{2}(\mathrm{C}[4])_{2}\right]$ single molecule magnets ${ }^{3 b, c}$ (SMMs, 2, Fig. 1B) that feature the aforementioned butterfly-like cluster; in this case the oxidation state distribution is the reverse of those reported in the literature for other ligand types. ${ }^{7}$ A family of $\left[\mathrm{Mn}^{\mathrm{II}}{ }_{4} \mathrm{Ln}{ }^{\mathrm{II}}{ }_{4}(\mathrm{C}[4])_{4}\right]$ clusters was obtained in the presence of both TM and $\operatorname{Ln}$ ions, and these can be best described as four [ $\mathrm{Mn}^{\text {III }}(\mathrm{C}[4])$ )- moieties capping the edges of a Ln"II square ( $\mathrm{Ln}=$ $\mathrm{Gd}, \mathrm{Tb}$ Dy). ${ }^{5 a}$ Finally, $\left[\mathrm{Ln}{ }^{n \prime \prime}{ }_{6}(\mathrm{C}[4])_{2}\right]$ octahedra were isolated when the latter reaction was carried out in the absence of TM ions. ${ }^{4}$

It should be noted that the vast majority of the examples of $\mathrm{C}[4]$-supported clusters outlined above were obtained under mild conditions, ${ }^{\mathrm{bb}-\mathrm{d}, 4,5}$ but similar species can also be obtained using microwave ${ }^{3 e, f}$ or solvothermal ${ }^{3 a, 8}$ synthesis. Markedly different structural topologies can be obtained when using Schlenk-line conditions, as this generally involves the use of bases that promote the incorporation of additional metal ions (e.g. alkali metals), dramatically affecting the resulting cluster topology. ${ }^{9}$ Thia-, sulfinyl-, and sulfonylcalix[4]arenes have also been used widely in cluster synthesis, and again, the prevailing coordination chemistry is drastically different to that found when using $\mathrm{C}[4] \mathrm{s}$ as cluster supports; this is due to the
incorporation of additional donor atoms in the ligand framework, the result of which is formation of common structural fragments comprising the relevant calixarene and four $3 d, 4 f$ or $3 d-4 f$ metal ions. A detailed discussion of this vast coordination chemistry is far beyond the scope of this introduction, and for the sake of brevity the reader is directed to recent reviews on the topic, ${ }^{10}$ as well as examples of sulfonyl-C[4]-supported manganese clusters. ${ }^{11}$


Fig. 1 Single crystal X-ray structures of 1 (A), ${ }^{2 a} \mathbf{2}$ (B), $,^{3 b} \mathrm{H}_{8} \mathrm{~L} 1(C),,^{14} \mathbf{3}$ (D),,$^{14} \mathbf{4}$ (E), ${ }^{15}$ and 5 (F). ${ }^{16}$ Colour code C - grey, O - red, N - royal blue, $\mathrm{Mn} n^{\text {II }}$ - pale blue, $\mathrm{Mn}^{\text {III }}$ purple, $\mathrm{Cu}^{\text {II }}$ - light blue, Ln"II - green. Hydrogen atoms (except those involved in
 in C), ligated solvent molecules in D, E and F, and co-crystallised solvent/anions omitted for clarity. Figures not to scale.

With the aforementioned coordination chemistry of $\mathrm{C}[4]$ in mind, we recently turned our attention to bis-p-t ${ }^{\text {t }}$ Bucalix[4]arene (BisTBC[4], $\mathrm{H}_{8}$ L1, Fig. 1C), a relatively new ligand in which two $\mathrm{H}_{4} \mathrm{C}[4]$ s are directly linked via a methylene bridge position. ${ }^{12}$ Being conformationally mobile, we envisaged that it would act in a similar manner to $\mathrm{H}_{4} \mathrm{C}[4]$, but that it would exhibit double structure capping behaviour and thus considerably enhance the nuclearity of any resulting polymetallic cluster. ${ }^{13}$ We recently reported the formation of a $\left[\mathrm{Mn}^{\mathrm{II}}{ }_{4} \mathrm{Mn}^{\mathrm{I}}{ }_{4}(\mathrm{~L} 1)_{2}\right]$ cluster (3, Fig. 1D) in which the polymetallic core can be thought as two fused and highly distorted $\left[\mathrm{Mn}^{\mathrm{II} 2} \mathrm{Mn}^{\mathrm{I}}{ }_{2}\right]$ butterflies. ${ }^{14}$ Perhaps the most important feature of this structure is the positions occupied by $\mathrm{Mn}^{\prime \prime}$ ions, located in binding pockets between the constituent C[4] lower-rims that are generated by ligand inversion. A remarkably similar topology is encountered in a related $\left[\mathrm{Mn}^{\prime \prime \prime}{ }_{4} \mathrm{Mn}^{\prime \prime} \mathrm{Ln}^{\prime \prime \prime}{ }_{2}(\mathrm{~L} 1)_{2}\right]$ cluster, obtained via interchange of two $\mathrm{Mn}^{\text {"I }}$ with Ln"II ions. ${ }^{14}$ Control over reactant stoichiometry afforded new clusters of formula $\left[\mathrm{Mn}^{\mathrm{II}}{ }_{6} \mathrm{Mn}^{\mathrm{IN}}{ }_{4}(\mathrm{L1})_{2}\right]$ and $\left[\mathrm{Mn}^{\mathrm{II}}{ }_{6} \mathrm{Mn}^{\mathrm{II}} \mathrm{Ln}^{\mathrm{IH}}{ }_{2}(\mathrm{L1})_{2}\right]$ (4, Fig. 1E), and these were obtained via 'insertion' of two additional methoxy-bridged $\mathrm{Mn}{ }^{\prime \prime \prime}$ ions to the $\left[\mathrm{Mn}^{\prime \prime \prime}{ }_{4} \mathrm{Mn}^{\prime \prime}{ }_{4}(\mathrm{LL})_{2}\right]$ or
$\left[\mathrm{Mn}^{\mathrm{II}}{ }_{4} \mathrm{Mn}^{\mathrm{II}} \mathrm{Ln}^{\mathrm{III}}{ }_{2}(\mathrm{LL})_{2}\right]$ cores. ${ }^{15}$ Our exploratory chemistry with $\mathrm{H}_{8} \mathrm{~L} 1$ also recently afforded a new family of clusters of general formula [TM ${ }^{I I / / I I} \mathrm{In}^{\prime \prime \prime}{ }_{y}(\mathrm{~L})_{2}$ ] where the TM was Cu , Fe or Mn , the Ln was Gd, Tb or Dy, and the $x: y$ ratio was 4:0, 5:4, $4: 5$ or 0:4 (e.g. 5, Fig. 1F). ${ }^{16}$ Although these new clusters have rather different topologies, they all share common features that follow established binding rules and structural capping behaviours. In this contribution we report our initial findings from multi-component cluster-forming reactions incorporating an $\mathrm{N}, \mathrm{O}$-co-ligand as well as $\mathrm{H}_{8} \mathrm{L1}$ in a one-pot synthesis. The remarkable $\mathrm{Mn}_{20}$ cluster formed displays coordination modes that are typical of both ligand types, but also features new structural behaviour for L1 which we attribute to the competitive metal ion binding nature of the co-ligand employed.

Reaction of 1:10:4 equivalents of $\mathrm{H}_{8} \mathrm{L1}$ with manganese(II) chloride tetrahydrate and diethanolamine ( $\mathrm{H}_{2} \mathrm{DEA}$ ) in a $\mathrm{DMF} / \mathrm{MeOH}$ mixture (to aid solubility) and in the presence of $\mathrm{Et}_{3} \mathrm{~N}$ (XS) as a base, ${ }^{17}$ afforded dark purple single crystals of $\left[\mathrm{Mn}^{\prime \mathrm{V}} \mathrm{V}_{2} \mathrm{Mn}^{\prime \prime{ }^{10}}{ }_{10} \mathrm{Mn}^{\mathrm{I}}{ }_{8}(\mathrm{~L} 1)_{2}(\mathrm{DEA})_{6}\left(\mu_{4}-\mathrm{O}\right)_{4}\left(\mu_{3^{-}}\right.\right.$
$\left.\mathrm{O}_{6}(\mathrm{dmf})_{10}(\mathrm{Cl})_{6}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right](\mathrm{dmf})_{2}(\mathrm{MeOH})\left(\mathrm{H}_{2} \mathrm{O}\right)_{3} \quad$ (6, Fig. 2) upon vapour diffusion of $\mathrm{Et}_{2} \mathrm{O}$ into the mother liquor. + The crystals were found to be in a monoclinic cell and structure solution was carried out in the space group C2/c. The asymmetric unit (ASU) comprises half of the reported formula, with ten Mn cations, two of which reside in the tetra-phenolato cavities in perfect accordance with the established binding rules for both $\mathrm{C}[4]$ and L1. The remaining eight cations propagate horizontally from L1, forming a polymetallic core supported by DEA molecules and bridging hydroxides / chlorides (Fig. 3A).


Fig. 2 Asymmetric unit in the single crystal X-ray structure of 6 with selected atoms labelled according to discussion. Colour code $\mathrm{C}-$ grey, O - red, N - royal blue, $\mathrm{Mn}^{\text {II }}$ - pale blue, $\mathrm{Mn}{ }^{\text {III }}$ - purple, $\mathrm{Mn}^{\text {IV }}$ - orange, Cl - dark green. H atoms, ${ }^{\text {t }} \mathrm{Bu}$ groups of L1, ligated solvent and co-crystallised solvent/anions are omitted.

Analysis of the structure shows a variety of coordination modes and oxidation states of the metal centres, the latter being confirmed by BVS calculations (Supporting Information).

Given the complexity of the structure it is necessary to include a detailed description of the coordination environment of the constituent metal ions. As expected, Mn 1 is in the $3+$ oxidation state and is bound in a C[4] lower-rim pocket described by O1O4 (Mn-O distances in the range $1.892(4)-1.967(3) \AA$ ). The coordination sphere of Mn1 is completed by a ligated dmf molecule residing in the C[4] cavity (Mn1-O10, 2.240(4) Å) and a $\mu_{4}$-oxide (Mn1-O8, 2.141(3) $\AA$ ) which bridges to $\mathrm{Mn} 3, \mathrm{Mn} 4$ and Mn6 (Mn3-O8, 2.417(4) Å; Mn4-O8, 1.896(3) Å; Mn6-O8, $1.858(4) \AA$ ). The Jahn-Teller axis deviates from linearity and is defined by the $\mathrm{O} 8-\mathrm{Mn} 1-\mathrm{O} 10$ vector $\left(170.79(15)^{\circ}\right) . \mathrm{Mn} 2$, also in the $3+$ oxidation state, has an analogous coordination environment, being bound to the lower-rim phenolic oxygens of one of the C[4] constituents of the L1 octa-anion (Mn2-O range 1.893(4) - 1.974(4) Å), a ligated dmf molecule (Mn2O11, 2.250(3) Å) and a $\mu_{4}$-oxide (Mn2-O9, 2.117(3) Å), the latter of which bridges to Mn3, Mn4 and Mn5 (Mn3-O9, 2.504(4) Å; Mn4-O9, 1.888(3) Å; Mn5-O9, 1.848(4) Å). The Jahn-Teller axis shows similar deviation from linearity and is defined by the O11-Mn2-O9 vector (173.88(15) ${ }^{\circ}$. Mn 3 is in the $2+$ oxidation state, is hepta-coordinate, has distorted facecapped octahedral geometry and, in addition to the aforementioned $\mu_{4}$-oxide ligands, is also bound to two phenolic oxygens belonging to the C[4] moieties of L1 (Mn3O1, 2.209(3) $\AA$ and $\mathrm{Mn} 3-07,2.209(3) \AA$ ), a ligated dmf molecule ( $\mathrm{Mn} 3-014,2.200(3) \AA$ ) and two oxygens from different DEA ligands (Mn3-O15, 2.180(3) Å and Mn3-O17, $2.168(3) \AA$ ). Mn4 is in the $3+$ oxidation state, is pentacoordinate and has a distorted square pyramidal geometry. The base of the pyramid is defined by the 08 and $09 \mu_{4}$-oxides, as well as two $\mu_{3}$-oxides (Mn4-O12, 1.866(3) $\AA$ and Mn4-O13, 1.866(3) $\AA$ ), whilst an oxo bridge is located at the apex ( $\mathrm{Mn} 4-$ O16, $2.284(3) \AA$ ). Mn5 is in the $3+$ oxidation state, has distorted octahedral geometry and is bound to a $\mu$-phenolate moiety ( $\mathrm{Mn} 5-06,2.232(3) \AA$ ) , the $\mathrm{O} 9 \mu_{4}$-oxide, a chloride anion ( $\mathrm{Mn} 5-\mathrm{Cl} 1,2.781(15) \AA$ ) that bridges to Mn 6 ( $\mathrm{Mn} 6-\mathrm{Cl} 1$, 2.827(15) Å) and a tridentate DEA ligand (Mn5-O17, 1.864(3) Å; Mn5-N4, 2.019(4) Å; Mn5-O18, 1.891(4) Å). The Jahn-Teller axis is located along the $\mathrm{O} 6-\mathrm{Mn5}-\mathrm{Cl} 1$ vector and shows significant deviation from linearity (165.27(10) ${ }^{\circ}$. The coordination spheres of Mn2 (3+) and Mn6 (3+) are near identical to those of Mn1 (3+) and Mn5 (3+) respectively, with only negligible differences observed (Table S1); the Jahn-Teller axis for Mn 6 is defined by the $\mathrm{O} 2-\mathrm{Mn} 6-\mathrm{Cl} 1$ vector (164.79(11) ${ }^{\circ}$ ), again showing deviation from linearity. Mn7 is in the $2+$ oxidation state, is penta-coordinate and has distorted square pyramidal geometry. It is bound to a phenolic oxygen atom (Mn7-O5, 2.136(4) Å), a $\mu_{3}$-oxide (Mn7-O13, 2.028(3) Å), an oxygen of a ligated DEA (Mn7-O18, 2.135(4) Å), a ligated dmf molecule (Mn7-O19, 2.136(4) Å) and a $\mu-\mathrm{Cl}$ ( $\mathrm{Mn} 7-\mathrm{Cl} 2$, $2.521(14) \AA$ ) that bridges to Mn9. Mn8, Mn9 and their symmetry equivalent (s.e.) ions form a DEA-supported butterfly located at the centre of the large cluster, acting as a link between the two $\mathrm{Mn}_{8}$ moieties (Fig. 3A). Mn8 is hexacoordinate, is in a distorted octahedral geometry, and is in the 4+ oxidation state. Although not directly interacting with any calixarene moiety, this represents the first example in which a
$\mathrm{Mn}^{\text {IV }}$ is incorporated in an L1-supported cluster, along with frequently observed $M n^{111 / I I}$ ions. Mn8 is bound to three $\mu_{3^{-}}$ oxides (Mn8-O12, 1.820(3) Å; Mn8-O13, 1.828(3) Å; Mn8O20, 1.917(3) Å) and a ligated DEA molecule (Mn8-O21, 1.925(4) Å; Mn8-N7, 2.041(4) Å; Mn8-O22, 1.923(3) Å). Mn9 is in the $2+$ oxidation state, has distorted octahedral geometry, and is bound to two $\mu_{3}$-oxides ( $\mathrm{Mn} 9-\mathrm{O} 20,2.239(3) \AA$ and Mn9-O20', 2.254(3) Å), two oxygens from DEA ligands (Mn9O21', 2.110(4) $\AA$ and Mn9-O22, 2.109(4) $\AA$ ) and two $\mu$ chlorides (Mn9-Cl2, 2.497(14) $\AA$ and $\mathrm{Mn} 9-\mathrm{Cl} 3,2.492(14) ~ \AA ̊)$ that bridge to Mn 7 and Mn 10 ( $\mathrm{Mn} 7-\mathrm{Cl} 2$ distance given above, $\mathrm{Mn} 10-\mathrm{Cl} 3,2.531(15) \mathrm{A})$. Finally, Mn 10 is in the $2+$ oxidation state, has distorted trigonal bipyramidal geometry, and is bound to the $\mu$-chloride, a $\mu_{3}$-oxide ( $\mathrm{Mn} 10-\mathrm{O} 12^{\prime}, 2.029$ (3) Å), an oxygen atom of a DEA ligand (Mn10-O25, 2.152(4) Å), a phenolic oxygen (Mn10-O23, 2.122(4) Å) and a ligated dmf molecule (Mn10-O24, 2.126(4) Å).


Fig. 3 A) Symmetry-expanded single crystal X-ray structure of 6. B) top-down view of the cluster core in 6 showing the presence of a central $\mathrm{Mn}^{\mathrm{IV}} \mathrm{V}_{2} \mathrm{Mn}_{2}$ butterfly. Selected atoms are labelled according to discussion. Colour code C grey, O - red, N - royal blue, $\mathrm{Mn}^{\prime \prime}$ - pale blue, $\mathrm{Mn}^{\text {III }}$ - purple, $\mathrm{Mn}^{\text {'V }}$ - orange, Cl dark green. H atoms, ${ }^{\text {t }} \mathrm{Bu}$ groups of L 1 , ligated solvent and co-crystallised solvent/anions are omitted.

Symmetry expansion of the ASU affords the entire cluster as shown in Figure 3A, which can be visualised as two $\mathrm{Mn}^{11 I_{5}} \mathrm{Mn}^{\prime \prime}{ }_{3}$ moieties linked via the central DEA-supported $\mathrm{Mn}^{\mid V_{2}} \mathrm{Mn}^{1{ }^{\prime \prime}}$ fragment. This fragment displays coordination modes that are typical for DEA and compound 6 can be considered an excellent example in which the nuclearity of clusters supported by one ligand type can be augmented (or greatly enhanced) via the incorporation of complementary and / or competing co-ligands; the complex topology of 6 (Fig. 3B) displays several recurring coordination modes typical for both L1- ${ }^{10}$ and DEA-supported clusters (Fig. S1). ${ }^{2 b}$ Capping behaviour is observed with four $\left[\mathrm{Mn}^{\text {III }}(\mathrm{C}[4])\right]^{-}$moieties (Mn1,

Mn2 and s.e.) 'encapsulating' one Mn" cation (Mn3) located in one of the binding pockets generated upon inversion of L1, whereas the other binding site remains unoccupied. This is unprecedented, and we propose that the strongly competing nature of DEA gives rise to this new structural feature; the presence of two additional DEA-supported $\mathrm{Mn}^{\text {III }}$ cations (Mn5 and Mn 6 ) appears to create steric hindrance in that region of the cluster, preventing it from being occupied by a metal ion. This also reflects on the tetrahedral geometry of Mn4, which is unusual and unprecedented in L1-supported cluster chemistry thus far. A CSD search for $\mathrm{Mn}_{20}$ clusters returned 18 hits with disparate topologies, the metallic cores of which are supported by a variety of ligands including phosphonate, ${ }^{18}$ triethanolamine, ${ }^{19}$ pivalate ${ }^{20}$ and other $N$-containing polydentates. ${ }^{21}$ These clusters possess Mn ions in oxidation states between 1+ and $3+$ in either mixed or non-mixed valence arrangements, but none were found to contain $\mathrm{Mn}^{\mathrm{IV}}$ ions. The topology of 6 is thus found to be unique, as is the oxidation state distribution and mixed-valence arrangement. Inspection of the expanded structure of 6 shows that neighbouring clusters are well-isolated, with no significant intermolecular interactions being observed between symmetry equivalents; the shortest metal-metal inter-cluster distance is found between Mn1 and Mn7 ~12.1 A along the crystallographic $b$ axis (Fig. S2).

The dc (direct current) molar magnetic susceptibility, $\chi_{\mathrm{M}}$, of a freshly filtered polycrystalline sample (Euan???) of 6 was measured in an applied magnetic field, $B$, of 0.1 T , over the $T=5-300 \mathrm{~K}$ temperature range. The experimental results are shown in Figure $S 3$ in the form of the $\chi_{M} T$ product versus $T$, where $\chi_{M}=M / B$, and $M$ is the magnetisation of the sample. At room temperature, the $\chi_{\mathrm{M}} T$ product is approximately 68 $\mathrm{cm}^{3} \mathrm{~K} \mathrm{~mol}^{-1}$, in good agreement with the sum of Curie constants for a $\left[\mathrm{Mn}^{1 \mathrm{~V}}{ }_{2} \mathrm{Mn}^{\prime I I}{ }_{10} \mathrm{Mn}^{\prime \prime}{ }_{8}\right.$ ] unit ( $68.75 \mathrm{~cm}^{3} \mathrm{~K} \mathrm{~mol}^{-1}, g=$ 2.0). Upon cooling, the $\chi_{M} T$ product decreases to a minimum value of $53.4 \mathrm{~cm}^{3} \mathrm{~K} \mathrm{~mol}^{-1}$ at $T=34 \mathrm{~K}$, then rises to a value of $58.3 \mathrm{~cm}^{3} \mathrm{~K} \mathrm{~mol}^{-1}$ at $T=8 \mathrm{~K}$, before decreasing again to a value of $57.5 \mathrm{~cm}^{3} \mathrm{~K} \mathrm{~mol}^{-1}$ at $T=5 \mathrm{~K}$. This behaviour is consistent with competing (weak) ferro- and antiferromagnetic exchange interactions between the Mn centres. The decrease in $\chi_{\mathrm{M}} T$ below 8 K can be attributed to zero-field splitting effects and / or the presence of antiferromagnetic inter-molecular interactions. The large nuclearity and complex topology of the [ $\mathrm{Mn}_{20}$ ] core prevents any quantitative analysis of the exchange constants, but the overall behaviour is entirely consistent with that observed for other $\mathrm{C}[n]$-constructed, O -atom bridged, heterovalent Mn cages, where typical coupling constants are of the order $|J| \leq 10 \mathrm{~cm}^{-1} .{ }^{22,23}$ Note also that $|J|$ is likely of the same order of magnitude as $\left|D_{\mathrm{Mn}(\mathrm{III})}\right|$. The low temperature variable-temperature-and-variable-field (VTVB) magnetisation data collected in fields of up to $B=7 \mathrm{~T}$ (Fig. S3, inset) are also consistent with this picture, showing $M$ increasing in a near linear fashion with $B$, without saturating ( $M=44.7 \mu_{\mathrm{B}}$ at $T=2 \mathrm{~K}$ and $B=7 \mathrm{~T}$ ). Complex 6 does not display any frequencydependent signals in out-of-phase ( $\chi_{M}{ }^{\prime \prime}$ ) ac susceptibility measurements, and is thus not an SMM.

In conclusion, we have shown that the use of BisTBC[4] with DEA as a co-ligand leads to the formation of a very high nuclearity mixed-valence Mn cluster that displays typical coordination modes relative to each ligand type. The competitive metal ion binding of DEA appears to influence that of BisTBC[4], and this delicate balance in ligand composition may be a route towards unearthing a large library of such cluster species in $\mathrm{C}[n]$ chemistry, whilst simultaneously increasing / enhancing metal ion composition. This strategy may also allow one to control the incorporation of metal ions with coordination numbers and oxidation states that are otherwise unobtainable using just BisTBC[4] as a ligand; this may also apply to all $\mathrm{C}[n]$ ligands. This will have concomitant effects on the magnetic properties for these multi-component systems, the results of which will be reported in due course.

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## Notes and references

$\mathrm{H}_{8} \mathrm{~L} 1$ was synthesised according to literature procedure. ${ }^{12}$ +Synthesis of $\left[\mathrm{Mn}^{1 V_{2}} \mathrm{Mn}^{111}{ }_{10} \mathrm{Mn}^{\prime \prime}{ }_{8}(\mathrm{L1})_{2}(\mathrm{DEA})_{6}\left(\mu_{4}-\mathrm{O}\right)_{4}\left(\mu_{3}-\right.\right.$ O) $\left.\mathbf{6}_{6}(\mathrm{dmf})_{10}(\mathrm{Cl})_{6}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right](\mathrm{dmf})_{2}(\mathrm{MeOH})\left(\mathrm{H}_{2} \mathrm{O}\right)_{3}, 6: \mathrm{H} 8 \mathrm{~L} 1(500 \mathrm{mg}, 0.39$ $\mathrm{mmol}), \mathrm{MnCl}_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O}(610 \mathrm{mg}, 3.08 \mathrm{mmol})$ and diethanolamine ( $0.148 \mathrm{~mL}, 1.54 \mathrm{mmol}$ ) were suspended in a $1: 1 \mathrm{dmf} / \mathrm{MeOH}$ mixture ( 20 mL ) and stirred for 10 minutes. $\mathrm{Et}_{3} \mathrm{~N}(0.6 \mathrm{~mL}, \mathrm{XS})$ was added and the resulting purple solution was stirred for additional 2 hours and then filtered. The mother liquor was slowly allowed to diffuse with diethyl ether, affording dark purple crystals suitable for $X$-ray studies. Elemental Analysis (\%) calculated for 6, $\mathrm{C}_{237} \mathrm{H}_{350} \mathrm{Mn}_{20} \mathrm{~N}_{18} \mathrm{O}_{56} \mathrm{Cl}_{6}(\mathrm{M}=5659): \mathrm{C}, 50.3 \% ; \mathrm{H}, 6.23 \% ; \mathrm{N}, 4.46 \%$. Found: C, 49.97\%; H, 5.89\%; N, 4.16\%. Yield 404 mg (18.3 \%). Crystal Data for 6 (CCDC 1573336): $\mathrm{C}_{237} \mathrm{H}_{350} \mathrm{Cl}_{6} \mathrm{Mn}_{20} \mathrm{~N}_{18} \mathrm{O}_{56}$, $M=5658.83 \mathrm{~g} / \mathrm{mol}$ ), monoclinic, space group $C 2 / c$ (no. 15), $a=$ 18.3953(7) $\AA, b=\quad 45.6912(18) \AA, c=\quad 40.7908(16) \AA, b=$ 99.212(2) ${ }^{\circ}, V=33843(2) \AA^{3}, Z=4, T=100(2) \mathrm{K}, 163555$ reflections measured $\left(4.198^{\circ} \leq 2 \Theta \leq 58.238^{\circ}\right), 34860$ unique ( $R_{\text {int }}=0.0610$, $\mathrm{R}_{\text {sigma }}=0.0498$ ) which were used in all calculations. The final $R_{1}$ was $0.0828(I>2 \sigma(I))$ and $w R_{2}$ was 0.2223 (all data).

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