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"Squaring the clusters": a $Mn^{III}_4Ni^{II}_4$ molecular square from nickel(II)-induced structural transformation of a $Mn^{II/III/IV}_{12}$ cage[†]

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A $Mn^{III}_4Ni^{II}_4$ molecular square exhibiting slow magnetization relaxation has been prepared from the reaction of a $Mn^{II}_4Mn^{III}_6Mn^{IV}_2$ cluster and a simple Ni^{II} source.

Mixed-metal materials are still an attractive research area for many groups worldwide in the fields of solid-state chemistry and condensed-matter physics.¹ Molecular synthetic chemists have also shown an intense interest in mixed-metal complexes during the last two decades. A major reason for this is the search for complexes with interesting magnetic properties, such as singlemolecule magnets (SMMs),² single-chain magnets (SCMs),³ and 3D molecule-based magnets.⁴

SMMs often possess high spin (S) ground states and easyaxis-type magnetic anisotropy (as reflected in a large and negative zero-field splitting parameter, D), giving a significant energy barrier to reversal of the magnetization vector. To date, the vast majority of SMMs have been found among polynuclear homometallic manganese complexes (clusters) containing Mn^{III} atoms.⁵ This is due to the often large S values they possess, and the large and negative magnetoanisotropy associated with the presence of Jahn-Teller distorted Mn^{III} centres. Polynuclear heterometallic 3d-4f and 3d-3d' complexes occupy a special place among mixed-metal molecular materials because they offer an alternative⁶ to homometallic transition-metal SMMs and often exhibit unprecedented metal topologies and beautiful structural motifs. The hope has been that the combination of different metal ions will lead to new molecular species with larger magnetic anisotropies and higher S values, the latter arising from the different nature and strength of the magnetic exchange interactions between the heterospin carriers. Indeed, this approach has successfully led to several 3d-4f high-spin molecules and SMMs,⁷ but the 3d–3d' heterometallic analogues are still not so

developed,⁸ very likely due to the difficulties encountered in their synthesis.

From a synthetic viewpoint, methods must be devised to combine the two different 3d-metal ions within a cluster. One of the common routes is the "one-pot" procedure involving a mixture of 3d- and 3d'-metal salts, and a ligand possessing coordination affinity for both 3d metal ions. A more synthetically logical strategy deals with the use of "3d-metal complexes as ligands" (building blocks)⁹ for reactions with an additional 3d' metal source. A variety of anionic 2-pyridylmonoximes have been widely employed to date in the synthesis of structurally and magnetically interesting homometallic 3d and 3d-4f metal complexes,¹⁰ but their use in high-nuclearity 3d-3d' chemistry is rather limited to a few clusters.¹¹ These ligands are particularly attractive when one of the 3d metals is divalent, favoring their coordination with the softer N atoms, whereas the harder oximato O atom will favor binding to the trivalent 3d (i.e., Cr^{III}, Mn^{III}, Fe^{III}) or 4f metal.

Distorted octahedral Ni(II) complexes with an S = 1 spin state can have large D values;¹² the magnetic coupling between Ni^{II} and Mn^{III} is known to be stronger than that between Mn^{II} and Mn^{III,13} thus preventing complications from low-lying excited states in the analysis of the low-temperature magnetic susceptibility data. In addition, polynuclear heterometallic Mn^{III}–Ni^{II} complexes are relatively scarce.^{8a,11b,14} For such reasons, we have been targeting new synthetic procedures that might yield large-nuclearity Mn^{III}–Ni^{II} clusters. We have now discovered a synthetic entry into an unusual Mn^{III}₄Ni₄ molecular square from the reaction between a new Mn^{II/III/IV}₁₂ oxido–oximato cage-like cluster and a simple Ni^{II} source. We believe this work presages a fruitful new area in high nuclearity 3d–3d' metal cluster chemistry with unprecedented architectures and interesting magnetic properties.

The reaction of $Mn(ClO_4)_2 \cdot 6H_2O$, phenyl 2-pyridyl ketone oxime (ppkoH), and NEt₃ in a 1:1:1 molar ratio in MeCN gave a dark brown solution that upon slow evaporation at room temperature gave brown crystals of $[Mn_{12}O_8(OH)_2(ppko)_{12}-(H_2O)_2](OH)(ClO_4)_3 \cdot 2MeCN$ (1·2MeCN) in 80% yield.† Dissolution of **1** in CH₂Cl₂ and addition of 6 equivalents of Ni(ClO₄)₂ \cdot 6H₂O gave a dark red precipitate upon overnight stirring. The solid was dissolved in MeCN, and careful layering with Et₂O afforded red crystals of the heterometallic [Mn₄Ni₄-(OH)₈(ppko)₈(H₂O)₄](ClO₄)₄ (**2**) complex in 45% yield.† Note that neither "one-pot" Mn(ClO₄)₂/Ni(ClO₄)₂/ppkoH/NEt₃

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[†]Electronic supplementary information (ESI) available: Details for the preparations of **1** and **2** including microanalytical and IR data, and various structural and magnetic plots for both complexes. CCDC 860120 and 860119. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt00030j

procedures nor reactions between the known $[Ni(ppkoH)_3]$ - $(ClO_4)_2$ "metalloligand"¹⁵ and various Mn^{III} sources led to complex **2** under several conditions (*i.e.* conventional synthetic methods, solvothermal techniques, *etc.*).

The structure[†] of the cation of **1** lies on a crystallographic inversion center, and consists of a mixed-valent (Mn^{II}₄Mn^{III}₆-Mn^{IV}₂) Mn₁₂ cage-like cluster (Fig. 1, top) with an irregular structural conformation. The two μ_4 -O²⁻, six μ_3 -O²⁻ and two μ_3 -OH⁻ ions hold the twelve metal ions together (Fig. S1⁺), whereas peripheral ligation is provided by twelve chelatingbridging η^1 : η^1 : η^1 : μ ppko⁻ groups and two terminal H₂O molecules. The metallic skeleton of 1 can be conveniently dissected into three layers of two types with an ABA arrangement (Fig. S2[†]). Layer A is a $Mn^{II}_2Mn^{III}$ triangle with a capping μ_3 - OH^- ion, and layer **B** is a nearly planar $Mn^{III}_{4}Mn^{IV}_{2}$ 'rod' comprising four edge-sharing triangles. Each layer is held together and linked to its neighboring layer(s) by a combination of oxido, hydroxido and oximato bridges, the latter arising from the twelve ppko⁻ groups. The complex thus contains an overall $[Mn_{12}(\mu_4 O_{2}(\mu_{3}-O)_{6}(\mu_{3}-OH)_{2}(\mu-ON)_{12}]^{4+}$ core (Fig. 1, bottom). All Mn atoms are six-coordinate with distorted octahedral geometry, except five-coordinate Mn3 and Mn3' with intermediate geometry. The Mn^{II}-Mn^{III}-Mn^{IV} oxidation states were established from the metric parameters, bond valence sum (BVS) calculations,^{†16} and the presence of Jahn-Teller (JT) distortions at octahedral Mn³⁺. The protonation level of O²⁻ and OH⁻ groups was also confirmed by BVS calculations.

Complex 1 joins only a handful of previous Mn_{12} clusters containing Mn ions at three different oxidation levels. The previous $Mn^{II/III/IV}_{12}$ complexes are the various



Fig. 1 (top) Molecular structure of the cation of complex **1**. H atoms have been omitted for clarity. (bottom) The $[Mn_{12}(\mu_4-O)_2(\mu_3-O)_6(\mu_3-OH)_2(\mu-ON)_{12}]^{4+}$ core. Symmetry code: ' = -x, 1 - y, 2 - z. O7 (and its symmetry equivalent) is the hydroxido oxygen atom. Colour scheme: Mn^{II} yellow; Mn^{III} blue; Mn^{IV} olive; O red; N green; C grey.

$$\begin{split} & [Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]^{z-} \ (z=1-3)^{17a} \ \text{reduced versions} \\ & \text{of the } Mn_{12} \ \text{family of SMMs, and the } [Mn_{12}O_6-(OH)_4(OMe)_2(pko)_{12}]^{4+} \ \text{cation},^{17b} \ \text{featuring the anion of di-2-} \\ & \text{pyridyl ketone oxime.} \end{split}$$

The cation of 2 (Fig. 2, top) has crystallographic D_{4d} symmetry and is a [4 + 4] heterometallic molecular square comprising alternating Mn^{III} "side" and Ni^{II} "corner" ions linked by the oximate N–O⁻ arms of eight $\eta^1 : \eta^1 : \eta^1 : \mu$ ppko⁻ ligands and eight μ -OH⁻ groups.[†] The complex thus contains a $\left[Mn_4Ni_4(\mu\text{-OH})_8(\mu\text{-ON})_8\right]^{4+}$ core (Fig. S3†). Peripheral ligation around the Ni^{II} atoms is provided by eight pairs of N atoms (N1, N2, and their symmetry equivalents) that belong to the 'chelating' parts of the ppko- ligands and around Mn^{III} atoms by four terminal H₂O molecules (O3, and its symmetry equivalents). All $\mathrm{Ni}^{\mathrm{II}}$ and $\mathrm{Mn}^{\mathrm{III}}$ atoms are bound to an $\mathrm{O}_2\mathrm{N}_4$ and O_5 set of donor atoms, respectively. Thus, the Ni^{II} atoms are six-coordinate with distorted octahedral geometries, whereas the Mn^{III} atoms are five-coordinate with almost ideal square pyramidal geometries; the coordinated H₂O molecules occupy the apical positions, while each Mn^{III} atom lies 0.075 Å above the O₄ least-squares basal plane. The metal oxidation states and the protonation level of OH⁻ and H₂O groups were again established from metric parameters and BVS calculations.[†]



Fig. 2 (top) Labelled PovRay representation of the cation of complex **2**, with H atoms omitted for clarity. (bottom) A space-filling representation of **2**. Symmetry codes: (a) = x, -y, -z; (b) = -x, -y, z; (c) = -x, y, -z. Colour scheme: Mn^{III} blue; Ni^{II} cyan; O red; N green; C grey; H orange.

The $[Mn_4Ni_4]^{4+}$ "square" is not planar. The Mn…Ni, Mn…Mn, and Ni…Ni distances are within the 3.367–7.727, 5.348–7.353, and 6.570–9.292 Å ranges, respectively, while the Mn–OH–Ni angles and the Mn–O–N–Ni torsion angles are 117.8 and 2.6°, respectively. A space-filling representation (Fig. 2, bottom) shows that the cation of **2** has a diameter of 18.1 Å, with a central hole of 6.2 Å diameter defined by the shortest O(H)…O(H) distance; the voids between the cations are occupied by disordered counterions and lattice solvate molecules. The aesthetically pleasing symmetry of **2** extends to the packing of the $[Mn_4Ni_4]^{4+}$ cations in the crystal, as shown in Fig. S4[†].

Complex **2** is the first 3d–3d' molecular square synthesized to date and the first Mn–Ni cluster with a [4 + 4] metal ion stoichiometry. It is also one of the largest Mn–Ni clusters prepared to date and the first 3d–3d' complex containing ppkoH, with only three examples at higher nuclearities, Mn_6Ni_{12} , ¹⁸ Mn_4Ni_5 , ^{14g} and Mn_3Ni_6 .

Solid-state dc (direct current) magnetic susceptibility $(\chi_{\rm M})$ data were collected on 1 and 2 in a 1 kG (0.1 T) field in the 5.0–300 K range. The data are plotted as $\chi_{\rm M}T$ vs. T in Fig. S5⁺ and Fig. 3, respectively, and both 1 and 2 clearly have non-zero ground state spin (S) values. $\chi_{\rm M}T$ for 1 steadily decreases from 22.71 cm³ K mol⁻¹ at 300 K to 14.50 cm³ K mol⁻¹ at 50.0 K, and then rapidly decreases further to 7.40 cm³ K mol⁻¹ at 5.0 K. The overall shape of the curve and its low temperature value suggest a relatively small ground state spin value for 1 of $S \approx 3$, probably with low-lying excited states as expected for a highnuclearity, spin-frustrated system; the spin frustration is consistent with the many triangular units within the core topology of 1. For 2, $\chi_{\rm M}T$ steadily decreases from 16.46 cm³ K mol⁻¹ at 300 K to 8.97 cm³ K mol⁻¹ at 5.0 K, indicating antiferromagnetic $Mn^{III} \cdots Ni^{II}$ exchange interactions leading to an S = 4; the spinonly (g = 2) value for S = 4 is 10 cm³ K mol⁻¹. This is the expected ground state spin value for a 4Mn^{III},4Ni^{II} square topology and a simple 'spin-up'/'spin-down' alignment.

To determine the ground states of 1 and 2, magnetization (M) data were collected at various fields and at low temperature (1.8–10.0 K). For 1, several attempted fits assuming that only the ground state is populated were poor, suggesting population of low-lying excited states, as expected for such a high



Fig. 3 $\chi_M T vs. T$ data for **2**. (inset) Out-of-phase $\chi_M'' vs. T$ ac susceptibility signals in a 3.5 G field oscillating at the indicated frequencies.

nuclearity compound containing Mn^{II} atoms and exhibiting spin frustration effects. In contrast, the corresponding data for **2**, plotted as $M/N\mu_{\rm B}$ vs. H/T in Fig. S6,[†] were successfully fit by matrix diagonalization to a model that assumes only the ground state is populated, includes axial zero-field splitting and the Zeeman interaction, and carries out a full powder average. The best fit (solid lines in Fig. S6)[†] gave S = 4, g = 1.90(5) and D = -0.69(9) cm⁻¹.

The S = 3 and 4 ground states for 1 and 2, respectively, were further confirmed by ac (alternating current) susceptibility studies, and particularly by extrapolating to 0 K the $\chi_M'T$ data (Fig. S7 and S8)† above ~3 K. At lower temperatures than 3 K, both 1 (Fig. S9)† and 2 (Fig. 3, inset) display a weak frequencydependent decrease in $\chi_M'T$ and concomitant appearance of weak frequency-dependent tails of out-of-phase (χ_M'') ac susceptibility signals, whose maxima lie below the operating minimum temperature of our SQUID instrument. Such signals are indicative of the superparamagnet-like slow relaxation of an SMM, albeit with very small barriers for both compounds.

In conclusion, we have reported the first example of a heterometallic 3d–3d' molecular square from a Ni^{II}-induced structural transformation of a new, homometallic Mn^{II/III/IV}₁₂ cage-like cluster built with phenyl 2-pyridyl ketone oxime. Both the homo- and heterometallic products show evidence for SMM behavior, but with small barriers arising from the small ground state spin values. Further, complex **2** can be also viewed as a "magnetic precursor" to a Mn(III)–Ni(II) heterometallic chain, revealing an additional interesting aspect of this work. We are currently trying to (i) raise the value of *S* in **2** by replacing the μ -OH⁻ ions with end-on bridging pseudohalides (N₃⁻, OCN⁻, *etc.*), (ii) replace Ni^{II} or/and Mn^{III} ions in **2** with other paramagnetic divalent or/and trivalent metals, respectively, in order to alter the magnetic coupling and magnetoanisotropy, and (iii) prepare analogues of **1** with other 2-pyridyl oximes to be used as starting reagents for reactions with various 3d' metal sources.

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Notes and references

‡Crystal data for 1·4MeCN·6H₂O (including the contribution of disordered solvate molecules): C₁₅₆H₁₂₁Mn₁₂Cl₃N₃₀O₃₄, $M_w = 3725.46$, monoclinic, space group $P2_1/n$ with a = 17.9483(3), b = 21.9148(3), c = 21.9379(4) Å, $\beta = 98.882(2)^\circ$, V = 8525.4(2) Å³, T = 100(2) K, Z = 2, $D_c = 1.451$ g cm⁻³, 74 336 reflections collected, 10 832 unique ($R_{int} = 0.0575$), R1 [$I > 2\sigma(I)$] = 0.0428, $wR_2 = 0.1236$ (F^2 , all data). Crystal data for 2·4CH₂Cl₂·21.5H₂O (including the contribution of disordered solvate molecules): C₁₀₀H₁₂₃Mn₄Ni₄Cl₈N₁₆O_{57.5}, $M_w = 3207.34$, tetragonal, space group $I\overline{42}m$ with a = b = 16.7927(8), c = 25.9583(10) Å, $a = \beta = \gamma = 90$, V = 7320.1(6) Å³, T = 100(2) K, Z = 2, $D_c = 1.455$ g cm⁻³, 9559 reflections collected, 2391 unique ($R_{int} = 0.0742$), R1 [$I > 2\sigma(I)$] = 0.0751, $wR_2 = 0.2120$ (F^2 , all data), Flack parameter = -0.21(4).

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- (a) M. C. Francisco, C. D. Malliakas, P. M. B. Piccoli, M. J. Gutmann, A. J. Schultz and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2010, **132**, 8998; (b) N. Ikeda, H. Oshumi, K. Ohwada, K. Ishii, T. Inami and T. Kakurai, *Nature*, 2005, **436**, 1136.
- 2 E. J. Schelter, F. Karadas, C. Avendano, A. V. Prosvirin, W. Wernsdorfer and K. R. Dunbar, J. Am. Chem. Soc., 2007, 129, 8139.
- 3 H. Miyasaka, M. Julve, M. Yamashita and R. Clérac, *Inorg. Chem.*, 2009, 48, 3420.
- 4 O. Kahn, Acc. Chem. Res., 2000, 33, 647.
- 5 (a) C. J. Milios, S. Piligkos and E. K. Brechin, *Dalton Trans.*, 2008, 1809; (b) Th. C. Stamatatos and G. Christou, *Inorg. Chem.*, 2009, 48, 3308.
- 6 (a) R. Sessoli and A. K. Powell, *Coord. Chem. Rev.*, 2009, **253**, 2328; (b) M. Andruh, J.-P. Costes, C. Diaz and S. Gao, *Inorg. Chem.*, 2009, **48**, 3342; (c) X.-Y. Wang, C. Avendano and K. R. Dunbar, *Chem. Soc. Rev.*, 2011, **40**, 3213.
- 7 (a) S. Osa, T. Kido, N. Matsumoto, N. Re, A. Pochaba and J. Mrozinski, J. Am. Chem. Soc., 2004, 126, 420; (b) Th. C. Stamatatos, S. J. Teat, W. Wernsdorfer and G. Christou, Angew. Chem., Int. Ed., 2009, 48, 521; (c) A. M. Ako, V. Mereacre, R. Clérac, W. Wernsdorfer, I. J. Hewitt, C. E. Anson and A. K. Powell, Chem. Commun., 2009, 544; (d) S. K. Langley, B. Moubaraki and K. S. Murray, Dalton Trans., 2010, 39, 5066; (e) C. M. Zaleski, E. C. Depperman, J. W. Kampf, M. L. Kirk and V. L. Pecoraro, Angew. Chem., Int. Ed., 2004, 43, 3912; (f) C. Papatriantafyllopoulou, W. Wernsdorfer, K. A. Abboud and G. Christou, Inorg. Chem., 2011, 50, 421; (g) M. Holyńska, D. Premužić, I.-R. Jeon, W. Wernsdorfer, R. Clérac and S. Dehnen, Chem.–Eur. J., 2011, 17, 9605.
- A. Das, K. Gieb, Y. Krupskaya, S. Demeshko, S. Dechert, R. Klingeler, V. Kataev, B. Büchner, P. Müler and F. Meyer, J. Am. Chem. Soc., 2011, 133, 3433; (b) D. Li, S. Parkin, G. Wang, T. G. Yee, R. Clérac, W. Wernsdorfer and M. S. Holmes, J. Am. Chem. Soc., 2006, 128, 4214; (c) H. Oshio, M. Nihei, A. Yoshida, H. Nojiri, M. Nakano, A. Yamaguchi, Y. Karaki and H. Ishimoto, Chem.-Eur. J., 2005, 11, 843.
 For example: L. Lecren, W. Wernsdorfer, Y. G. Li, A. Vindigni,
- H. Miyasaka and R. Clérac, J. Am. Chem. Soc., 2007, **129**, 5045.
- 10 (a) P. Chaudhuri, Coord. Chem. Rev., 2003, 243, 143; (b) C. J. Milios, Th. C. Stamatatos and S. P. Perlepes, Polyhedron, 2006, 25, 134;

(c) C. Papatriantafyllopoulou, Th. C. Stamatatos, C. G. Efthymiou, L. Cunha-Silva, F. A. Almeida Paz, S. P. Perlepes and G. Christou, *Inorg. Chem.*, 2010, **49**, 9743; (d) C. Papatriantafyllopoulou, M. Estrader, C. G. Efthymiou, D. Dermitzaki, C. Gkotsis, A. Terzis, C. Diaz and S. P. Perlepes, *Polyhedron*, 2009, **28**, 1652.

- (a) H. Miyasaka, T. Nezu, F. Iwahori, S. Furukawa, K. Sugimoto, R. Clérac, K. Sugiura and M. Yamashita, *Inorg. Chem.*, 2003, 42, 4501;
 (b) G. Psomas, A. J. Stemmler, C. Dendrinou-Samara, J. J. Bodwin, M. Schneider, M. Alexiou, J. W. Kampf, D. P. Kessissoglou and V. L. Pecoraro, *Inorg. Chem.*, 2001, 40, 1562.
- 12 O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, 1993.
- 13 G. Rogez, J.-N. Rebilly, A.-L. Barra, L. Sorace, G. Blondin, N. Kirchner, M. Duran, J. van Slageren, S. Parsons, L. Ricard, A. Marvilliers and T. Mallah, *Angew. Chem.*, *Int. Ed.*, 2005, 44, 1876.
- (a) H. Oshio, M. Nihei, S. Koizumi, T. Shiga, H. Nojiri, M. Nakano, N. Shirakawa and M. Akatsu, J. Am. Chem. Soc., 2005, 127, 4568;
 (b) H. Miyasaka, T. Nezu, K. Sugimoto, K. Sugiura, M. Yamashita and R. Clérac, Inorg. Chem., 2004, 43, 5486;
 (c) M. Nihei, A. Yoshida, S. Koizumi and H. Oshio, Polyhedron, 2007, 26, 1997;
 (d) K. S. Gavrilenko, S. V. Punin, O. Cador, S. Golhen, L. Ouahab and V. V. Pavlishchuk, Inorg. Chem., 2005, 44, 5903;
 (e) H.-P. Jia, W. Li, Z.-F. Ju and J. Zhang, Inorg. Chem. Commun., 2007, 10, 397;
 (f) Y. Sunatsuki, H. Shimada, T. Matsuo, M. Nakamura, F. Kai, N. Matsumoto and N. Re, Inorg. Chem., 1998, 37, 5566;
 (g) H. Chen, C.-B. Ma, D.-Q. Yuan, M.-Q. Hu, H.-M. Wen, Q.-T. Liu and C.-N. Chen, Inorg. Chem., 2011, 50, 10342.
- 15 D. Dermitzaki, Th. C. Stamatatos and S. P. Perlepes, manuscript in preparation.
- 16 (a) I. D. Brown and D. Altermatt, Acta Crystallogr., Sect. B: Struct. Sci., 1985, 41, 244; (b) W. Liu and H. H. Thorp, Inorg. Chem., 1993, 32, 4102.
- 17 (a) R. Bagai and G. Christou, Chem. Soc. Rev., 2009, 38, 1011; (b) C. Dendrinou-Samara, C. M. Zaleski, A. Evagorou, J. W. Kampf, V. L. Pecoraro and D. P. Kessissoglou, Chem. Commun., 2003, 2668.
- 18 G. Wu, R. Clérac, W. Wernsdorfer, S. Qiu, C. E. Anson, I. J. Hewitt and A. K. Powell, *Eur. J. Inorg. Chem.*, 2006, 1927.