Magnetic Clusters

DOI: 10.1002/anie.200600691

High-Nuclearity, High-Symmetry, High-Spin Molecules: A Mixed-Valence Mn_{10} Cage Possessing Rare T symmetry and an $S = 22$ Ground State**

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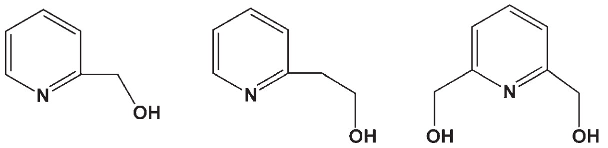
Polynuclear transition-metal clusters in intermediate oxidation states continue to attract great attention, mainly because of their fascinating physical properties and the aesthetic beauty and complexity of their structures. An interesting subarea of this chemistry is the small but growing family of molecules that, in their ground states, have unusually large numbers of unpaired electrons. Several molecular cluster compounds with abnormally high spin (S) values have been prepared, with the highest values to date being $S = 51/2$ for a $[Mn^{II}_6Mn^{III}_{18}Mn^{IV}]$ complex[1] and a cyano-bridged $[Mn^{II}_9Mo^{V}_6]$ system.[2] The study of such molecules has shown that the large S value results from either ferromagnetic (or ferrimagnetic) exchange interactions between the metal centers and/or spin-frustration effects from the presence in certain M_x topologies of competing antiferromagnetic exchange interactions that prevent (frustrate) the preferred spin alignments that would normally yield low-spin species.[3] In addition, it has recently become apparent that a fairly large ground-state S value is one of the necessary (but not sufficient) requirements for molecules to be able to exhibit the phenomenon of single-molecule magnetism.[4] The synthesis of new high-spin molecules is thus of great interest and importance. However, it is difficult to predict what type of topology and structure will lead to a high-spin cluster and even more difficult to then achieve the synthesis of such a species.[5]

In the majority of polynuclear clusters, magnetic exchange interactions are propagated mainly by bridging OH^-, OR^-, O^{2-}, or RCO_2^- groups (or a combination of these), ligands which usually lead to antiferromagnetic coupling. One approach to increasing the ground state S value is replacement of some or all of the above ligands with groups that give ferromagnetic coupling. One of the best of the latter is the azide (N_3^-) group when it bridges metal ions in the 1,1 (end-on) fashion, in which case the exchange coupling is ferromagnetic for a wide range of M-N-M angles.[6] We also have a long-standing interest in the use of pyridine-based alkoxide ligands (Scheme 1) in Mn cluster chemistry, and have found that the anion of 2-(hydroxymethyl)pyridine (hmp$^-$) is a versatile N,O-chelating and -bridging ligand whose alkoxide arm often supports ferromagnetic coupling between the metal atoms it bridges.[7,8]



Scheme 1. Pyridyl alcohol ligands (from left to the right) 2-(hydroxymethyl)pyridine (hmpH), 2-(2-hydroxyethyl)pyridine (hepH), and 2,6-pyridinedimethanol (pdmH$_2$).

We now report that use of both N_3^- and hmp$^-$ groups in certain reactions with Mn salts leads to the two remarkable decanuclear, mixed-valence complexes $[Mn^{II}_4Mn^{III}_6O_4(N_3)_4(hmp)_{12}](X)_2$ [$X = N_3^-$ (**1**), ClO_4^- (**2**)]. The Mn_{10} cation in each of these complexes possesses an aesthetically pleasing structure of high (T) symmetry, is completely ferromagnetically coupled, and has a resulting $S = 22$ ground state, one of the highest values yet reported. In addition, this cation is the first example in which μ_3-1,1,1-azido ligands bridge *exclu-*

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[**] This work was supported by the U.S. National Science Foundation (Grant CHE-0414155).

sively Mn^{3+} ions, and thus presages a potentially rich new area of Mn^{III} clusters with high spin values.

The reaction of $Mn(NO_3)_2{\cdot}H_2O$, hmpH, Et_3N, and NaN_3 in a 1:1:1:1 ratio in MeCN/MeOH gave a dark brown solution from which crystals of $[Mn_{10}O_4(N_3)_4(hmp)_{12}](N_3)_2$ (**1**) were subsequently isolated in 20% yield. Use of $Mn(ClO_4)_2{\cdot}6H_2O$ gave the isostructural complex $[Mn_{10}O_4(N_3)_4(hmp)_{12}](ClO_4)_2{\cdot}MeCN$ (**2**·MeCN) in a much higher yield of 75%. The same reaction in which only MeOH was used gave the known complex $[Mn^{II}{}_2Mn^{III}{}_2(N_3)_2(hmp)_6]_n(ClO_4)_{2n}$ (**3**), which is a one-dimensional chain.[8]

The structure of the cation $[Mn_{10}O_4(N_3)_4(hmp)_{12}]^{2+}$ (Figure 1)[9] consists of ten Mn ions with a tetra-face-capped octahedral topology. The central octahedron comprises six Mn^{3+} ions, and the eight faces of this octahedron are bridged by four μ_3-N_3^- ions and four μ_4-O^{2-} ions (Figure 2), with the latter also bridging to four external Mn^{2+} ions that thus cap four non-adjacent faces of the octahedron. The μ_3-N_3^- ions bind in an η^1:η^1:η^1 (end-on) fashion. The Mn^{II}/Mn^{III} oxidation states were established by consideration of bond lengths, bond-valence-sum (BVS) calculations,[10] and the presence of the Jahn–Teller distortions expected for octahedral Mn^{III} centers. All Mn^{3+} ions (Mn2 and its symmetry-related counterparts) are six-coordinate with near-octahedral geometry and thus display a Jahn–Teller distortion, which is observed in the form of an axial elongation of the two *trans* $Mn{-}N_{azide}$ bonds (2.412(3) Å). The four Mn^{2+} ions (Mn1 and its symmetry-related counterparts) are seven-coordinate with distorted face-capped octahedral geometry in which the capping atom is the oxide atom O1 ($d(Mn^{2+}{-}O^{2-})$: 2.304(4) Å). The peripheral ligation about the $[Mn_{10}(\mu_4\text{-}O)_4(\mu_3\text{-}N_3)_4]^{14+}$ core is provided by the twelve hmp^- groups; three hmp^- groups bind terminally through their N atoms to each of the exterior Mn^{2+} ions, and their alkoxide arms bridge each Mn^{2+} ion (Mn1) to Mn^{3+} ions (Mn2). There are only weak intermolecular interactions, which involve the hmp pyridyl rings.

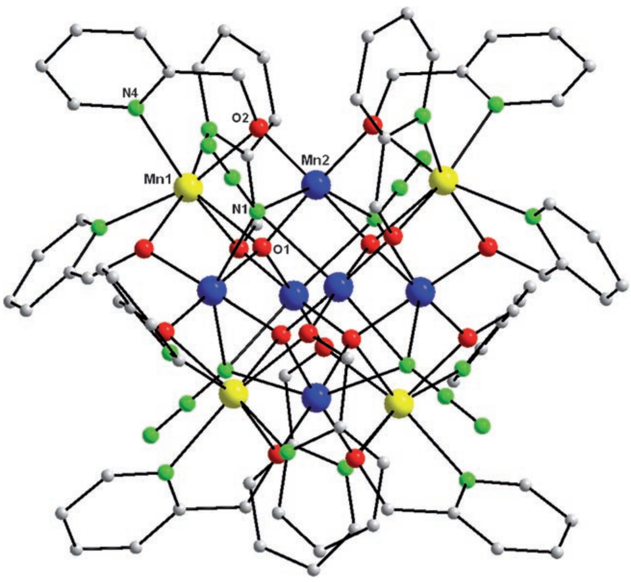

Figure 1. Partially labelled PovRay representation of the cation of **1** (Mn^{II} yellow, Mn^{III} blue, O red, N green, C gray). H atoms have been omitted for clarity.

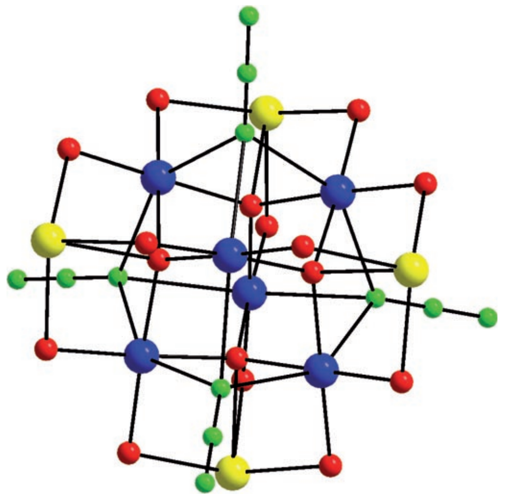

Figure 2. The core of complex **1** (Mn^{II} yellow, Mn^{III} blue, O red, N green, C gray). The hmp^- ligands, except for their O atoms, have been omitted.

Complexes **1** and **2** join only a handful of previously described mixed-valence Mn_{10} clusters[11] and are the first of the $[Mn^{II}{}_4Mn^{III}{}_6]$ type. The $[Mn_{10}(\mu_4\text{-}O)_4(\mu_3\text{-}N_3)_4]^{14+}$ core has T_d symmetry, but inclusion of the hmp groups removes the σ_d planes and S_4 axes of symmetry, and the complete $[Mn^{II}{}_4Mn^{III}{}_6O_4(N_3)_4(hmp)_{12}]^{2+}$ cation consequently has the rare T point-group symmetry, which is crystallographically imposed; the point group T is the rotational subgroup of T_d.

Solid-state direct current (dc) magnetic susceptibility (χ_M) data for complex **2**·MeCN were collected in the temperature range 5.0–300 K in an applied field of 1 kG (0.1 T).[12] The $\chi_M T$ value steadily increases from 53.78 $cm^3\,mol^{-1}\,K$ at 300 K to a maximum of 231.56 $cm^3\,mol^{-1}\,K$ at 10 K, before dropping to 220.23 $cm^3\,mol^{-1}\,K$ at 5.0 K (Figure 3). The spin-only ($g=2$) value for a non-interacting $[Mn^{II}{}_4Mn^{III}{}_6]$ unit is 35.5 $cm^3\,mol^{-1}\,K$. This value indicates ferromagnetic exchange interactions within **2**, and the value at 10 K strongly suggests a very large ground-state spin value; the sharp decrease at the lowest temperatures is assigned to Zeeman

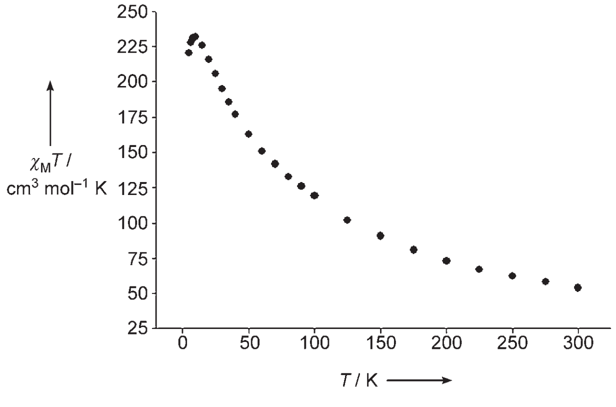

Figure 3. $\chi_M T$ versus T plot for complex **2**·MeCN in a 1-kG field.

effects, zero-field splitting (ZFS), and/or weak intermolecular interactions. The value at 10 K is consistent with an $S=22$ ground state, the maximum possible value for this cluster, and a g factor slightly less than 2.0, as expected for a $\mathrm{Mn^{II}/Mn^{III}}$ complex; the spin-only ($g=2$) value for a state with $S=22$ is 253 $\mathrm{cm^3\,mol^{-1}\,K}$.

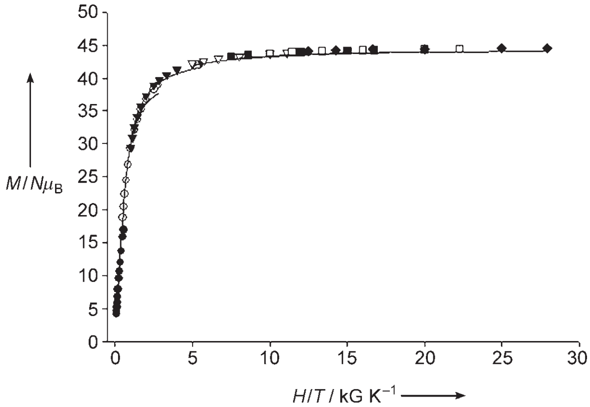

Figure 4. Plot of reduced magnetization ($M/N\mu_B$) versus H/T for **2**·MeCN in the temperature range 1.8–10 K and in fields of 0.1 T (●), 0.5 T (○), 1.0 T (▼), 2.0 T (▽), 3.0 T (■), 4.0 T (□), 5.0 T (◆). Solid lines are the fit; see the text for the fitting parameters.

In order to confirm the ground state of **2**·MeCN, magnetization (M) data were collected in the ranges 0.1–5 T and 1.8–10.0 K, and these are plotted as $M/N\mu_B$ versus H/T in Figure 4. The various isofield lines are virtually superimposed, thus indicating essentially no zero-field splitting within the ground state, and the saturation value of $M/N\mu_B \approx 44$ is consistent with a spin value of $S=22$. The data were fit by matrix diagonalization to a model that assumes only the ground state is populated, includes axial zero-field splitting ($D\hat{S}_z^2$) and the Zeeman interaction, and carries out a full powder average. The best fit (solid lines in Figure 4) gave $S=22$, $g=2.00\pm0.0013$, and $D=-0.0112\pm0.0003\ \mathrm{cm^{-1}}$, thus confirming a very high-spin ground state with little or no magnetic anisotropy. The latter attribute was anticipated from the high (cubic) symmetry of the molecule because, although $\mathrm{Mn^{3+}}$ ions have significant single-ion anisotropy, the molecular anisotropy is the tensoral sum of the single-ion values, and this sum should be essentially zero given the cubic symmetry and the resulting orientations of the six $\mathrm{Mn^{III}}$ Jahn–Teller axes.[3,13] This supposition is borne out by the experimental observation of $D\approx0$ for **1** and **2**.

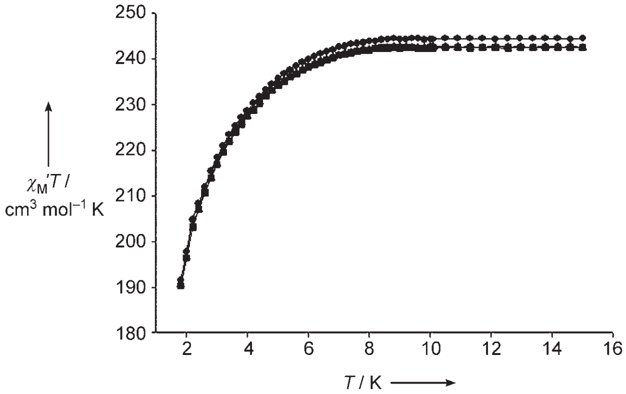

Figure 5. In-phase ac susceptibility ($\chi_M'T$) measurements of complex **2**·MeCN measured below 15.0 K at 50 Hz (▲), 250 Hz (■), and 1000 Hz (●).

The presence of the $S=22$ ground state was further supported by alternating current (ac) susceptibility experiments, in which a weak field of 3.5 G that was oscillating at a particular frequency was applied to the sample. Alternating current susceptibility studies use no dc field and thus are an excellent complementary tool for determining S by avoiding potential complications from a large dc field. The in-phase susceptibility (χ_M') for **2**·MeCN is shown as $\chi_M'T$ versus T in Figure 5, and $\chi_M'T$ is temperature-independent at about 244 $\mathrm{cm^3\,mol^{-1}\,K}$ from 15 K down to about 8 K. This temperature-independent value is consistent with a spin value of $S=22$ and a g factor of about 1.96, thus in satisfying agreement with the dc magnetization fits. The temperature-independent $\chi_M'T$ value also indicates no population of excited states in this temperature range. At lower temperatures, $\chi_M'T$ decreases slightly, and we assign this effect to weak intermolecular interactions, both dipolar and superexchange in nature.

There is no out-of-phase (χ_M'') ac susceptibility signal down to 1.8 K, which indicates an insignificant barrier (vs. kT, where k is the Boltzmann constant) to magnetization relaxation. To explore whether slow relaxation might become apparent at even lower temperatures, magnetization versus dc field scans were performed on a single crystal of **2**·MeCN down to 0.04 K, with the field applied in turn along three perpendicular axes of the crystal. All of the measurements gave essentially superimposable scans, as shown for one field direction in Figure 6. There is also clearly no hysteresis observed. The combined results indicate an isotropic crystal and fast magnetization relaxation even at 0.04 K, thus consistent with $D\approx0$.

In summary, the combination of azide and hmp$^-$ ligands in Mn cluster chemistry has yielded an unusual cation that has both a very high ($S=22$) ground-state spin value and high (T)

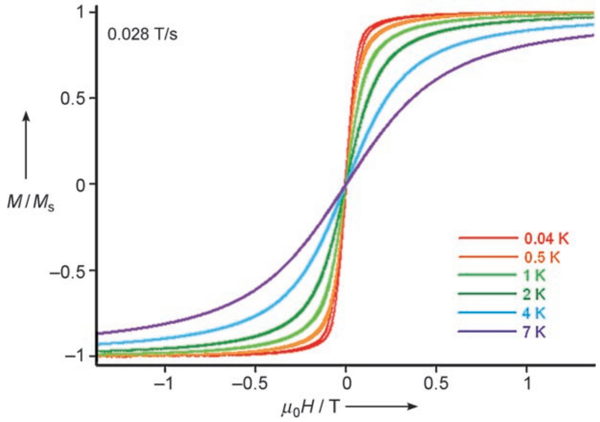

Figure 6. Plot of magnetization versus applied dc field scans for a single crystal of complex **2**·MeCN at the indicated field sweep rate and temperatures. The magnetization is normalized to its saturation value.

symmetry. Such a high S value is extremely rare; in fact, it is the second-highest in Mn chemistry to date and very similar in magnitude to the value $S = 23$ for an Fe_{14} cluster, which is the largest spin value in Fe chemistry.[14] The value $S = 22$ for **1** and **2** is the maximum for a $[Mn^{II}_4Mn^{III}_6]$ species, thus indicating that all interactions are ferromagnetic. This attribute is consistent with the presence of end-on-bridging N_3^- groups on the $\{Mn^{III}_3\}$ faces of the central octahedron, as well as with the bridging of each $Mn^{II}Mn^{III}$ pair by two separate O atoms with rather acute Mn-O-Mn angles (ca. 101–105°), as both of these bridging modes are known to yield ferromagnetic interactions.[6,7,15] Also rare is the high, aesthetically pleasing symmetry of this cation, which continues to emphasize the versatility of Mn chemistry.

Experimental Section

1: Solid NaN_3 (0.13 g, 2.0 mmol) was added to a stirred, pale yellow solution of hmpH (0.19 mL, 2.0 mmol) and Et_3N (0.28 mL, 2.0 mmol) in MeCN/MeOH (20 mL, 20:1 v/v). To this solution was added solid $Mn(NO_3)_2\cdot H_2O$ (0.36 g, 2.0 mmol), which caused a rapid color change to dark brown. The resulting dark brown solution was stirred for a further 2 h and filtered, and the filtrate was left undisturbed at ambient temperature. After 3 days, X-ray quality dark brown hexagonal crystals appeared and were collected by filtration, washed with MeCN (2 × 5 mL), and dried in vacuo. The yield was 20%. Elemental analysis (%) calcd for $C_{72}H_{72}Mn_{10}N_{30}O_{16}$: C 39.98, H 3.36, N 19.43; found: C 39.77, H 3.32, N 19.54.

2·MeCN: This complex was prepared in the same manner as complex **1**, except that $Mn(ClO_4)_2\cdot 6H_2O$ (0.50 g, 2.0 mmol) was used in place of $Mn(NO_3)_2\cdot H_2O$. Dark brown hexagonal crystals of the product were isolated, collected by filtration, washed with MeCN (2 × 5 mL), and dried in vacuo. The yield was 75%. Elemental analysis (%) calcd for $C_{74}H_{75}Mn_{10}N_{25}O_{24}Cl_2$: C 38.33, H 3.26, N 15.10; found: C 38.31, H 3.10, N 14.98; selected IR data (KBr): $\tilde{\nu} = 3334$ (m), 3068 (m), 2902 (w), 2784 (m), 2048 (vs), 1602 (s), 1567 (m), 1482 (m), 1434 (s), 1367 (m), 1210 (m), 1291 (m), 1248 (w), 1223 (w), 1153 (m), 1082 (vs), 1048 (m), 1010 (m), 817 (m), 758 (s), 729 (m), 671 (vs), 622 (vs), 549 (m), 467 cm^{-1} (m).

Safety note: Perchlorate and azide salts are potentially explosive; such compounds should be synthesized and used in small quantities, and should be treated with utmost care at all times.

Received: February 21, 2006
Revised: March 23, 2006

Keywords: azides · cluster compounds · magnetic properties · manganese · N,O ligands

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[9] a) Crystal-structure data for **1**: $C_{72}H_{72}Mn_{10}N_{30}O_{16}$, $M_r = 2163.00$, cubic, space group $P4_3/n$, $a = 16.3101(3)$ Å, $V = 4338.80(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.656\ g\,cm^{-3}$, $T = 173(2)$ K, 25543 reflections collected, 1670 unique ($R_{int} = 0.1262$), $R1 = 0.0266$ and $wR2 = 0.0577$, based on 1670 reflections with $I > 2\sigma(I)$. The asymmetric unit consists of half of the Mn_{10} cluster and one-eighth of a combination of N_3^- and MeCN disordered in the same position. The disorder of the counter ion and MeCN molecule is the only possibility of balancing the crystal charges whereby the ratio of cluster to counter ion is 3:1, thus necessitating two-thirds occupancy of the N_3^- anion with one-third of MeCN. Crystal-structure data for **2**·MeCN: $C_{74}H_{75}Cl_2Mn_{10}N_{25}O_{24}$, $M_r = 2283.44$, cubic, space group $P4_3/n$, $a = 16.5474(5)$ Å, $V = 4531.0(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.674\ g\,cm^{-3}$, $T = 173(2)$ K, 27284 reflections collected, 1755 unique ($R_{int} = 0.0582$), $R1 = 0.0351$ and $wR2 = 0.0840$, based on 1755 reflections with $I > 2\sigma(I)$; b) CCDC-298873 and CCDC-298874 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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