

Structure and magnetic properties of a high-spin $\text{Mn}_6^{\text{II}}\text{Cr}^{\text{III}}$ cluster containing cyano bridges and Mn centres capped by pentadentate ligands

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The formation of an elaborate H-bonding network between heptanuclear cations, consisting of a hexacyanochromate capped by six $[\text{Mn}(\text{dmptacn})]^{2+}$ moieties, and hexacyanochromate counterions results in the assembly of novel 1-D chains with short-range ferrimagnetic behaviour occurring between the $S = 27/2$ clusters and $S = 3/2$ ions.

A major challenge in the field of molecular magnetism is to design discrete polynuclear entities with high-spin ground states and tunable magnetic properties.^{1–3} Such materials allow the study of the transition from molecular to bulk-like magnetic behaviour exhibited by, for example, bulk ferromagnets. An important area is that of ‘single-molecule’ magnets based on high-spin clusters, e.g. $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{OH}_2)_4$, for which magnetic anisotropy and negative zero-field splitting are prerequisites.^{1,2} One approach to isolating discrete molecules with high-spin states, albeit of a symmetrical type, has focussed on the use of hexacyanometallates as building blocks in the construction of heterometallic assemblies.^{4–7} We have reported the structure of $[\text{Fe}\{\text{CN}\}\text{Cu}(\text{tpa})]_6(\text{ClO}_4)_8 \cdot 3\text{H}_2\text{O}$, [tpa = tris(2-pyridylmethyl)amine]. While this was the first heptanuclear complex of this type to be structurally characterized, new techniques, such as X-ray MCD, have since been applied to probe the magnetisation in $\text{Mn}_6^{\text{II}}\text{Cr}^{\text{III}}$ and $\text{Ni}_6^{\text{II}}\text{Cr}^{\text{III}}$ complexes, for which X-ray structures were not obtained.⁶ Two other structurally characterised cyano-bridged clusters with large high-spin ground states were reported recently.^{8,9} Based on octacyanometallates, they consist of $\text{Mn}^{\text{II}}\text{M}^{\text{V}}\text{V}_6$ fully-capped cubane structures but, surprisingly, that with $\text{M} = \text{W}^8$ has an $S = 39/2$ ground state (i.e. $S = 9S_{\text{Mn}} - 6S_{\text{W}}$) while that with $\text{M} = \text{Mo}^9$ is reported to have an $S = 51/2$ ground state (i.e. $S = 9S_{\text{Mn}} + 6S_{\text{Mo}}$). Inter-cluster coupling, via H-bonded pathways, led to long-range order being observed in the Mo case⁹ while some features of single molecule magnetism were noted in the W case.⁸ We report here the structure and magnetism of $[\{\text{Mn}(\text{dmptacn})(\text{CN})\}_6\text{Cr}][\text{Cr}(\text{CN})_6](\text{ClO}_4)_6 \cdot 6\text{H}_2\text{O}$ **1** [dmptacn = 1,4-bis(2-methylpyridyl)-1,4,7-triazacyclononane], a complex featuring intimate H-bonding between heptanuclear $[\{\text{Mn}^{\text{II}}(\text{dmptacn})(\text{CN})\}_6\text{Cr}^{\text{III}}]^{9+}$ cations and $[\text{Cr}(\text{CN})_6]^{3-}$ counter anions.

Complex **1** initially formed in an aqueous solution containing a 1:6 mixture of $[\text{Cr}(\text{CN})_6]^{3-}$ and $[\text{Mn}(\text{dmptacn})(\text{OH}_2)]^{2+}$, a reactant ratio expected to yield a heptanuclear complex. However, microanalysis and crystallography confirmed a Mn:Cr ratio of 3:1, and the IR spectrum exhibited CN stretches attributable to both bridging and terminal CN groups. Reactant ratios corresponding to the product stoichiometry afforded better yields of **1**.[†] The encapsulation of $[\text{Cr}(\text{CN})_6]^{3-}$ by six $[\text{Mn}(\text{dmptacn})]^{2+}$ moieties has generated a heptanuclear cation [Fig. 1(a)] whose 9+ charge is balanced by one $[\text{Cr}(\text{CN})_6]^{3-}$ and six perchlorates even in the presence of excess ClO_4^- . This gives rise to a novel crystallographic feature described below.[‡]

The geometry of the Cr centres in **1** is little distorted from octahedral, viz., C–Cr–C(*cis*) and C–Cr–C(*trans*) angles are

close to 90 and 180°, respectively, and the Cr–C–N angles in both the ‘capped $\text{Cr}(\text{CN})_6$ ’ core and $[\text{Cr}(\text{CN})_6]^{3-}$ anions are almost linear. These features are common to clusters incorporating $[\text{Cr}(\text{CN})_6]^{3-}$ except for $(\text{VO})_3[\text{Cr}(\text{CN})_6]_2 \cdot 10\text{H}_2\text{O}$.^{10,11} The Mn–N–C(CN) angles in **1** [158.4(5)°] deviate from linearity [Fig. 1(b)]. Such deviations have been found in extended lattices formed by cyanometallates and manganese chelates¹² but not in discrete molecules like **1**. For each Mn^{II} centre, the CN ligand is *cis* to the secondary amine of dmptacn,¹³ and the Mn^{II} cations adopt a geometry intermediate between trigonal prismatic and octahedral. A trigonal twist angle of 29.2° is calculated from the orientation of the three tacn N atoms relative to the two pyridyl and cyano N atoms. The slightly bent *trans*-C≡N–Mn–N angles [164.9(2)°] cause the three sets of *trans*-Cr–C≡N–Mn units to adopt *anti*-configurations.

Intimate H-bonding interactions exist between the terminal CN nitrogens in the $[\text{Cr}(\text{CN})_6]^{3-}$ counter ion and the hydrogen on the sec. amine of dmptacn [Fig. 1(c)]. The C≡N...H–N distance is 2.53 Å while the C≡N...N distance is 3.075(7) Å.

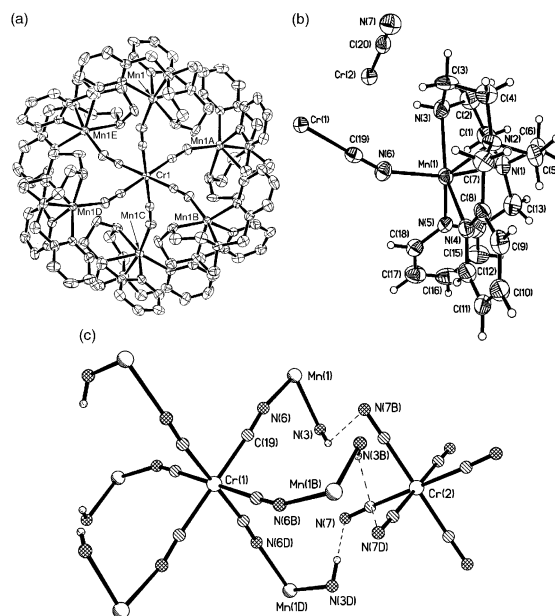


Fig. 1 (a) View of the heptanuclear cation in **1**; (b) atomic labeling scheme (50% probability ellipsoids); (c) 1-D chains formed by H-bonding between the cyano groups on the $[\text{Cr}(\text{CN})_6]^{3-}$ counter ion and the secondary amine proton on each dmptacn. Selected bond lengths (Å) and angles (°): Cr1–C19 2.074(6), Cr2–C20 2.050(6), Mn1–N1 2.316(4), Mn1–N2 2.306(4), Mn1–N3 2.236(5), Mn1–N4 2.308(4), Mn1–N5 2.197(4), Mn1–N6 2.196(5), C19–N6 1.150(6), C20–N7 1.173(7), Cr1...Mn1 5.318, Cr2...Mn1 5.849, Cr1...Cr2 6.882, N3...N7b 3.075(7); Cr1–C19–N6 175.0(5), Cr2–C20–N7 177.5(5), Mn1–N6–C19 158.4(5), N1–Mn1–N2 75.4(1), N1–Mn1–N3 76.7(2), N1–Mn1–N5 75.4(2), N1–Mn1–N6 164.9(2), N2–Mn1–N5 140.0(2), N3–Mn1–N4 146.6(2), N3–Mn1–N5 122.3(2), N3–Mn1–N6 88.7(2), N5–Mn1–N6 110.1(2).

This interaction results in a pseudo 1-D chain of alternating $[\{\text{Mn}(\text{dmptacn})(\text{CN})\}_6\text{Cr}]^{9+}$ cations and $[\text{Cr}(\text{CN})_6]^{3-}$ anions running along the c -axis. Each complex anion is sandwiched between two heptanuclear cations, forming three H-bonds to one of the two sets of three sec. amine N atoms on each cation. Of importance to the supramolecular assembly of the cations and anions into H-bonded 1-D chains is the geometric arrangement of each set of three sec. amine N atoms, and their hydrogens, at the corners of an equilateral triangle (thus, the cation has a C_{3v} axis of symmetry). The excellent match in the symmetry and size of the extended octahedral faces of $[\text{Cr}(\text{CN})_6]^{3-}$ and these triangular arrays of sec. N atoms facilitate the establishment of H-bonded contacts between the exposed N atoms on the anion and the heptanuclear cations.

Fig. 2 shows the temperature dependence of the $\chi_{\text{M}}T$, per Mn_6Cr_2 , measured in a field of 1 T. The room-temperature $\chi_{\text{M}}T$ value of $27.1 \text{ cm}^3 \text{ K mol}^{-1}$ is slightly lower than the spin-only value of 30.0 expected for an uncoupled spin system [$6(S_{\text{Mn}} = 5/2)$, $2(S_{\text{Cr}} = 3/2)$] with $g = 2.0$. As the temperature is lowered, $\chi_{\text{M}}T$ decreases slightly to a broad minimum of 26.3 at 203 K and then slowly increases to 30.1 at 100 K. As the temperature is decreased further, $\chi_{\text{M}}T$ increases rapidly to a maximum of 71.0 at 12 K. This is below the value expected for a fully antiferromagnetically coupled heptanuclear spin system plus $[\text{Cr}(\text{CN})_6]^{3-}$ [*viz.*, $99.9 \text{ cm}^3 \text{ K mol}^{-1}$ for $\{6(S_{\text{Mn}} = 5/2) - (S_{\text{Cr}} = 3/2)\} + (S_{\text{Cr}} = 3/2)$]. The drop in $\chi_{\text{M}}T$ observed below 12 K can be attributed to a competing intermolecular anti-ferromagnetic interaction and/or thermal population of low lying Zeeman levels, as noted in other clusters.¹⁴ The χ_{M} values obey the Curie–Weiss law above *ca.* 140 K with a Weiss constant $\theta = -4.2 \text{ K}$. This is consistent with intracluster antiferromagnetic coupling. A ground-state spin value of 27/2 for the cluster corresponds to the spins on the Mn^{II} atoms being antiparallel to those on the central Cr^{III} , *i.e.* $6S_{\text{Mn}} - S_{\text{Cr}}$. This was also the case for the related $\text{Mn}^{\text{II}}_6\text{Cr}^{\text{III}}$ cluster^{5,6} and the $\text{Mn}^{\text{II}}_9\text{W}^{\text{V}}_6$ cluster.⁸ Indeed, a good fit to the $\chi_{\text{M}}T$ vs. T data in a field of 1 T was obtained using the spin Hamiltonian of Sculler *et al.*,⁵ allowing for an additional $S_{\text{Cr}} = 3/2$ Curie contribution in **1**. The best-fit, shown in Fig. 2, corresponds to the parameters of $g = 1.96$ and $J_{\text{Cr-Mn}} = -5 \text{ cm}^{-1}$ ($J_{\text{Mn-Mn}} = 0$) which are similar to those for $[\text{Mn}(\text{L})(\text{NC})_6\text{Cr}]^{9+}$ [$g = 1.97$; $J_{\text{Cr-Mn}} = -8.0 \text{ cm}^{-1}$, $\text{L} = N,N,N'$ -[tris(2-pyridylmethyl)- N' -methyl-ethane]-1,2-diamine].^{5,6} The ability to simulate the maximum in $\chi_{\text{M}}T$ at 12 K, using the thermodynamic form of the susceptibility,¹⁴ shows that field-dependent Zeeman level depopulation effects are responsible for this maximum.

The broad minimum in $\chi_{\text{M}}T$ noted at 203 K most likely reflects short-range 1D-ferrimagnetic behaviour occurring through weak antiferromagnetic coupling between the $S = 27/2$ cation and the $S = 3/2$ $[\text{Cr}(\text{CN})_6]^{3-}$ *via* the H-bonding pathways that connect them. Tests for long-range order in **1** proved negative. Thus, the field-cooled and zero-field magnetization data at very low temperatures, in $H = 50 \text{ Oe}$, showed no bifurcation. At low-fields and 2 K, the magnetization, M , increases rapidly with increasing fields then saturates above H

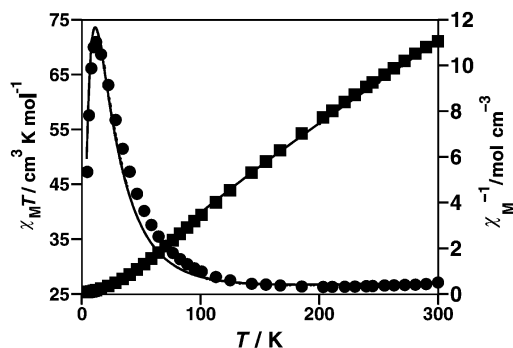


Fig. 2 Plots of $\chi_{\text{M}}T$ (■) and χ_{M}^{-1} (●) per $\text{Mn}_6^{\text{II}}\text{Cr}_2^{\text{III}}$, for **1** vs. T measured in a field of 1 T. The solid line was calculated using the heptanuclear model (see text).

$\approx 2 \text{ T}$ to a M_{sat} value of $24 \mu_{\text{B}}$, a value consistent with the 1D-ferrimagnet proposal. There is no hysteresis in magnetization at 2 K. Further, the rapid increase in M observed at low fields, such as 100 and 50 Oe, lead to values of $\chi_{\text{M}}T$, as a function of temperature (50–2 K) which do not show the maximum of Fig. 2. Anomalous high values are observed, that continue increasing as T is decreased, reaching $\chi_{\text{M}}T$ of $358 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. Such behaviour gives further confirmation of **1** being a 1D-ferrimagnet. However, further work, including ac susceptibility measurements, is needed to fully understand this unusual behaviour at low temperatures and variable fields. Finally, we note that Hashimoto and coworkers,¹⁵ have obtained a 3-D network in their octacyanotungstate(v)– $\text{Mn}(\text{II})$ species which is a ferrimagnet displaying long-range order ($T_{\text{c}} = 54 \text{ K}$) and with W–CN–Mn chains linking the clusters.

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Notes and references

† *Experimental details:* **Caution!** Perchlorates are potentially explosive and should be handled in small quantities. An aqueous solution of $\text{K}_3[\text{Cr}(\text{CN})_6]$ (0.05 g, 0.15 mmol) was added to a stirring solution of $[\text{Mn}(\text{dmptacn})-(\text{OH}_2)](\text{ClO}_4)_2$ ¹³ (0.26 g, 0.44 mmol) in water (45 ml), resulting in a change from colourless to pale yellow. Evaporation of this solution gave yellow needles of $[\text{Cr}\{\text{CN}\}(\text{Mn}(\text{dmptacn})_6)[\text{Cr}(\text{CN})_6](\text{ClO}_4)_6 \cdot 6\text{H}_2\text{O}$ suitable for crystallography (yield: 0.16 g, 37%). Anal. Calc. for $\text{C}_{120}\text{H}_{162}\text{N}_{42}\text{Cl}_6\text{O}_{30}\text{Mn}_6\text{Cr}_2$: C, 43.4; H, 4.9; N, 17.7. Found: C, 43.3; H, 5.0; N, 17.5%. IR (KBr, cm^{-1}): 3632, 3543 (H_2O); 3330 (N–H); 2142, 2118 ($\text{C}\equiv\text{N}$); 1608vs, 1572m (py); 1097vs, 624 (ClO_4).

‡ *Crystal data* for **1**: $\text{C}_{120}\text{H}_{162}\text{N}_{42}\text{Cl}_6\text{O}_{30}\text{Mn}_6\text{Cr}_2$, $M = 3319.2$, trigonal, space group $R\bar{3}$ (no. 148), $a = 30.1382(9)$, $c = 13.7641(9) \text{ \AA}$, $V = 10827.1(7) \text{ \AA}^3$, $Z = 3$, $D_{\text{c}} = 1.386 \text{ g cm}^{-3}$, $\mu = 8.31 \text{ cm}^{-1}$, $F(000) = 4686$, $T = 173 \text{ K}$, Nonius Kappa CCD, Mo– $\text{K}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$), $2\theta_{\text{max}} = 56.5^\circ$, ϕ -scans, 5378 unique data, final $R = 0.062$, $wR = 0.056$ for 2908 observed reflections [$I > 3.00\sigma(I)$] and 311 variables. The structure was solved by and expanded using Fourier techniques and non-hydrogen atoms refined anisotropically. CCDC 182/1889. See <http://www.rsc.org/suppdata/cc/b0/b007113g/> for crystallographic files in .cif format.

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