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Synthesis and Structure of the Octanuclear Manganese(II) Cage $[(\eta\text{-Cp})\text{Mn}\{2\text{-NH}(4,6\text{-Me}_2\text{pm})\}\cdot\text{Mn}\{2\text{-N}(4,6\text{-Me}_2\text{Pm})\}]_4$ (Cp = C_5H_5, pm = Pyrimidine)

Carmen Soria Aluarez, Andrew D. Bond, Eilis A. Harron, Richard A. Layfield,
Judith A. McAllister, Christopher M. Pask, Jeremy M. Rawson, and
Dominic S. Wright*

Chemistry Department, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, U.K.

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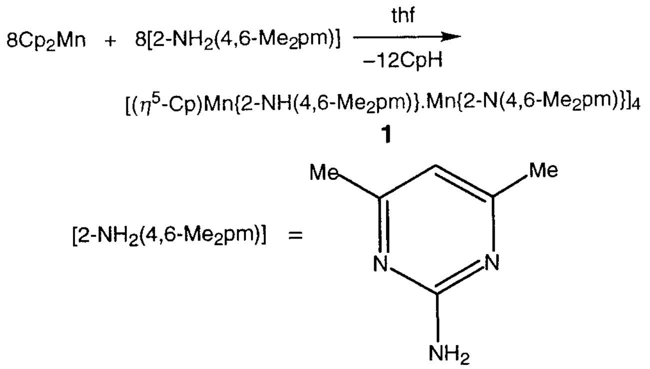
*Summary: The 1:1 reaction of $2\text{-NH}_2(4,6\text{-Me}_2\text{pm})$ with Cp_2Mn in thf gives the novel heteroleptic imido/amido Mn(II) cage $[(\eta\text{-Cp})\text{Mn}\{2\text{-NH}(4,6\text{-Me}_2\text{pm})\}\cdot\text{Mn}\{2\text{-N}(4,6\text{-Me}_2\text{pm})\}]_4$ (**1**), composed of a central Mn(II) imido $[\text{Mn}_4\{2\text{-N}(4,6\text{-Me}_2\text{pm})\}_4]$ core coordinated at the periphery by four $[(\eta\text{-Cp})\text{Mn}\{2\text{-NH}(4,6\text{-Me}_2\text{pm})\}]$ monomer units.*

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 properties of related nitrogen-based manganese cluster compounds have been less explored, and so far very few imido manganese cluster compounds have been structurally characterized.[2] Our interest in this area has arisen from a general interest in the applications of main-group and transition-metal metallocenes as precursors in the synthesis of amido and imido compounds.[3] Although the lability and basicity of the C−metal bonds in stannocene (Cp_2Sn) and related p-block metallocenes have long been appreciated,[4] the use of transition-metal metallocenes as soluble sources of low-oxidation-state metals has been investigated far less extensively. There is, however, ample evidence for the emergence of polarity of the C−metal bonds in these species (particularly at the right-hand side of the transition-metal series),[5] as is illustrated by the deprotonation of weaker organic monoacids using Cp_2Mn.[6] The latter route provides a more convenient method of preparing metallo-organic derivatives than the use of highly air-sensitive $[\text{Mn}\{\text{N}(\text{SiMe}_3)\}_2]$ as the base.[7] We report here that Cp_2Mn is also capable of *double* deprotonation of primary amines, giving easy access to little-studied Mn(II) imido compounds, as exemplified by the synthesis of the novel Mn_8 cage $[(\eta\text{-Cp})\text{Mn}\{2\text{-NH}(4,6\text{-Me}_2\text{pm})\}\cdot\text{Mn}\{2\text{-N}(4,6\text{-Me}_2\text{pm})\}]_4$ (**1**) (pm = pyrimidinyl).

Scheme 1



The reaction of $2\text{-NH}_2(4,6\text{-Me}_2\text{pm})$ with Cp_2Mn[8] (1:1 molar equiv) at −78 °C in thf, followed by storage at room temperature, gives the crystalline title compound **1** in 27% yield (Scheme 1).[9] Little information concerning the structure of the complex could be gained from NMR spectroscopy, owing to the paramagnetic nature of the complex and its low solubility even in polar organic solvents such as DMSO (as well as to the likely deaggregation of the complex in such a strong donor

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* To whom correspondence should be addressed. Fax: 01223 336362. E-mail: dsw1000@cus.cam.ac.uk.

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[9] Synthesis of **1**: a solution of 4,6-dimethyl-2-pyrimidine (0.186 g, 1.5 mmol) in thf (20 mL) was added dropwise to a solution of Cp_2Mn (0.28 g, 1.5 mmol) in thf (10 mL) at −78 °C (under argon, prescrubbed with activated molecular sieves and Cu columns). The faint yellow mixture was warmed to 5 °C and stored at room temperature for 12 h. This gave a golden yellow solution and a crop of finely faceted amber crystals of **1**. Yield: 0.102 g, 27%. Dec pt: >200 °C to black solid. IR (Nujol, NaCl; $\nu_{\text{max}}/\text{cm}^{-1}$): 3340 (w, N−H str), 3068 (w, C−H str, Cp). ^{1}H NMR (400.16 MHz, 25 °C, d_6-DMSO; δ/ppm): 6.24 (s br, C−H aryl), 3.51 (s br, Cp H), 1.67 (s br, Me) (no accurate integrals could be obtained, owing to the poor quality of the spectrum and the paramagnetic nature of the complex). Anal. Found: C, 51.9; H, 6.0; N, 16.4. Calcd for $\mathbf{1}\cdot 5\text{thf}$: C, 52.0; H, 5.9; N, 16.5.

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solvent). However, the IR spectrum reveals the presence of both N−H and Cp functionalities and therefore indicates that the deprotonation of the NH_2 group of 2-NH_2(4,6-Me_2pm) is incomplete.

The low-temperature X-ray structure of **1**[10] shows that it consists of discrete molecules of formula [(η-Cp)-Mn{2-NH(4,6-Me_2pm)}·Mn{2-N(4,6-Me_2pm)}]$_4$, possessing exact $\bar{4}$ symmetry (Figure 1). In addition, there are five molecules of thf in the lattice for each molecule of **1**. The structure of **1** is best regarded as a co-complex of four Mn(II) imido (Mn{2-N(4,6-Me_2pm)}) and four organo/amido ((η-Cp)Mn{2-NH(4,6-Me_2pm)}) monomer units. The central core of the molecule is formed from the association of the [Mn{2-N(4,6-Me_2pm)}] units, giving a distorted-tetrahedral arrangement of the Mn centers (Mn(1)···Mn(1A) = 3.1594(8), Mn(1)···Mn(1C) = 3.543(1) Å). This fragment can be visualized as a highly distorted Mn_4N_4 cubane unit, in which four opposite edges (defined by Mn(1)···N(1C), Mn(1A)···N(1B), Mn(1B)···N(1A), and Mn(1C)···N(1)) have been broken. The anionic imido-N centers of the 2-N(4,6-Me_2pm) ligands in this unit bridge the symmetry-related Mn atoms of the core (Mn(1)−N(1) = 2.085(3), Mn(1A)−N(1) = 2.110(3) Å), with one of the neutral N centers of each pm ring spanning the four broken edges of the Mn_4N_4 core via longer donor interactions (Mn(1)−N(6C) = 2.160(3) Å). As a result, the Mn centers of the core attain a highly distorted tetrahedral geometry. The [(η-Cp)-Mn{2-NH(4,6-Me_2pm)}] units are located at the periphery of the cage (Mn(1)···Mn(2) = 3.2335(7) Å). The MnCp fragments of these are chelated by the imido N center (Mn(2)−N(1) = 2.208(3) Å) and the second N center (Mn(2)−N(5) = 2.262(3) Å) of each of the 2-N(4,6-Me_2-pm) ligands of the central Mn_4N_4 core. The {2-NH(4,6-Me_2pm)} groups of the [(η-Cp)Mn{2-NH(4,6-Me_2pm)}] units adopt a chelating bonding mode similar to that found for the 2-N(4,6-Me_2pm) groups within the Mn_4N_4 core, with the anionic N(H) centers and one of the pm ring N centers being involved in bridging the core Mn and Mn(Cp) atoms (Mn(1)−N(2) = 2.117(3), Mn(2)−N(3) = 2.200(3) Å). The Mn atom within each [(η-Cp)Mn{2-NH(4,6-Me_2pm)}] monomer therefore achieves a “piano-stool” coordination geometry similar to that found in metal carbonyls such as [CpMn(CO)$_3$].[11] However, these Mn centers are clearly high spin (formally 17e) in **1** at 180 K. This conclusion is supported by the long C−Mn distances involved (range 2.408(5)−2.616(5) Å), which are significantly greater than the values expected for low-spin Mn(II) (ca. 2.11−2.14 Å).[12,13]

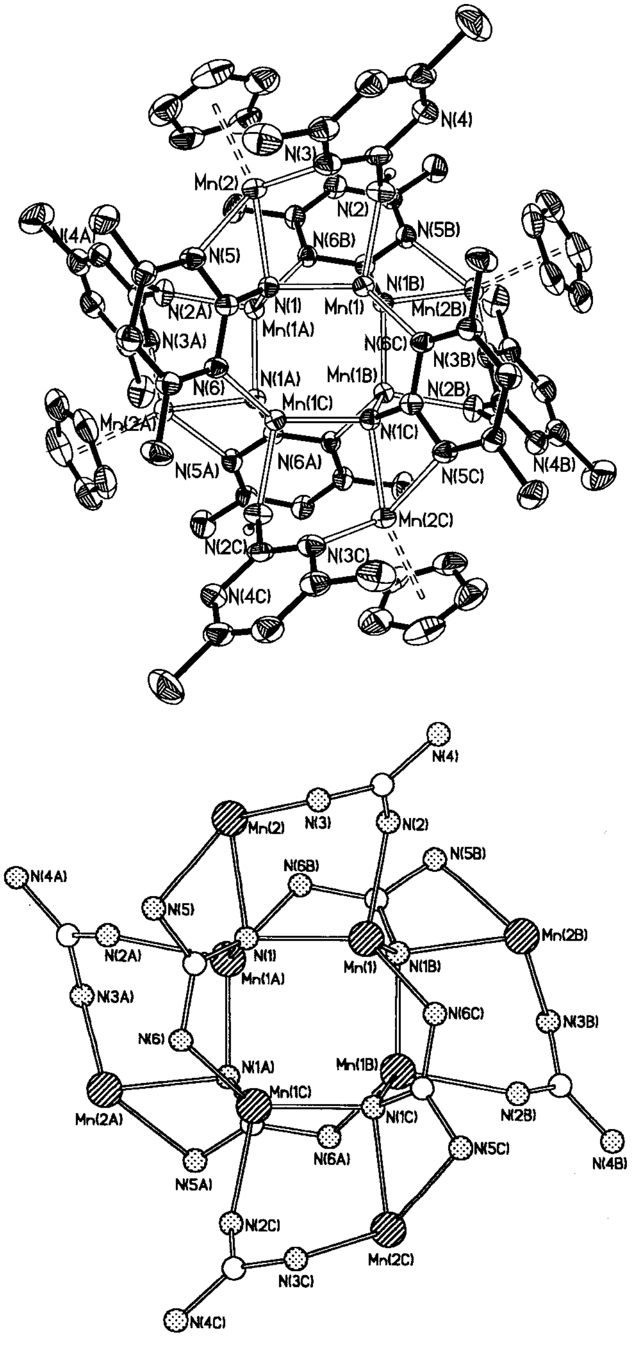

Figure 1. (a, top) Structure of the cage molecules of **1**. Thermal ellipsoids are drawn at the 40% probability level. H atoms (except those attached to N) and lattice-bound thf atoms have been omitted for clarity. Key bond lengths (Å) and angles (deg): Mn(1)−N(1) = 2.085(3), Mn(1)−N(1B) = 2.110(3), Mn(1)−N(2) = 2.117(3), Mn(1)−N(6C) = 2.160(3), Mn(2)−N(1) = 2.208(3), Mn(2)−N(3) = 2.200(3), Mn(2)−N(5) = 2.262(3), Mn(1)···$Cp_{centroid}$ = 2.23 (C−Mn range 2.408(5)−2.616(5)), Mn(1)···Mn(1A) = 3.1594(8), Mn(1)···Mn(2) = 3.2335(7), Mn(1)···Mn(1C) = 3.543(1); N(1)−Mn(1)−N(1B) = 106.1(1), N(1)−Mn(1)−N(2) = 100.3(1), N(1A)−Mn(1)−N(2) = 102.3(1), N(1)−Mn(1)−N(6C) = 122.7(1), N(1)−Mn(1)−N(6C) = 109.8(1), N(2)−Mn(1)−N(6C) = 113.4(1), Mn(1A)−N(1)−Mn(1B) = 97.7(1), N(1)−Mn(2)−N(3) = 104.7(1), N(1)−Mn(2)−N(5) = 61.9(1), N(3)−Mn(2)−N(5) = 102.6(1). (b, bottom) Core structure of **1**. Only the guanidide fragments of the 4,6-Me_2pm ligands are shown for the symmetry-related monomer units, and the Cp ligands attached to the symmetry-related atoms of Mn(2) have been omitted for clarity.

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[10] Crystal data for **1**: $C_{88}H_{120}Mn_8N_{24}O_5$, M_r = 2033.60, tetragonal, space group $I\bar{4}$, Z = 2, a = b = 19.4971(6) Å, c = 12.3496(3) Å, V = 4694.5(2) Å^3, μ(Mo Kα) = 1.103 mm^{-1}, T = 180(2) K. Data were collected on a Nonius KappaCCD diffractometer. A total of 15 251 reflections were collected, 5099 of which were independent (R_{int} = 0.038). The structure was solved by direct methods and refined by full-matrix least squares on F^2. Final R1 = 0.043 ($I > 2\sigma(I)$) and wR2 = 0.122 (all data).[17] The absolute structure parameter was0.00(2). The H atoms attached to the [2-NH(4,6-Me_2pm)] groups were located in the difference map but were fixed geometrically in the final refinement. One of the thf molecules in the lattice of **1** is disordered about a 4-fold axis. X-ray data for **1** have been submitted to the Cambridge Crystallographic Database (CCDC No. 159430).

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Although amido Mn(II) compounds (containing R_2N^- anions) are now fairly common,[6a,14] very few Mn imido compounds such as **1** have been structurally characterized.[2] Of these the majority are Mn(V−VII) complexes such as the nitrido anion $[Mn^{VII}(N)(N^tBu)_3]^-$ and the dimers $[Mn^V(R)(N^tBu)(\mu\text{-}N^tBu)]_2$ (R = CH_2CMe_3, CH_2Ph), prepared by transmetalation reactions of $[Mn(N^tBu)_3Cl]$.[2a] The only structurally authenticated example of a Mn(II) imido compound is the hexanuclear adamantane-like cation $[Mn_6(\mu_3\text{-}NPh)_4(thf)_4]^{4+}$, obtained by the transmetalation reaction of $[Mg(NPh)(thf)_6]$ with $MnBr_2$ in thf (the Mn−N bond lengths (2.035(9)−2.080(9) Å) being similar to those found in the Mn_4N_4 core of **1**).[2b] The structure of **1** contains many novel features, not least of which is the fact that the complex is the highest nuclearity imido or amido Mn cage to be structurally characterized. The incorporation of four CpMn units within this cage arrangement is also unprecedented. The most closely related situation is found in $[(CpMn)_3(\mu_2\text{-}NO)_3(\mu_3\text{-}NO)_3]$, containing three CpMn fragments.[15]

An X-band powder EPR spectrum of solid **1** exhibited a broad singlet at room temperature ($g = 2.004$ G, $\Delta H_{pp} = 218$ G), together with a shoulder at lower field ($g = 2.367$ G). At 77 K the lower-field resonance becomes more pronounced. The effective magnetic moment of **1** exhibits an unusual evolution with temperature (Figure 2).[16] The room-temperature moment of 12.0 μ_B is somewhat less than that expected for eight high-spin ($S = {}^5/_2$) Mn(II) ions (16.7 μ_B). The magnetic moment decreases steadily to a minimum of 8.7 μ_B at 33 K before rising to a smaller maximum of 9.6 μ_B at 9 K. Below this temperature the moment decreases again down to 5 K. While it is tempting to interpret the magnetic behavior in terms of exchange interactions between imido- and amido-bridged Mn(II) ions, the temperature-dependent behavior of the complex could be explained, in part, by single-ion effects: e.g., a change in spin state of the CpMn units caused by the strong-field Cp ligand,[12] or zero-field splitting (which is known to be significant for manganocenes[12a]). An isothermal magnetization study of **1** at 5 K up to 7 T showed no evidence for saturation. Further detailed studies are planned to analyze this behavior.

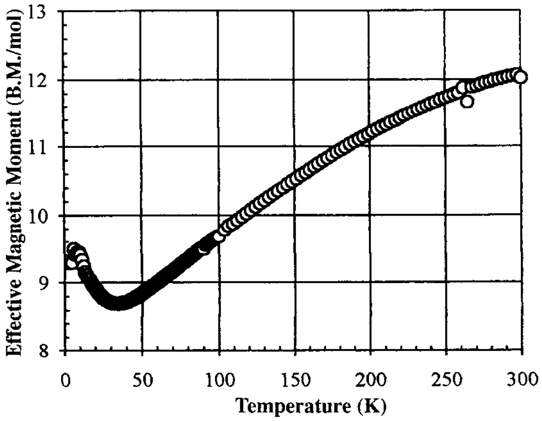

Figure 2. Variable-temperature magnetic data for **1** (data points are shown as open circles).

Ongoing studies are aimed at extending the use of Cp_2Mn and other polar metallocenes of transition metals as sources of low-oxidation-state metals in the synthesis of imido and phosphinidine cages. These investigations have the potential to provide simple access to a range of previously rarely studied complexes of these types as well as new magnetic materials. The structural type identified in **1** may well be a general one where the 2-pyrimidine functionality is present, as is indicated by the formation of an isostructural complex in the reaction of 4,6-dimethoxy-2-pyrimidine with Cp_2Mn.

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[13] The C−Mn interactions in **1** are similar to those observed in paramagnetic $[\{E_2(NCy)_4\}(MnCp)_2]$ (E = As, Sb): Bashall, A.; Beswick, M. A.; Ehlenberg, H.; Kidd, S. J.; McPartlin, M.; Palmer, J. S.; Raithby, P. R.; Rawson, J. M.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **2000**, 749 (C−Mn range 2.389(10)−2.615(8) Å).

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[16] The magnetic behavior of the complex was studied between 5 and 300 K on a Quantum Design MPMS-XL SQUID magnetometer in an applied field of 500 G. A correction for diamagnetism was made using Pascal's constant ($\chi_d = -1.181 \times 10^{-3}$). The variable-field experiment was carried out at 5 K using field strengths between 0 and 700 G (the upper limit of the magnetometer).

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