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COMMUNICATION

A Mn₃₆Ni₄ 'loop-of-loops-and-supertetrahedra' aggregate possessing a high $S_{\rm T} = 26 \pm 1$ spin ground state[†]

Maria Charalambous,^{*a*} Eleni E. Moushi,^{*a*} Constantina Papatriantafyllopoulou,^{*ab*} Wolfgang Wernsdorfer,^{*c*} Vassilios Nastopoulos,^{*d*} George Christou^{*b*} and Anastasios J. Tasiopoulos*^{*a*}

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The initial use of 1,3-propanediol in mixed Mn/3d cluster chemistry has led to a $Mn^{III}_{28}Mn^{II}_{8}Ni^{II}_{4}$ molecular aggregate which consists of two $Mn^{III}_{8}Ni_{2}$ loops and two $Mn^{III}_{6}Mn^{II}_{4}$ supertetrahedral units and displays a high ground spin state value $S_{\rm T} = 26 \pm 1$.

Polynuclear clusters of paramagnetic 3d metal ions have attracted intense interest in the last two decades for a number of reasons including their novel crystal structures and magnetic properties.¹⁻³ One important challenge for coordination chemists is the utilization of polynuclear complexes with interesting magnetic properties for the construction of larger clusters or polymeric networks. Such compounds would combine novel structural features (large size, high symmetry, and aesthetically pleasing shapes and architectures) with retention and possibly enhancement of the magnetic properties of their 'magnetic' "buildingblocks". However, although there are a few coordination polymers composed of magnetically interesting Mn₃,⁴ Mn₄,⁵ Mn₆,⁶ Mn₁₀,⁷ Mn₁₇⁸ and Mn₁₉⁹ units, the list of discrete polynuclear complexes containing such "building-blocks" is very small, being limited mainly to some polynuclear clusters comprising linked trinuclear units.^{1b,10}

We recently reported a family of large molecular aggregates consisting of four smaller clusters linked through Na⁺ or Mn²⁺ ions.¹¹ These large tetrameric [Mn₁₀M(μ_3 -O)₂(O₂CCH₃)₁₃(pd)₆-(py)₂]₄^{x+} (**Mn**₄₀**M**₄; pd = the dianion of 1,3-propanediol; M =Na⁺, x = 0; $M = Mn^{2+}$, x = 1), clusters contain four Mn₁₀ loops linked through Na⁺ or Mn²⁺ ions and have a saddle-like topology. The **Mn**₄₄ analogue of this family displays a spin $S_T = 6$ ground state and SMM behaviour. Further investigation of the reactions that afforded the **Mn**₄₀**M**₄ clusters involved the use of various 3d paramagnetic metal ions in an attempt to isolate a series of heterometallic Mn/3d analogues and/or other large aggregates composed of smaller clusters.

We herein report the initial result of these studies, which is the new molecular aggregate $[Mn^{II}_{28}Mn^{I}_{8}Ni_4O_{12}Cl_{10}(O_2CCH_3)_{26}-(pd)_{24}(py)_4(H_2O)_2]$ (1) that possesses an unprecedented 'loopof-loops-and-supertetrahedra' structural topology. It consists of two $Mn^{III}_{8}Ni_2$ loops, which are related to the Mn_{10} loops of the $Mn_{40}M_4$ complexes, and two $Mn^{III}_{6}Mn^{II}_{4}$ units exhibiting a supertetrahedral structural motif. The latter has appeared in several $Mn^{III}_{6}Mn^{II}_{4}$ discrete complexes¹² and is known to display intracluster ferromagnetic exchange interactions and a high $S_T = 22$ ground state. The large $Mn^{III}_{28}Mn^{II}_{8}Ni^{II}_{4}$ cluster thus represents an unusual example of a molecular aggregate consisting of magnetically interesting polynuclear M_x (x > 6) repeating units. In addition, it possesses a high spin ground state $S_T = 26 \pm 1$, the highest yet observed for a mixed metal cluster and one of the highest for any metal cluster.

The reaction of $[Mn_3O(O_2CMe)_6(py)_3]$ ·py (py = pyridine) with H₂pd and NiCl₂·6H₂O in a 1:10:1 molar ratio in CH₃CN resulted in a dark-brown slurry, which was filtered to give a brown filtrate. The filtrate was left undisturbed at room temperature for a few days, and it slowly gave redbrown crystals of 1.2CH₃CN·12.30H₂O in 35% yield; dried solid was analyzed as $1.10H_2O$.‡ The molecular structure of 1(Fig 1, top) consists of two mixed-metal [Mn^{III}₈Ni₂(µ₃-O)₂-(O₂CCH₃)₁₂(pd)₆(py)₂] loops (Fig. 1, bottom, right) and two $[Mn^{III}_{6}Mn^{II}_{4}(\mu_{4}-O)_{4}(\mu_{3}-Cl)_{4}(O_{2}CCH_{3})Cl(pd)_{6}(H_{2}O)]$ supertetrahedral units (Fig 1, bottom, left). The Mn^{III}₈Ni₂ loops are related to the Mn₁₀ loops of the Mn₄₀M₄ clusters, with the main difference being the existence of the two Ni²⁺ ions in the former instead of two Mn²⁺ ions. Thus, each Mn^{III}₈Ni₂ unit consists of two $[Mn^{III}_{3}O]^{7+}$ triangles and two dinuclear $Mn^{III}Ni^{II}$ subunits linked by $pd^{2-}\mu$ -O atoms, and bridging CH₃CO₂⁻ groups. The peripheral ligation of the Mn^{III}₈Ni₂ loop is provided by six syn, syn- η^1 : η^1 : μ_2 , four η^1 : η^2 : μ_3 and two $\eta^2:\eta^2:\mu_4$ CH₃CO₂⁻ groups, six $\eta^2:\eta^2:\mu_3$ pd²⁻ ligands (the coordination modes of pd^{2-} ligand in 1 is illustrated in Fig. S1, in ESI^{\dagger}) and two terminal py molecules. Two μ_3 and one μ CH₃CO₂⁻ ligands connect the Mn ions of each [Mn^{III}₃O]⁷⁺ triangle of the Mn^{III}₈Ni₂ loops to a Mn^{II} ion of a Mn^{III}₆Mn^{II}₄ supertetrahedral unit (Fig. S2, in ESI[†]) resulting in the formation of the nearly-planar Mn^{III}₂₈Mn^{II}₈Ni₄

^a Department of Chemistry, University of Cyprus, 1678 Nicosia, Cyprus. E-mail: atasio@ucy.ac.cy; Fax: +357 22892801; Tel: +357 22892765

^b Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, USA

FL 32011-7200, USA

^c Institut Néel, CNRS, BP-166, Grenoble Cedex 9, France

^d Department of Chemistry, University of Patras, 26500 Patras, Greece † Electronic supplementary information (ESI) available: Various structural and magnetism figures. CCDC 862029 (1·2CH₃CN·12.30H₂O). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc30654a



Fig. 1 Representations of the molecular structure of 1 (top) and its $Mn_{16}^{III}Mn_{4}^{II}$ supertetrahedral (bottom, left) and $Mn_{8}^{III}Ni_{2}$ loop (bottom, right) subunits. Colour code: Mn_{11}^{III} , blue; Mn_{1}^{II} , lavender; Ni_{1}^{II} , orange; O, red; N, light green; Cl, green; C, gray. H atoms are omitted.

'loop-of-loops-and-supertetrahedra' aggregate. The [Mn^{III}₆Mn^{II}₄- $(\mu_4-O)_4(\mu_3-Cl)_4(O_2CCH_3)Cl(pd)_6(H_2O)]$ subunit (Fig 1, bottom, left) consists of a $[Mn^{III}_{6}Mn^{II}_{4}(\mu_{4}-O)_{4}]^{18+}$ supertetrahedral core which is analogous to those observed in other discrete Mn₁₀ complexes reported recently.¹² Each Mn₁₀ supertetrahedron contains nine Mn ions in two stacked Mn₃ and Mn₆ isosceles triangles, and a tenth Mn at the apex position. Its Mn₆ base consists of three Mn^{II} and three Mn^{III} atoms located at the corners and the edges of an isosceles triangle, respectively. The Mn_{10} unit is held together by four $\mu_4\text{-}O^{2-}$ ligands resulting in a $[Mn^{II}_{4}Mn^{III}_{6}(\mu_4\text{-}O)_4]^{18+}$ core (Fig. S3 in ESI[†]). The peripheral ligation of the supertetrahedron is completed by one $syn, syn, \eta^1: \eta^1: \mu_2 \text{ CH}_3\text{CO}_2^-$ group, six η^2 : η^2 : μ_3 pd²⁻ ligands, four μ_3 and one terminal Cl⁻ ions and one monodentate H₂O molecule. The oxidation states of the Mn ions and the protonation levels of $O^{2-}/RO^{-}/RCO_{2}^{-}$ groups were determined by bond valence sum (BVS) calculations,¹³ charge balance considerations, and inspection of metric parameters.

Compound 1 possesses an aesthetically pleasing topology and displays an unusually large nuclearity and size, being one of the largest heterometallic Mn_xM_y (M = any metal ion) metal clusters.¹⁴ It is also interesting that the $Mn_{36}Ni_4$ cluster consists of two high nuclearity complexes which display structural cores that have appeared in the past in discrete complexes and/or in fragments of larger clusters. In particular, the $[Mn^{II}_4Mn^{III}_6(\mu_4-O_4)]^{18+}$ supertetrahedral core has appeared in several $Mn^{III}_6Mn^{II}_4$ discrete complexes¹² and also has been recognized as a fragment in larger, $Mn_{17}^{-8a,15}$ and Mn_{19} clusters.² In all cases, intracluster ferromagnetic exchange interactions were realized, which resulted in high $S_T = 22$ or abnormally



Fig. 2 Plot of $\chi_{\mathbf{M}}T$ vs. T for complex 1.

high $S_{\rm T} = 37$ and 83/2 spin ground state values for the discrete ${\rm Mn}^{\rm III}_{6}{\rm Mn}^{\rm II}_{4}$ and the ${\rm Mn}_{17}$ and ${\rm Mn}_{19}$ complexes, respectively. For these reasons, the ${\rm Mn}^{\rm III}_{6}{\rm Mn}^{\rm II}_{4}$ supertetrahedral unit represents a very attractive "building-block" for the construction of large clusters and multidimensional coordination polymers.⁷ Thus, the presence in 1 of the ${\rm Mn}^{\rm III}_{6}{\rm Mn}^{\rm II}_{4}$ unit is expected to result in dominant intracluster ferromagnetic exchange interactions and a very high spin ground state.

Solid-state, direct-current (dc) magnetic susceptibility (γ_M) data were collected in the 5-300 K range in a 1 kG (0.1 T) field and are plotted as $\chi_M T$ vs. T in Fig. 2. The $\chi_M T$ value at 300 K is 118.63 cm³ mol⁻¹ K and increases steadily with decreasing temperature to 325.63 cm³ mol⁻¹ K at 15 K, and then decreases to 304.34 cm³ mol⁻¹ K at 5.0 K. This behaviour is indicative of the existence of dominant ferromagnetic exchange interactions in 1. In addition, the maximum of $325.63 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 15 K is consistent with an S in the 25 to 27 range, depending on the g value. The small decrease at the lowest temperatures is assigned to Zeeman effects, zero-field splitting and/or weak intermolecular interactions. To determine the ground state of 1, magnetisation (M) data were collected in the 1–10 kG and 1.8-4.0 K ranges, and these are plotted as reduced magnetisation $(M/N\mu_{\rm B})$ vs. H/T in Fig. S4 (ESI[†]). The data were fit by assuming that only the ground state is populated and by including axial zero-field splitting $(D\hat{S}_{z}^{2})$ and isotropic Zeeman interactions. Equal quality fits were obtained for S = 25, 26, and 27 with parameters $g = 2.03(1)/D = -0.007(1) \text{ cm}^{-1}$, g = 1.96(1)/2 $D = -0.004(1) \text{ cm}^{-1}$, and $g = 1.91(1)/D = -0.004(1) \text{ cm}^{-1}$, respectively. We conclude that 1 has a ground state of $S_{\rm T}$ = 26 ± 1 , and a very small D value.

Confirmation of the ground state values proposed for **1** on the basis of the dc studies was obtained by alternating current (ac) susceptibility experiments. Ac 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.^{3a,9,11,12a} The in-phase susceptibility $\chi'_{\rm M}$ for **1** is shown as $\chi'_{\rm M} T$ versus *T* in Fig. 3, and extrapolation of the $\chi'_{\rm M} T$ signal to 0 K from above ~8 K (to avoid the effects of intermolecular interactions at lower temperatures) gives a value of ~340 cm³ mol⁻¹ K consistent with: (i) S = 25 and g = 2.05, (ii) S = 26 and g = 1.97, and (iii) S = 27 and g = 1.90. The AC data thus confirm that **1** possesses a high ground state spin value of $S_{\rm T} = 26 \pm 1$. Examination of the out-of-phase ac plot $\chi''_{\rm M}$ vs. *T*



Fig. 3 Plot of the in-phase (χ'_M) (as $\chi'_M T$) ac magnetic susceptibility *versus T* for complex **1** at the indicated frequencies.

(Fig. S5 in ESI[†]) reveals that complex **1** does not exhibit an out-of-phase ac magnetic susceptibility signal down to 1.8 K.

To confirm whether 1 is a SMM, magnetisation versus dc field scans were carried out on a single crystal of 1.2CH₃CN·12.30H₂O using a micro-SQUID apparatus.¹⁶ These studies revealed the existence of hysteresis loops below 0.3 K but with a very narrow coercivity (Fig. S6 in ESI[†]) that increased slightly with either decreasing temperature or increasing scan rate. This is not a typical SMM behaviour for which one would normally expect wider loops and a greater dependence of the coercivity on the temperature. We thus conclude that 1 is not a SMM. This could be attributed to its very small D value as determined by variable field-variable temperature magnetisation measurements. Such a small D value for 1 is not surprising since the highly symmetric Mn^{III}₆Mn^{II}₄ supertetrahedral unit that it contains is known to display a $D \approx 0$ and as a consequence not to be a SMM. Clearly there are remarkable analogies between the overall magnetic behaviour of 1 and its Mn^{III}₆Mn^{II}₄ supertetrahedral "building-block" as both clusters display ferromagnetic exchange interactions, high spin ground state, a nearly zero D, and do not exhibit SMM behaviour.¹²

In summary, the initial employment of H₂pd in mixed metal chemistry has led to a large Mn^{III}₂₈Mn^{II}₈Ni^{II}₄ cluster which consists of two Mn^{III}₈Ni₂ loops and two Mn^{III}₆Mn^{II}₄ supertetrahedral units. It represents a relatively rare example of a large cluster consisting of covalently linked polynuclear M_x (x > 6) complexes and the only one that contains a magnetically interesting polynuclear M_x repeating unit. The presence of the $S_T = 22$ Mn^{III}₆Mn^{II}₄ supertetrahedral unit in the structure of 1 affected dramatically the overall magnetic behaviour of the latter resulting in a high $S_{\rm T} = 26 \pm 1$ spin ground state, the highest observed in a heterometallic cluster. The isolation of 1 suggests that other aggregates that will contain only Mn^{III}₆Mn^{II}₄ or other magnetically interesting high nuclearity complexes as "building-blocks" are also possible. Such complexes could be of significant interest not only for their aesthetically pleasing structures but also for their magnetic properties since for example a cluster consisting of only Mn^{III}₆Mn^{II}₄ supertetrahedral units would likely have a giant ground spin state. Thus, further investigations targeting to the isolation of a series of analogues of 1 and/or large clusters composed of magnetically interesting Mn_xM_y complexes are in progress.

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Notes and references

‡ Vacuum-dried solid analyzed (C, H, N) as $1\cdot 10H_2O$. Calcd. (found): C, 26.19 (26.32); H, 4.06 (4.09); N, 0.85 (0.94)%. Metal analysis was performed *via* ICP-OES. Calcd. for $1\cdot 10H_2O$ (found): Mn, 29.94 (30.09); Ni, 3.55 (3.68)%.

Crystal data for 1·2CH₃CN·12.30H₂O: C₁₄₈H_{276.60}Cl₁₀Mn₃₆N₆O_{126.30}-Ni₄, M = 6728.33, monoclinic, a = 47.463(2) Å, b = 14.049(1) Å, c = 50.160 (2) Å, $\beta = 103.689(3)^\circ$, V = 32496(2) Å³, T = 100(2) K, space group I2/a, Z = 4, $\rho_{calcd} = 1.375$ g cm⁻³, 28 529 reflections collected, 11 651 reflections used, R_1 [$I > 2\sigma(I)$] = 0.0725, w $R_2 = 0.1702$. The asymmetric unit also contains severely disordered water molecules that could not be modeled properly. Thus, the SQUEEZE program was used to eliminate the contribution of the electron density in the disordered solvent region from the overall intensity data.

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