The paramagnetic, heterometallic manganese cubanes $[\{E_2(NCy)_4\}(MnCp)_2]$ (Cy = C_6H_{11}, Cp = C_5H_5, E = As, Sb)†

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The heterometallic cubanes $[\{E_2(NCy)_4\}(MnCp)_2]$ (E = Sb 1, As 2; Cy = C_6H_{11}, Cp = C_5H_5) are the first examples of complexes in which a paramagnetic metal ion has been incorporated into a p block ligand framework.

The coordination chemistry of ligand systems based on *p* block element imido frameworks has become increasingly studied in recent years.[1,2] Species such as the homologous group 15 dianions $[E_2(NR)_4]^{2-}$ (E = P–Bi)[1,3] offer readily accessible building blocks for the assembly of cage complexes containing a broad variety of mixed p block element/main group and transition element compositions.[1a] However, so far studies of the coordination chemistry of imido p block ligands have only involved main group and transition metal ions which possess closed-shell electronic configurations (for the transition metals d^0 or d^{10} only have been reported).[1,4,5] A current interest of ours involves utilising the differing geometric and bonding demands in homologous ligands of this type to control the degree of magnetic and/or bonding interactions between the ligand-supported metal frameworks present in these species.[4c] The heterometallic complexes $[\{Sb_2(NCy)_4\}(MnCp)_2]$ **1** and $[\{As_2(NCy)_4\}(MnCp)_2]$ **2**, presented here, provide the first opportunity to investigate ligand control of magnetic properties in these systems.

$[\{Sb_2(NCy)_4\}(MnCp)_2]$ **1** and $[\{As_2(NCy)_4\}(MnCp)_2]$ **2** were prepared by the nucleophilic substitution reactions of $MnCp_2$[6] with $[\{E_2(NCy)_4\}_2M_4]$ (E = Sb, M = Na;[6] E = As, M = Li[3b]), with the elimination of CpM (Scheme 1.‡ ^1H NMR studies of both showed only broad ill defined resonances which are consistent with paramagnetic materials.

The low-temperature X-ray structures of **1** (Fig. 1) and **2** (Fig. 2)§ reveal that both complexes have similar pseudo-cubane structures in the solid state, which are composed of two (formally 17e) $CpMn^+$ fragments[7] complexed by $[Sb_2(NCy)_4]^{2-}$ and $[As_2(NCy)_4]^{2-}$ dianions. The similarity of the endo- and exo-cyclic Sb–N and As–N bonds of their $[Sb_2(NCy)_4]^{2-}$ and $[As_2(NCy)_4]^{2-}$ anions with those observed in the precursor Na complexes $[\{Sb_2(NCy)_4\}_2Na_4]$[8] and $[\{As_2(NCy)_4\}_2Na_4]$[4c] illustrates that, like these complexes, the anion units have the primary role in dictating the overall structures of **1** and **2**. The reduction in the endo-cyclic Sb–N and As–N bond lengths from **1** to **2** (of *ca.* 0.19 Å) has a major affect on the Mn_2N_2 rings in both complexes. In order to retain similar Mn–N bond lengths within these units (*ca.* 2.20 Å in both complexes[9]), this ring is far more puckered in **2** (the angle between the MnN_2 planes being 161.9° in **1** and 142.6° in **2**).

$$[\{E_2(NCy)_4\}_2M_4] + 4MnCp_2 \xrightarrow{\text{THF–toluene}} 2[\{E_2(NCy)_4\}(MnCp)_2] + 4CpM$$

M = Na, E = Sb **1**
M = Li, E = As **2**

Scheme 1

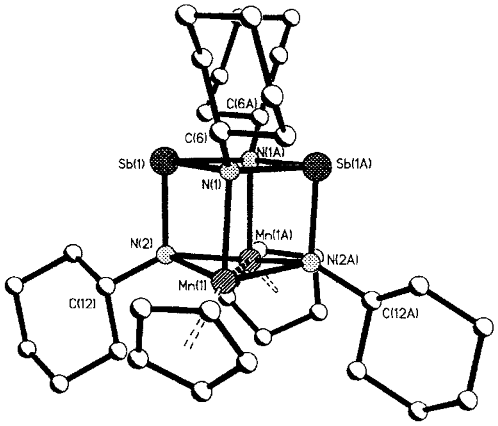

Fig. 1 Structure of the Sb_2Mn_2 cubane **1** with H-atoms omitted for clarity. Key bond lengths (Å): Sb(1)–N(1) 2.109(5), Sb(1)–N(1A) 2.128(5), Sb(1)–N(2) 2.039(5), N(1)–Mn(1) 2.269(6), N(2)–Mn(1) 2.215(5), N(2)–Mn(1A) 2.217(5), Mn(1)–Mn(1A) 3.041(2), Mn–C range 2.421(7)-2.615(8) ($Cp_{centroid}$–Mn 2.16). Bond angles (°); N(1)–Sb(1)–N(1A) 80.1(2), Sb(1)–N(1)–Sb(1A) 99.9(2), N(1,1A)–Sb(1)–N(2) mean 88.2, Sb(1)–N(2)–Mn(1,1A) mean 97.6, Sb(1,1A)–N(1)–Mn(1) mean 93.2, N(1)–Mn(1)–N(2,2A) mean 80.7, Mn(1)–N(2)–Mn(1A) 87.6(2), N(2)–Mn(1)–N(2A) 91.0(2). Dihedral angles (°) between planes; MnN_2 161.9, SbN_2 178.4.

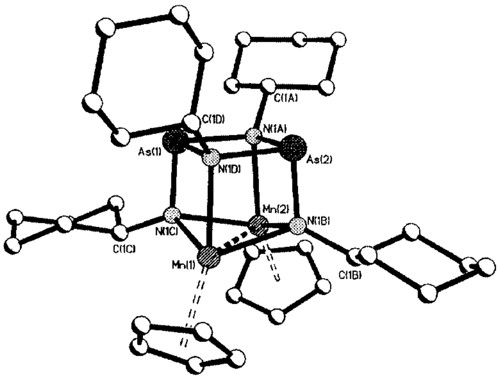

Fig. 2 Structure of the As_2Mn_2 cubane **2** with H-atoms omitted for clarity. Key bond lengths (Å): As(1)–N(1A) 1.940(8), As(1)–N(1C) 1.816(7), As(1)–N(1D) 1.912(7), As(2)–N(1A) 1.923(7), As(2)–N(1B) 1.820(7), As(2)–N(1D) 1.935(7), Mn(1)–N(1B) 2.202(7), Mn(1)–N(1C) 2.170(7), Mn(1)–N(1D) 2.264(7), Mn(2)–N(1A) 2.278(7), Mn(2)–N(1B) 2.199(7), Mn(2)–N(1C) 2.253(7), Mn(1)···Mn(2) 2.934(2), Mn–C range 2.39(1)–2.53(1) ($Cp_{centroid}$–Mn 2.16). Mean angles (°): N(1A)–As(1,2)–N(1D) 83.0, N(1C)–As(1)–N(1A,1D) 91.9, N(1B)–As(2)–N(1A,1D) 91.3, Mn(1)–N(1B,1C)–Mn(2) 83.4, N(1C)–Mn(1,2)–N(1B) 90.8. Dihedral angles (°) between planes; MnN_2 142.6, AsN_2 176.2.

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† Electronic supplementary information (ESI) available: plots of the effective magnetic moments of **1** and **2** as a function of temperature. See http://www.rsc.org/suppdata/cc/a9/a910196i/

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Although this distortion has only a small affect on the Mn–N–Mn and N–Mn–N angles within the Mn_2N_2 ring units, a consequence of the presence of the more compact $[As_2(NCy)_4]^{2-}$ ligand in **2** is a large reduction in Mn···Mn separation [from 3.041(2) Å in **1** to 2.934(2) Å in **2**]. The Mn···Mn separation in **2** is almost identical to that in $Mn_2(CO)_{10}$ (2.93 Å).[10]

Whilst Mn(II) ions are almost invariably high spin, the large ligand field associated with the π-donor Cp^- ligand makes the high- and low-spin electronic configurations energetically similar. Indeed, for manganocenes ($MnCp^R{}_2$; Cp^R = substituted Cp) examples of pure low-spin, pure high-spin and high-/low-spin equilibria have been observed (depending on the donor or acceptor character and steric demands of ring substituents).[11,12] For the half-sandwich ($MnCp^R$) derivatives, pure high-spin behaviour has been observed.[13] For **1** and **2**, the possibility of high-/low-spin equilibria is complicated by the potential for superexchange *via* the bridging imido ligands. Preliminary magnetic studies of **1** and **2** (5.5–380 K) show a marked temperature dependence of μ_{eff} (ESI†). Even at 380 K, the observed moments (6.0 and 6.6 μ_B for **1** and **2**, respectively) are significantly less than that expected for two high-spin Mn(II) ions per molecule (8.37 μ_B). The value of μ_{eff} decreases steadily on cooling, reaching 2.6 μ_B for **1** and 1.9 μ_B for **2** at 5.5 K. While the value for **1** is consistent with two non-interacting low-spin Mn(II) ions (2.5 μ_B), the significantly lower value for **2** may indicate intramolecular exchange between the Mn ions.

Attempts to model the data for **1** and **2** have so far proved inconclusive.¶ The suggestion that a high-/low-spin equilibrium may be occurring over a wide temperature range for both complexes is apparently inconsistent with the long Mn–C bond lengths in **1** and **2** [range 2.389(10)–2.615(8) Å], which are typical of high-spin manganocenes (*cf. ca.* 2.11–2.14 Å in low-spin species).[12] Although some shortening of the Mn–C bonds is anticipated for the high-/low-spin equilibrium at the temperatures at which the structures of the complexes were obtained (180 K for **1** and 223 K for **2**), a possible reason for the maintenance of long metal–ligand bonds in both complexes is the sterically congested nature of the $[E_2(NCy)_4]^{2-}$ ligand frameworks (making closer approach of the Cp ligands unfavourable[12b]). A detailed study of the magnetic behaviour (EPR and solid-state susceptibility) and variable-temperature X-ray diffraction studies of **1** and **2** will be the subject of a full paper.

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Notes and references

‡ *Syntheses*: **1**: solid $MnCp_2$ (0.273g, 1.48 mmol) and $[\{Sb_2(NCy)_4\}_2Na_4]$ (0.676 g, 0.74 mmol) were mixed together in a glove box under argon. The mixture was dissolved in toluene (20 ml) and brought to reflux, producing a fine gelatinous solid of CpNa which was separated by the addition of thf (10 ml) followed by filtration. The red filtrate was reduced to dryness under vacuum and the solid residue dissolved by the addition of hexane (10 ml) and toluene (10 ml) and gentle heating. Storage (25 °C, 12 h) gave red plates of **1**. Yield 0.520 g (81%). Decomp. *ca.* 200 °C. δ_H(+25 °C, thf-d_8, 250 MHz), 4.75 (Cp), 1.8–0.7 (Cy groups) (Found: C 46.2; H 6.0; N 5.3. Calc. for **1**: C, 46.8; H, 6.2; N, 6.4%).

2: $[\{As_2(NCy)_4\}_2Li_4]$ was prepared *in situ* by the reaction of $As(NMe_2)_3$ (5.0 ml, 2.43 mol dm^{-3} solution in toluene, 12.15 mmol) with a solution of $CyNH_2$ (1.39 ml, 12.15 mmol) in toluene (8 ml), followed by the addition of a suspension of CyNHLi (12.15 mmol) in toluene (8 ml). $MnCp_2$ (2.25 g, 12.15 mmol) in thf (10 ml) was added to this mixture and a white precipitate of CpLi was formed after bringing to reflux. Filtration gave a yellow solution which was stored (25 °C, 12 h) to give yellow plates of **2**. Yield 1.62 g (34%). Decomp. *ca.* 210 °C. δ_H(+25 °C, thf-d_8, 250 MHz), *ca.* 6.5 (Cp), 2.5–0.5 (Cy groups) (Found: C, 51.5; H, 6.6; N, 6.2. Calc. for **2**: C, 52.4; H, 6.9, N, 7.2%).

§ *Crystal data*: for **1**: $C_{34}H_{54}Mn_2N_4Sb_2$, M = 872.20, tetragonal, space group $P4_12_12$, Z = 4, a = 11.775(2), c = 26.095(5) Å, U = 3618.1(11) Å^3, D_c = 1.601 g cm^{-3}, $F(000)$ = 1752, μ(Mo–Kα) = 2.187 mm^{-1}, T = 180(2) K. Data in the θ range 1.90–25.06° were collected on a Nonius Kappa CCD diffractometer. The structure was solved by direct methods. Full-matrix least-squares refinement on F^2 with 190 parameters was based on 3156 independent data (total collected 5231, R_{int} = 0.044). Final R_1 = 0.028 [$I > 2\sigma(I)$], wR_2 = 0.126 (all data).[14] Largest peak and hole in the final difference map 0.808 and −1.750 e Å^{-3}. Absolute structure parameter −0.09(6).

For **2**: $C_{34}H_{54}As_2Mn_2N_4$, M = 778.53, monoclinic, space group $P2_1/c$, Z = 4, a = 10.336(2), b = 17.095(6), c = 20.506(5) Å, β = 103.99(2)°, U = 3516(2) Å^3, D_c = 1.471 g cm^{-3}, $F(000)$ = 1608, μ(Mo-Kα) = 2.615 mm^{-1}, T = 223(2) K. Data in the θ range 2.03–23.01° were collected on a Siemens P4 difractometer, and corrected for absorption effects using Ψ scans. The structure was solved by direct methods. Full-matrix least-squares refinement on F^2 with 379 parameters was based on 4893 independent data (total collected 6294, R_{int} = 0.0509). Final R_1 = 0.054 [$I > 2\sigma(I)$], wR_2 = 0.156 (all data).[14] Largest peak and hole in the final difference map 0.868 and −0.877 e Å^{-3}.

CCDC 182/1581. See http://www.rsc.org/suppdata/cc/a9/a910196i/ for crystallographic files in .cif format.

¶ *Magnetic behaviour* of **1** and **2**: solid samples were measured between 5.5 and 380 K using a SQUID magnetometer in fields of 100 (for **1**) and 1000 G (for **2**). They were corrected for diamagnetism using Pascals' constants. Attempts to model the magnetic behaviour as a low-spin ground state with a thermally accessible high-spin state were unsuccessful as was an attempt to fit the data to two interacting Heisenberg S = $\frac{5}{2}$ ions. For **1**, a high-spin/low-spin thermal equilibrium fits the data throughout the temperature range 5.5-380 K, and also for the range 25–380 K for **2**.

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