A Ferromagnetic Salicylaldoximate/Azide $Mn^{II}_2Mn^{III}_6$ Cluster with an S = 17 Ground State and a Single-Molecule-Magnet Response

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ABSTRACT:

One new $Mn^{II}_2Mn^{III}_6$ cluster exhibiting an S = 17 spin ground state and single-molecule-magnet properties has been designed linking Mn^{III}_3-salicylaldoximate triangles and tetracoordinated Mn^{II} cations by means of end-on azido bridges. The ferromagnètic coupling has been rationalized as a function of their structural parameters.

After the discovery of the first members of the Mn^{III}_6 family of single molecule magnets (SMMs) employing the salicylaldoxime (H_2salox) ligand[1] and further systematic study in the last 10 years by Brechin et al.,[2–11] $\{Mn^{III}_3(\mu_3\text{-O})\}$ triangular fragments with salicyloximato side bridges have been one of the most fruitful and better studied systems in the search for a SMM response. The factors that control the sign and magnitude of the magnetic interaction inside the triangular units were rationalized as a function of the Mn^{III}–N–O–Mn^{III} torsion angle, establishing the border between ferromagnetic (FM) and antiferromagnetic (AF) interaction around 31° [4,5].

The ground state for a $\{Mn^{III}_3(\mu_3\text{-O})\}$ triangle is restricted to the S = 0–6 range, but the hexanuclear systems, consisting of two linked triangles by means of η^2:η^1:η^1:μ_3-oximato bridges, can reach the larger S = 12 ground state (Chart 1). It is worth noting that for these systems the easy axes of the Mn^{III} cations are roughly parallel, and they reached the largest energy barrier to magnetization reversal for d transition-metal clusters.[6] In addition to the Mn^{III}_3 and Mn^{III}_6 cores, other molecular clusters, based in the $\{Mn^{III}_3(\mu_3\text{-O})\}$ fragment, are those consisting of four stacked triangles[12] (Mn^{III}_{12}), Mn^{II} bicapped triangles[13,14] with a $Mn^{II}_2\{Mn^{III}_3(\mu_3\text{-O})\}$ core, or Mn^{II} bicapped hexanuclears with a $Mn^{II}_2\{Mn^{III}_6(\mu_3\text{-O})_2\}$[15–17] core. The presence of two additional Mn^{II} cations can reduce or increase the S ground state by up to five units as a function of the sign and magnitude of the magnetic interactions. In fact, Hendrickson proved experimentally that the pentanuclear $Mn^{II}_2\{Mn^{III}_3(\mu_3\text{-O})\}$ core can reach up to the maximum S = 11 ground state,[14] whereas only AF interactions between the Mn^{II} and Mn^{III} cations have been found until now for the $Mn^{II}_2\{Mn^{III}_6(\mu_3\text{-O})_2\}$ core, resulting in S = 1 and 7 ground states.[15–17] On the basis of these premises, we have designed the synthesis of one new octanuclear compound with a $Mn^{II}_2\{Mn^{III}_6(\mu_3\text{-O})_2\}$ core with the goal of obtaining FM interactions between the inner hexanuclear fragment and the capping Mn^{II} cations and reaching the S = 17 record ground state for this wide family of complexes. The reaction of H_2salox, sodium azide, and manganese chloride in a methanolic medium, employing Pr_4NOH as a base, yields compound $(Pr_4N)_2[Mn^{II}_2Mn^{III}_6(O)_2(salox)_6(N_3)_6(Cl)_2(H_2O)_2]\cdot 2H_2O$ ($1\cdot 2H_2O$; Supporting Information, synthetic details). Analysis of its magnetic properties reveals a SMM response with a medium energy barrier. Complex 1 can be described as two stacked $\{Mn^{III}_3(\mu_3\text{-O})(salox)_3\}$ triangles bicapped by Mn^{II} cations (Figure 1, and BSV calculations in Table S1). The Mn^{III} cations are linked by $salox^{2-}$ ligands, four of them in the main plane of the triangular subunits in its η^1:η^1:η^1:μ^2 coordination mode and two in its η^1:η^2:η^1:μ^3 mode, connecting both triangles. Mn1 and Mn3 are hexacoordinated, whereas Mn2 shows a square-pyramidal environment, with weak contact with the phenoxo O3′ atom. Each triangular subunit is capped by one Mn^{II} cation, linked by means of three end-on azido bridges with similar Mn^{II}–N_{azido}–Mn^{III} bond angles close to 104.0°. The Mn^{II} cation is tetracoordinated, and the coordination sphere is fulfilled with one Cl^- anion. Mn–N–O–Mn torsion angles are relatively low with 13.7(5)°, 25.5(5)°, and 32.1(4)° values. Charge balance is achieved with two Pr_4N^+ cations, which efficiently isolate the octanuclear clusters. The only intermolecular interaction involves the coordinated and crystallization water molecules and one azidoNatom. Additional plots and structural data can be found in Tables S2 and S3 and Figures S1 and S2.

The room temperature $\chi_M T$ value is 28.96 $cm^3\cdot mol^{-1}\cdot K$, slightly larger than the expected value for two Mn^{II} and six Mn^{III} noninteracting ions (g = 2.00; Figure 2). Upon cooling, $\chi_M T$ increases up to a maximum value of 100.6$cm^3\cdot mol{-}1\cdot K$ at 5 K, and below this temperature, $\chi_M T$ decays to a final value of 85.4 $cm^3\cdot mol^{-1}\cdot K$ at 2 K. The most simplified coupling scheme to describe the system requires four J constants, assuming J_1 as the intertriangle interaction, J_2 and J_3 as the interactions mediated by the Mn–O–N–Mn pathways with torsions larger or lower than 30°, respectively, and J_4 as the $Mn^{II}\cdots Mn^{III}$ interaction mediated by end-on azido bridges (Figure S3).

The system was fitted[18] isotropically in the 25–300 K range of temperature to avoid low-temperature effects as zero-field splitting. Best-fit parameters under these conditions were J_1 = +3.9 cm^{-1}, J_2 = 14.0cm^{-1}, J_3 = −2.7 cm^{-1}, J_4 = +7.4 cm^{-1}, and g = 1.88 with $R = 6.0 \times 10^{-4}$, suggesting an S = 17 ground state. As will be further discussed, the sign and magnitude of the J and g constants lie in the normal range for these kinds of systems, but absolute values of J are obviously poorly reliable as a consequence of the simplified fit procedure.

Magnetization measurements at 2 K in the 0−5 T field range show a maximum unsaturated value equivalent to 28.2 electrons, which can be fitted[18] to the maximum spin $S = 17$ for $g = 1.87$ and $D \approx 0.15$ cm^{-1} (Figure 2). In light of these results and the more reliable further fit of the reduced magnetization, which gives a D value of −0.12 cm^{-1} (Figure S4), alternating-current measurements were performed in the 1488−10 Hz range of frequencies.

Well-defined χ'' peaks in the 3.96−2.85 K range were observed (Figure 3). The Arrhenius fit of the peak maxima gives $E_a = 35.2$ cm^{-1}, $\tau_0 = 3.25 \times 10^{-10}$ s, and $D = -0.12$ cm^{-1}, in excellent agreement with the D value obtained from the reduced magnetization measurement and indicating that tunnelling relaxation is not operative. Measurements at 2 K do not show magnetic hysteresis.

Nevertheless, an interesting question arises from analysis of the structural data: following the rule of the Mn^{III}–N–O–Mn^{III} torsion angle[5] and compared with Mn^{III}_6 complexes with a similar range of torsion angles (summarized in Table S4),[10,19–21] the inner hexanuclear unit should have an $S = 4$ local spin and, *apparently*, complex 1 should only reach $S = 9$ if the interaction with the Mn^{II} cations was FM. Thus, *why does this complex reach its maximum spin?*

The answer requires detailed analysis of selected bond parameters of the related octanuclear $[Mn_2^{II}Mn_6^{III}(O)_2(napthsalox)_6(N_3)_6(MeOH)_8]$ and $[Mn_2^{II}Mn_6^{III}(O)_2(Mesao)_6(N_3)_6(MeOH)_8]$ clusters (CCDC codes CIGYIB and CIGYOH)[15,16] and the pentanuclear $[Mn_2^{II}Mn_3^{III}(O)\text{-}(salox)_3(N_3)_6X_2]^{2-}$ (X = Cl, Br) and $[Mn_2^{II}Mn_3^{III}(O)(Mesao)_3(N_3)_6Cl_2]^{2-}$ complexes,[13,14] (CCDC codes TEZNES, WAJKOJ, and WAJKUP; Table S5). If the capping Mn^{II} cation is octahedrally coordinated, as occurs for CIGYIB and CIGYOH, the Mn^{II}–N_{azido} bond distances are larger than 2.2 Å, the N_{azido}–Mn^{II}–N_{azido} angles are close to 90°, and the Mn^{II}–N_{azido}–Mn^{III} bond angles are close to 120°. When the capping Mn^{II} cation is tetrahedrally coordinated, the N_{azido}–Mn^{II}–N_{azido} bond angles increase up to 110° and the remainder of the bond parameters are also modified: Mn^{II}–N_{azido} distances become 0.1 Å shorter, axial Mn^{III}–N_{azido} distances increase, the Mn^{II}–N_{azido}–Mn^{III} bond angles decrease below 110°, and the Mn^{II} cation is closer to the centroid of the Mn^{III}_3 plane, giving a compressed $\{Mn^{II}(N_3)_3Mn^{III}_3\}$ fragment (Figure 4).

End-on azido bridges usually induce FM interaction,[22] but for large Mn−N−Mn bond angles, it becomes AF, as was demonstrated by Alvarez et al.[23] Tetrahedral coordination of the capping Mn^{II} for 1 leads to Mn^{II}–N_{azido}–Mn^{III} bond angles in the typical range of FM interactions.

When the oximate torsion and azide bond angle rules are combined, the S ground state for the systems in which the interactions inside the $\{(\mu_3\text{-}O)Mn^{III}_3\}$ units are FM is trivial: S ground states become a combination of the local S_L spin of the inner hexanuclear or trinuclear fragments and the 5/2 spins of each Mn^{II}, and thus applying $S = |S_L \pm 5/2 \pm 5/2|$, we obtain $|12 - 5/2 - 5/2| = 7$ for CIGYOH, $|6 + 5/2 + 5/2| = 11$ for TEZNES or WAJKOJ, and $|6 - 5/2 + 5/2| = 6$ for WAJKUP, in full agreement with the experimental values (Table *S*5). In contrast, for the octanuclear systems with $S = 4$ local spin for the inner hexanuclear unit, the overall S ground state is a function of the dominant interaction, and in that case, the $S = |S_L \pm 5/2 \pm 5/2|$ sum is no longer applicable because all intermediate S ground states are possible. In fact, if the Mn^{II}–Mn^{III} interaction is AF and dominant, the ground state will be $S = 7$, and if this interaction is FM and dominant, the ground state will be $S = 17$. In contrast, if the Mn^{II}–Mn^{III} interaction is weakly AF, the ground state must be $S = 1$, as occurs for the octanuclear complex CIGYIB (Figure S5).

In conclusion, we have reported a new member of the $Mn^{II}_2Mn^{III}_6$ family of clusters based on bicapped stacked Mn^{III} triangles. The new system is FM, reaching the limit of the $S = 17$ ground state, and it is moderately anisotropic and exhibits a SMM response with $E_a = 35$ cm^{-1}. The FM response is attributed to a subtle combination of factors such as the tetrahedral environment of the Mn^{II} cation and the end-on azido bridges with low Mn^{II}–N–Mn^{III} bond angles.

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Legends to figures

Chart 1. Isolated, Stacked, or Capped Mn^{III}_3-Salox Triangles and Their Range of S Ground States[a]
[a]Color key: Mn^{II}, orange; Mn^{III}, dark green; O, red; N, navy blue.

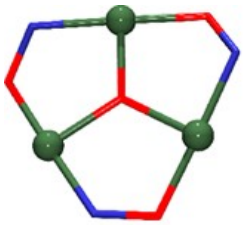
Figure 1. Labelled plot of the core of compound 1.

Figure 2. $\chi_M T$ product for compound 1. Inset: magnetization plot at 2 K. Solid lines show the best obtained fits.

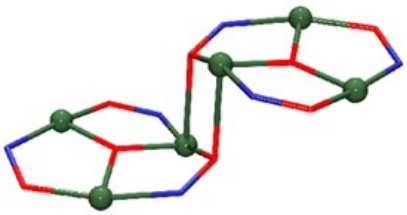
Figure 3. Alternating-current measurements for compound 1. Inset: Arrenhius plot from the position of the χ'' peaks.

Figure 4. Triangular $\{Mn^{III}_3(\mu_3\text{-}O)(\text{oximate})_3\}$ fragments with end-on azido bridges linking an additional Mn^{II} cation in octahedral or tetrahedral environments.

CHART 1



$S = 0 - 6$



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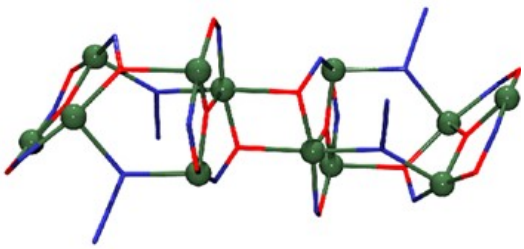

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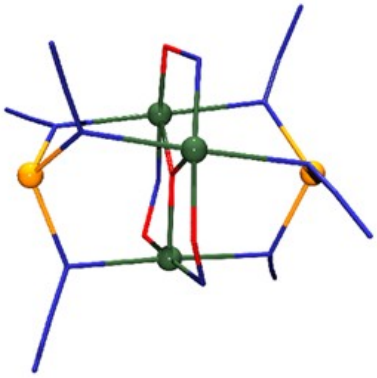
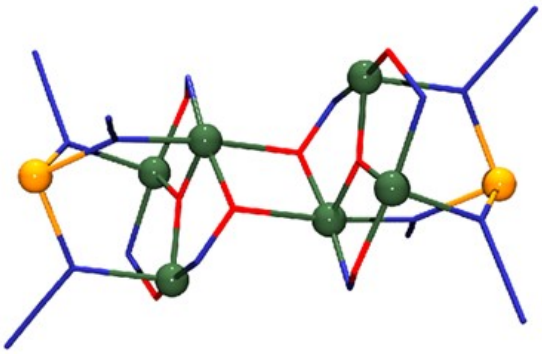


$S = 6, 11$



$S = 1, 7$

184
185 **FIGURE 1**
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FIGURE 2

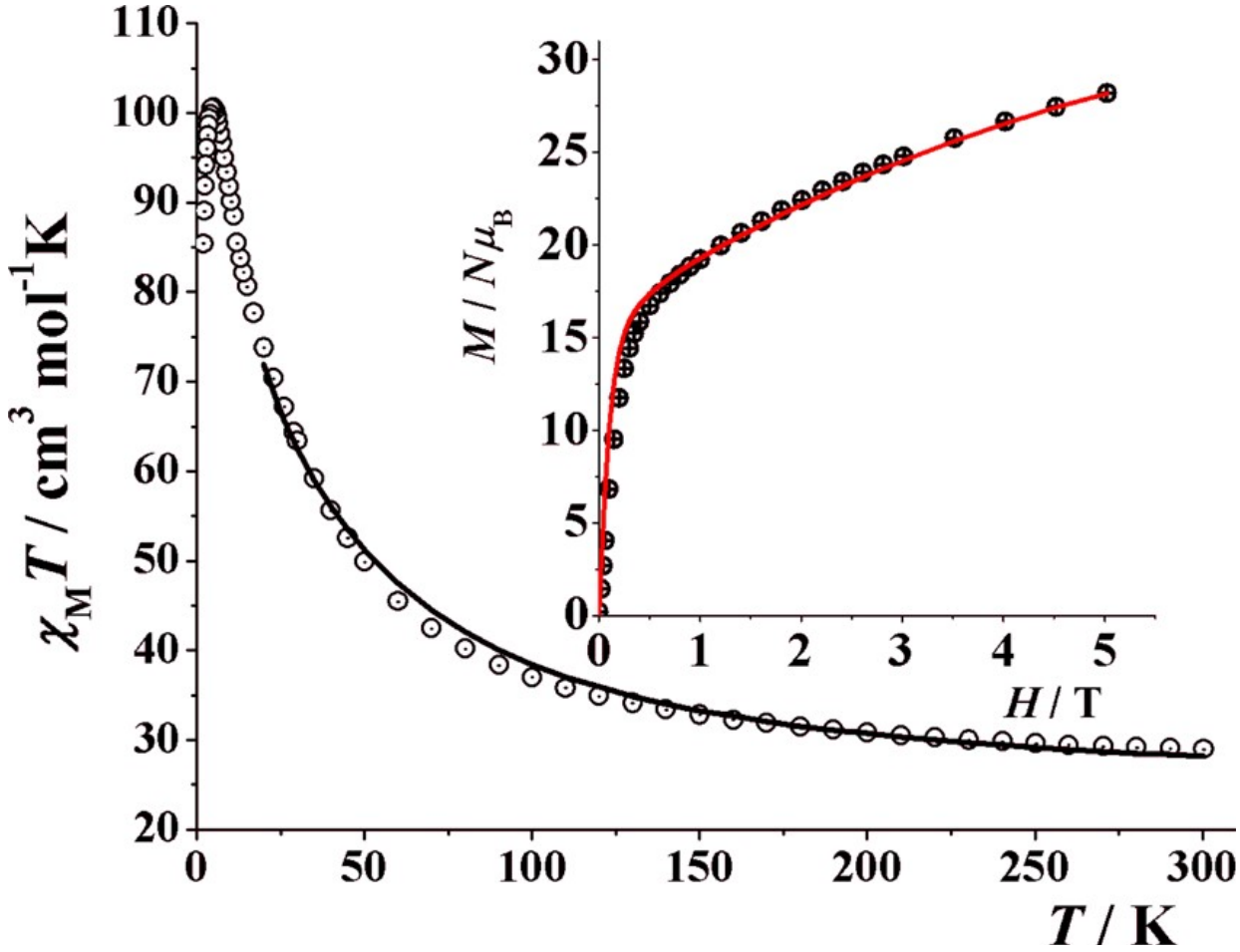
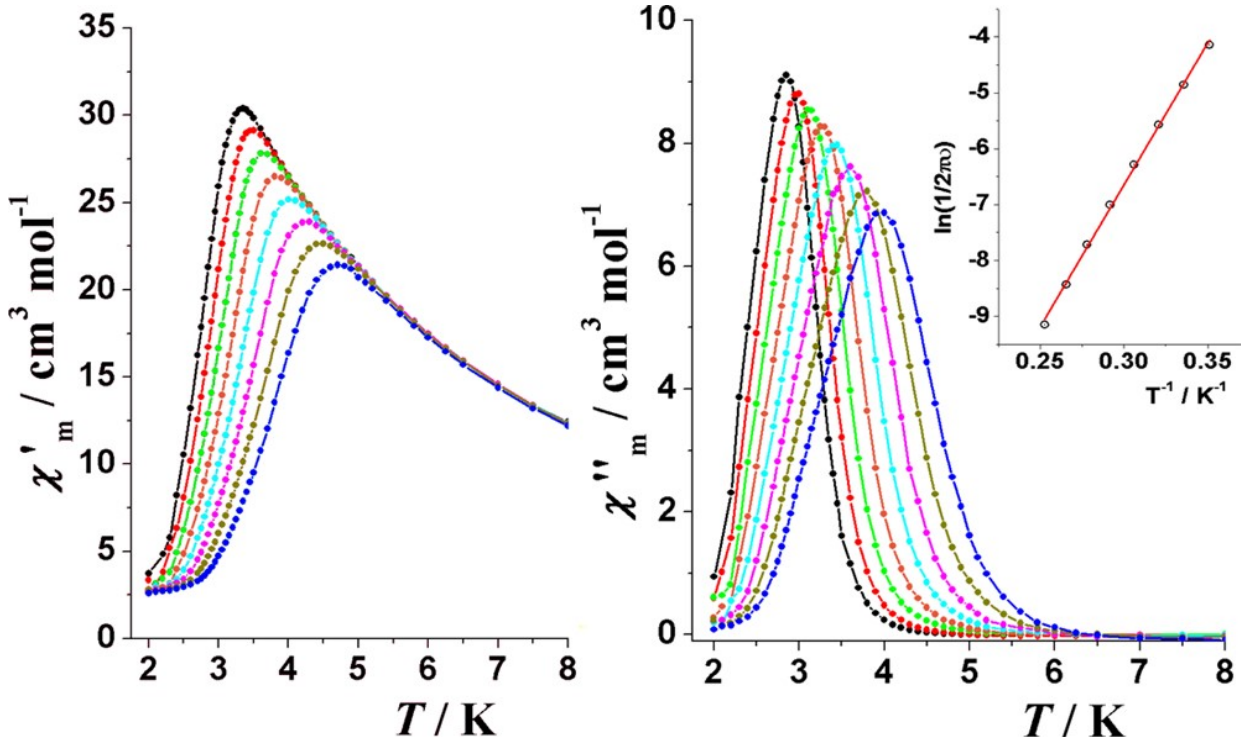


FIGURE 3



201
202 **FIGURE 4**
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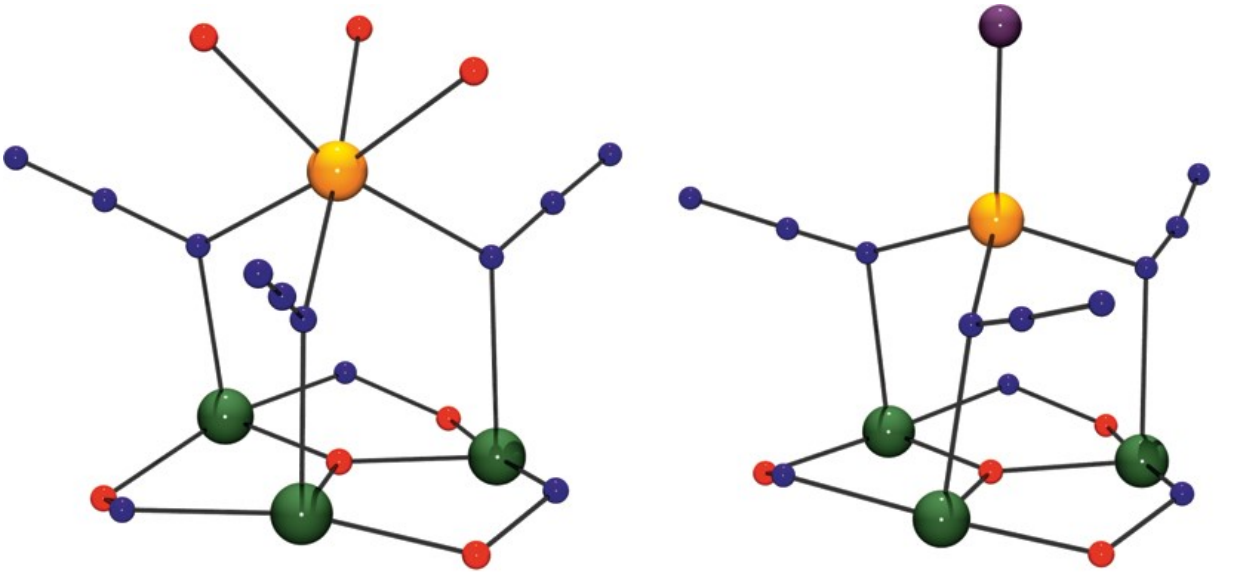

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