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Syntheses and magnetic properties of hexanuclear $[Cp_2Mn_3(L_1)_4]_2$ and octanuclear $[Mn_8(L_2)_{12}(\mu_4\text{-}O)_2]$ (L_1 = 2-HNC_5H_5N, L_2 = 2-NH-3-Br-5-MeC_5H_3N, Cp = C_5H_5)†

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The reactions of manganocene, Cp_2Mn, with 2-aminopyridine (L_1H) or 2-amino-3-bromo-5-methylpyridine (L_2H) give the novel hexanuclear and octanuclear Mn(II) amido cage compounds $[Cp_2Mn_3(L_1)_4]_2$ (1) and $[Mn_8(L_2)_{12}(\mu_4\text{-}O)_2]$ (2); magnetic measurements on which provide a rare insight into the magnetic properties of amido-bridged metal clusters.

The potential applications of manganese carboxylate cluster compounds as precursors to molecule-based magnetic materials or as molecular magnets in their own right, has attracted considerable interest in the past two decades.[1] Despite this, the chemistry and magnetic properties of related nitrogen-based manganese cluster compounds have been less explored, and so far only a handful of imido manganese compounds (containing RN^{2-} ligands) have been structurally characterised. The majority of these species contain Mn in the V to VII oxidation states,[2] the cationic species $[Mn_6(\mu_3\text{-}NPh)_4(THF)_4]^{4+}$ being the only structurally characterised Mn^{II} imido complex.[3d] Moreover, even for the more widely studied amido Mn complexes (containing R_2N^- ligands) only comparatively few solid-state structures of mono- and dinuclear Mn(II) complexes have been reported.[3] In a recent communication we showed for the first time that Cp_2Mn is capable of doubly-deprotonating the NH_2 groups of moderately acidic primary amines, providing a new route to high-nuclearity Mn(II) imido cage compounds.[4] We report here the syntheses and structures of the polynuclear amido cages $[Cp_2Mn_3(L_1)_4]_2$ (**1**) (L_1H = 2-aminopyridine) and $[Mn_8(L_2)_{12}(\mu_4\text{-}O)_2]$ (**2**) (L_2H = 2-amino-3-bromo-5-methylpyridine). This study illustrates the general applications of transition metal metallocenes in the synthesis of high-nuclearity transition metal amido cages.

The 1 : 1 stoichiometric reactions of Cp_2Mn with L_1H or L_2H in THF (under argon) give the new Mn(II) amido complexes $[Cp_2Mn_3(L_1)_4]_2$ (**1**) (93% yield) and $[Mn_8(L_2)_{12}(\mu_4\text{-}O)_2]$ (**2**) (32% yield), respectively, as the only crystalline products (see ESI†). Although the elaborate natures of these species (and, indeed, the exact composition in the case of **2**) were only apparent once their solid-state structures had been determined, the presence of N–H stretching bands in their IR spectra suggested that only partial deprotonation of the NH_2 groups of both amines had occurred during their reactions with Cp_2Mn. The presence of oxo-ligands in the structure of **2** is apparently due to water of crystallisation present in the amine. We have found that **2** is obtained reproducibly using commercially supplied samples of L_2H, without further purification or drying.

Molecules of **1** (Fig. 1) (see ESI†) are composed of two $[Cp_2Mn_3(L_1)_4]$ units which dimerise *via* pyridyl-N–Mn bonding into a hexanuclear arrangement (possessing exact C_2 symmetry). In addition, one toluene molecule is also present in the lattice for each cage molecule of **1**. The three, chemically distinct Mn(II) centres within the $[Cp_2Mn_3(L_1)_4]$ constituents form a metal triangle in which two of the Mn···Mn distances [Mn(1)···Mn(3) 3.2021(9) and Mn(2)···Mn(3) 3.2757(8)Å] are considerably shorter than the remaining Mn···Mn separation [Mn(1)···Mn(2) 3.490(1) Å]. These Mn···Mn distances can be compared to a range of 3.1594(8)–3.724(1) Å found in the structures of [{CpMn(NHpm)}{MnNpm}]$_4$ (pm = a substituted or unsubstituted pyrimidinyl ligand).[4–6] Two coordination modes are adopted by the L_1 ligands in **1**, either a bridging bidentate N,N′-coordination mode bridging [Mn(2)/Mn(3a) and Mn(1)/Mn(3)] or a bridging tridentate μ_2-N,N′-mode [*i.e.*, for the L_1 ligands bridging Mn(3), Mn(1) and Mn(2) and Mn(3), Mn(2) and Mn(3a)]. The Mn(1) and Mn(2) centres have similar, pseudo-tetrahedral (piano-stool) coordination geometries within their η^5-$CpMnN_3$ units. However, whereas Mn(1) is coordinated by the anionic NH centres of *three* L_1 groups [N(1) 2.215(4), N(3) 2.077(5), N(5) 2.240(4) Å], Mn(2) is bonded to *two* anionic NH centres [N(5) 2.166(5), N(7) 2.149(3) Å] and to a neutral pyridyl-ring N centre [N(2) 2.207(4) Å]. Both of these Mn atoms are η^5-bonded to Cp ligands, the range of C–Mn bond lengths [Mn(1)–C 2.475(5)–2.566(5), Mn(2)–C 2.384(8)–2.627(9) Å] being similar to those found in [{CpMn(NHpm)}{MnNpm}]$_4$. These bond lengths are consistent with high-spin (17e) electronic arrangements for these metal centres.[7] A distorted trigonal bipyramidal coordination geometry is found for Mn(3), in which two pyridyl-N centres [N(6) 2.188(4) and N(8A) 2.200(4) Å] and an anionic pyNH [N(1) 2.160(4) Å] coordinate Mn(3) at equatorial positions, with an anionic pyNH [N(4) 2.230(4) Å] and a neutral pyridyl-N centre [N(7) 2.293(3) Å] coordinating at axial positions.

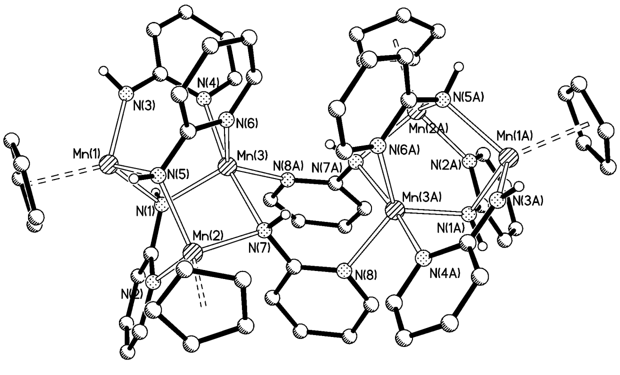

Fig. 1 Structure of the hexanuclear cage $[Cp_2Mn_3(L_1)_4]_2$ (**1**). H-atoms, except those attached to N, and the lattice-bound toluene solvent has been omitted for clarity.

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† Electronic supplementary information (ESI) available: synthesis and crystal data of **1** and **2**·2THF, key bond lengths and angles for **1** and **2**, models employed for **1** and **2**, and χT *vs.* T plots for **1** and **2**. See http://www.rsc.org/suppdata/cc/b2/b209496g/

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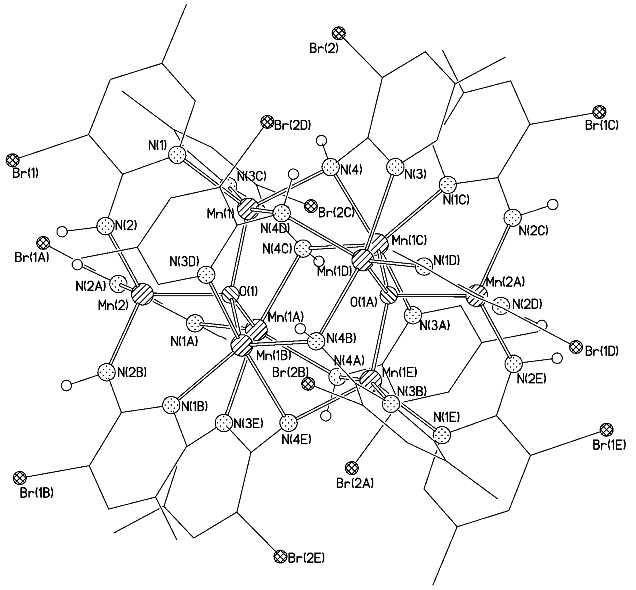

Fig. 2 (a) Structure of the octanuclear cage $[Mn_8(L_2)_{10}(\mu_4\text{-}O)_2]$ (**2**). H-atoms, except those attached to N, have been omitted for clarity.

Molecules of the octanuclear complex **2** (Fig. 2) exhibit S_6 symmetry [about the axis of the Mn(2)–O(1) bond vector].† In addition, there are two uncoordinated molecules of THF for each molecule of **2** within the crystal lattice. The core structure of the complex is composed of two tetrahedral $Mn_4(\mu_4\text{-}O)$ units which are linked together by bridging L_2 ligands. The μ_4-bonded O centres within these units are bound equally (within the crystallographic errors) to all four of the Mn atoms [Mn(1)–O(1) 2.027(2), Mn(2)–O(1) 2.029(7) Å].[8] The Mn$\cdots$Mn contacts within the core [range 3.154(2)–3.433(2) Å] are similar to those found in **1** and in the structures of $[\{CpMn(NHpm)\}\{MnNpm\}]_4$,[4,5] with the Mn(1)$\cdots$Mn(2) contact being the shortest. The L_2 ligands adopt the same two bidentate and tridentate bonding modes as found in the structure of **1**, with three L_2 ligands N,N′-bridging between Mn(1) and Mn(2) within the two $Mn_4(\mu_4\text{-}O)$ units and with six μ_2-N,N′-bonded ligands being responsible for the association of the $Mn_4(\mu_4\text{-}O)$ units. The terminal Mn(2) centres of the core are bonded to the anionic NH centres of three symmetry-related 2-NH-3-Br-5-Me-py ligands [Mn(2)-N(2) 2.088(6) Å], giving these centres distorted tetrahedral geometries. The remaining six symmetry-related Mn centres [Mn(1)] have distorted trigonal bipyramidal coordination geometries; being coordinated by the μ_4-O ligand, an anionic NH centre [N(4) 2.171(5) Å] and by a neutral pyN centre [N(1) 2.176(6) Å] at the equatorial positions, and by an anionic NH [N(4D) 2.317(6) Å] and a neutral pyN centre [N(3C) 2.334(5) Å] at the axial positions.

Complexes **1** and **2** exhibit many unusual structural features. Perhaps most importantly, the vast majority of structurally characterised polynuclear manganese complexes contain carboxylate or related oxygen-containing ligands. As a consequence of the hardness of these ligand sets and the reaction conditions employed, the vast majority of structurally characterised polynuclear manganese complexes exhibit higher (and often mixed $Mn^{II/III/IV}$) oxidation states.[8] Comparable examples of Mn^{II} cage compounds containing nitrogen-based ligands are rare and the magnetic properties of these species have been the subject of few reports.[4,9] The magnetic behaviour of **1** and **2** was studied between 2 and 300 K using a Quantum Design SQUID magnetometer. The significant positive slopes in graphs of χT *vs.* T (ESI†) indicates significant antiferromagnetic coupling as the dominant interaction. For compound **1** the most significant exchange pathway is likely to be *via* the μ_2-NH groups within the unsymmetrical Mn_3units [N(1), N(5) and N(7)]. Although the coordination spheres of the three manganese ions within the triangles are very different, the Mn–N–Mn bridge angles fall in a relatively narrow range [94.1(2) to 104.7(2)°]. We should therefore expect the coupling constants to be of similar magnitude. Modelling the data for **1** assuming the cluster consists of two non-interacting equilateral triangles yielded a fit that is reasonable at lower temperatures but deviates significantly at higher temperatures.† Introducing a second intra-triangle exchange parameter improves the fit in all regions and yields $J_1 = -3.0$ K, $J_2 = -5.4$ K.† It is assumed that superexchange *via* the inter-triangle Mn–NCN–Mn is negligible. For compound **2** the geometry of the μ-NH groups linking the $Mn_4(\mu_4\text{-}O)$ [Mn(1)–N(4)–Mn(1C) 99.6(2)°] units is similar to those in compound **1** and is likely to give an exchange coupling of the same magnitude as that observed for **1**. The substantially stronger exchange coupling evident from the slope of χT (ESI†) is therefore likely to result from the μ_4-O bridge. The behaviour was modelled based on (a) two non-interacting symmetrical tetrahedra and (b) two coupled tetrahedra in which the inter-tetrahedral interaction is modelled using a simple Mean Field term.† The simpler model gives $J = -40.0(3)$ K and fits the data well at intermediate temperatures but deviates very markedly below 50 and above 250 K. Introduction of the inter-tetrahedron term produces a good fit across the whole temperature range giving $J = -21.7(7)$ and $J' = -9.3(5)$ K. Hence the inter-tetrahedron coupling is of a similar size to that *via* NH bridges in **1**.

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