

Octanuclearity and tetradecanuclearity in manganese chemistry: an octanuclear manganese(II)/(III) complex featuring the novel $[\text{Mn}_8(\mu_4\text{-O})_2(\mu_3\text{-OH})_2]^{14+}$ core and $[\text{Mn}_{10}^{\text{II}}\text{Mn}_4^{\text{III}}\text{O}_4(\text{O}_2\text{CMe})_{20}\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_4]$ ($2\text{-py} = 2\text{-pyridyl}$)

Constantinos J. Milios,^a Elena Kefalloniti,^a Catherine P. Raptopoulou,^b Aris Terzis,^b Ramon Vicente,^c Nikolia Lalioti,^{*d} Albert Escuer^{*c} and Spyros P. Perlepes^{*a}

^a Department of Chemistry, University of Patras, 265 04 Patras, Greece.

E-mail: perlepes@patreas.upatras.gr

^b Institute of Materials Science, NCSR "Demokritos", 153 10 Aghia Paraskevi Attikis, Greece

^c Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain.

E-mail: albert.escuer@qi.ub.es

^d Department of Materials Science, University of Patras, 265 04 Patras, Greece. E-mail: lali@upatras.gr

Received (in Cambridge, UK) 23rd January 2003, Accepted 18th February 2003

First published as an Advance Article on the web 5th March 2003

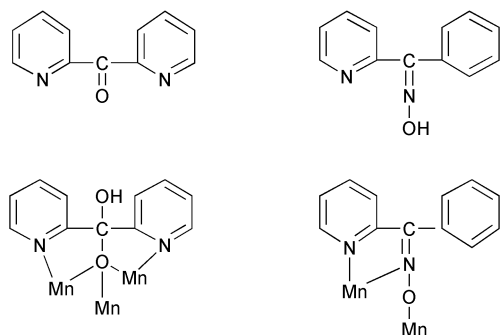
Reactions of Mn sources with di-2-pyridyl ketone, $(2\text{-py})_2\text{CO}$, and phenyl 2-pyridyl ketone oxime, $(\text{ph})(2\text{-py})\text{CNOH}$, give the novel clusters $[\text{Mn}_{10}^{\text{II}}\text{Mn}_4^{\text{III}}\text{O}_4(\text{O}_2\text{CMe})_{20}\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_4]$ **1** and $[\text{Mn}_4^{\text{II}}\text{Mn}_4^{\text{III}}\text{O}_2(\text{OH})_2(\text{O}_2\text{CPh})_{10}\{(\text{ph})(2\text{-py})\text{CNO}\}_4]$ **2**, respectively, which possess low-spin ground states; the observed tetradecanuclearity in **1** is extremely rare in 3d-metal chemistry, while the core of **2** has a unique topology consisting of two linked $[\text{Mn}_2^{\text{II}}\text{Mn}_2^{\text{III}}\text{O}(\text{OH})]$ units.

Manganese cluster chemistry is of current interest from a variety of viewpoints, including magnetic materials¹ and bioinorganic chemistry.² For example, in the former area, such clusters often possess large numbers of unpaired electrons making them attractive as potential precursors to molecule-based magnetic materials or as discrete, nanoscale magnetic particles in their own right ('single-molecule magnets').¹ While the number of polynuclear Mn complexes reported continues to grow rapidly, some nuclearities remain extremely rare.³ There is a small family of Mn clusters of nuclearity eight, which currently comprise the metal oxidation states Mn_8^{II} ,⁴ $\text{Mn}_6^{\text{II}}\text{Mn}_2^{\text{III}}$,⁵ $\text{Mn}_2^{\text{II}}\text{Mn}_6^{\text{III}}$ ⁶ and Mn_8^{III} .⁷ Only one tetradecanuclear Mn cluster has been structurally characterised; this is the impressive mixed-valent $[\text{Mn}_{12}^{\text{II}}\text{Mn}_2^{\text{III}}\text{O}_2(\text{OH})_4(\text{ppo})_{18}(\text{Hppo})_4(\text{NO}_3)_4(\text{MeCN})_4]$ molecule reported very recently by Winpenny⁸ (Hppo = 3-phenyl-3-pyrazolin-5-one). Here we report studies of two new $\{\text{Mn}14\}$ and $\{\text{Mn}8\}$ clusters which are the first members of the $\text{Mn}_{10}^{\text{II}}\text{Mn}_4^{\text{III}}$ and $\text{Mn}_4^{\text{II}}\text{Mn}_4^{\text{III}}$ sub-families, respectively.

The ligand system used for the preparation of the $\{\text{Mn}14\}$ compound is the $\text{MeCO}_2\text{-}/(2\text{-py})_2\text{CO}$ 'blend', where $(2\text{-py})_2\text{CO}$ is di-2-pyridyl ketone (Scheme 1). Several groups,⁹ including our group,¹⁰ have been exploring reaction schemes,

where the monoanion, $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$, or the dianion, $(2\text{-py})_2\text{CO}_2^{2-}$, of the *gem*-diol form of $(2\text{-py})_2\text{CO}$ (these anions are stabilised *only* in the presence of metal ions) and carboxylates are present in the same reaction. This has led to a large family of Co, Ni and Cu clusters with nuclearities ranging from three to twelve. We were wondering whether extension of this general ligand 'blend' in manganese chemistry would prove exciting. The ligand system used for the preparation of the $\{\text{Mn}8\}$ compound is the $\text{PhCO}_2\text{-}/(\text{ph})(2\text{-py})\text{CNOH}$ 'blend', where $(\text{ph})(2\text{-py})\text{CNOH}$ is phenyl 2-pyridyl ketone oxime (Scheme 1). The reason for the use of $(\text{ph})(2\text{-py})\text{CNOH}$ is that we have decided to extend our studies in the area of the polynuclear complexes of 3d-metals in moderate oxidation states by including ligands that present a similarity to $(2\text{-py})_2\text{CO}$. Our goal is to investigate to what extent such ligands might affect the identity of isolated products compared to $(2\text{-py})_2\text{CO}$ and to what extent this might thus prove a route to new cluster types. Our initial work was concentrated on di-2-pyridyl ketone oxime, $(2\text{-py})_2\text{CNOH}$, a ligand whose employment in Mn carboxylate chemistry gave a new family of mixed-valence $\text{Mn}_2^{\text{II}}\text{Mn}_2^{\text{III}}$ complexes.¹¹ In attempting to extend this family and to create new topologies, we have begun reactions featuring $(\text{ph})(2\text{-py})\text{CNOH}$. This ligand has different electronic properties compared with those of $(2\text{-py})_2\text{CNOH}$ and has never been employed in coordination chemistry.

In a typical experiment, $\text{Mn}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$ (0.110 g, 0.45 mmol) and $(2\text{-py})_2\text{CO}$ (0.084 g, 0.45 mmol) were stirred together in MeCN (20 mL) for 45 min in an *open* reaction flask. The reaction mixture was filtered to remove a small amount of pink-grey solid. The brownish-pink filtrate was layered with Et_2O (45 mL) to give X-ray quality, pale brown crystals of $[\text{Mn}_{14}\text{O}_4(\text{O}_2\text{CMe})_{20}\{(2\text{-py})_2\text{C}(\text{OH})\text{O}\}_4] \cdot 3.4\text{MeCN} \cdot 2.5\text{H}_2\text{O} \cdot 1.3.4\text{MeCN} \cdot 2.5\text{H}_2\text{O}$ in *ca.* 35% yield. The dried sample analysed as solvent free. †. The centrosymmetric molecule of **1** (Fig. 1) ‡. is mixed-valent containing four Mn^{III} [$\text{Mn}(1)$, $\text{Mn}(3)$ and their symmetry related partners] and ten Mn^{II} centres. A possible description of the core (Fig. 2) is based on $\{\text{Mn}7\}$ fragments. Each fragment contains the known¹² $[\text{Mn}_4^{\text{II}}\text{Mn}_2^{\text{III}}(\mu_4\text{-O})_2]^{10+}$ sub-core [the oxide ions are $\text{O}(41)$, $\text{O}(42)$, $\text{O}(41')$ and $\text{O}(42')$]. A seventh metal ion, $\text{Mn}(4)$, is attached to four metal ions of this sub-core by three 2.21 acetates (Harris notation¹³) and one 3.22 acetate [the one containing $\text{O}(39)$ and $\text{O}(40)$]; the latter and its symmetry equivalent serve to link the two heptanuclear fragments. Peripheral ligation is provided by four 3.311 $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$ ligands (Scheme 1) and twelve 2.11 acetates; the peripheral ligands bridge metal ions within the $[\text{Mn}_4^{\text{II}}\text{Mn}_2^{\text{III}}(\mu_4\text{-O})_2]^{10+}$ subcore. The topology of the latter consists of six Mn ions arranged as two edge-sharing $[\text{Mn}(1) \cdots \text{Mn}(3)]$ tetrahedra; at the centre of each tetrahedron lies a $\mu_4\text{-O}^{2-}$ ion.



Scheme 1 The neutral ligands $(2\text{-py})_2\text{CO}$ (top left), $(\text{ph})(2\text{-py})\text{CNOH}$ (top right) and their monoanions $(2\text{-py})_2\text{C}(\text{OH})\text{O}^-$, $(\text{ph})(2\text{-py})\text{CNO}^-$ in the 3.311, 2.111 coordination modes, respectively (bottom).

In addition to 'the edge-sharing tetrahedra' description of the sub-core, another way of describing it emphasizes its structural relationship to known smaller nuclearity Mn/O units. The Mn_6O_2 sub-core can be considered to contain the $[Mn_2^{II}Mn_2^{III}(\mu_3-O)_2]^{6+}$ unit¹⁴ and completion of the sub-core requires merely the conversion of the two μ_3-O^{2-} to μ_4-O^{2-} by ligation to additional Mn^{II} sites.

Bond valence sum (BVS) calculations indicate that Mn(1) and Mn(3) are Mn^{III} , while the remaining metal centres are Mn^{II} . In addition, Mn(1) and Mn(3) display Jahn–Teller (JT) elongation (as expected for high-spin $3d^4$ ions in near octahedral geometry), with the JT axes avoiding the short strong $Mn^{III}-O^{2-}$ bonds. Mn(1, 2, 3, 7) are bound to an octahedral O_6 set of donor atoms, while Mn(5, 6) to an O_4N_2 set. Mn(4) is seven coordinate, possessing a distorted pentagonal bipyramidal geometry, with the axial positions comprising O(40) and O(34) from the $3.22 MeCO_2^-$ and one $2.21 MeCO_2^-$, respectively.

Complex **1** represents a new addition to the family of known Mn clusters containing N- or O- donor ligands with nuclearities higher than 12.^{8, 15–22} Tetradecanuclear clusters are particularly uncommon in 3d-metal chemistry. Several polyoxovanadate cages are known,²³ and a few copper sulfide²⁴ and phosphide²⁵ clusters as well. Only one {M14} complex containing N- or O-donor ligands, with a 3d-metal other than Mn, has been structurally characterized; this is a beautiful hexacation containing an $[Fe_{14}O_{12}(OH)_{16}]^{2+}$ core.²⁶

Solid state dc magnetic susceptibility measurements were performed on **1** in the range 2.0–300 K in a field of 0.1 T. The $\chi_M T$ value of $42.7 cm^3 mol^{-1} K$ at room temperature decreases gradually with decreasing temperature to $2.36 cm^3 mol^{-1} K$ at 2.0 K. The spin-only ($g = 2$) value for a unit composed of non-interacting $10Mn^{II}, 4Mn^{III}$ ions is $55.8 cm^3 mol^{-1} K$. Hence, the molecule appears to possess strong intramolecular antiferromagnetic interactions.¹⁷ Magnetization data at 2 K were

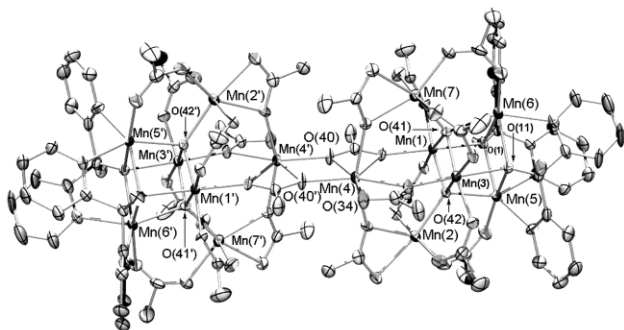


Fig. 1 ORTEP representation of **1**. Thermal ellipsoids are at the 30% probability level. Primed and unprimed atoms are related by the crystallographic inversion centre.

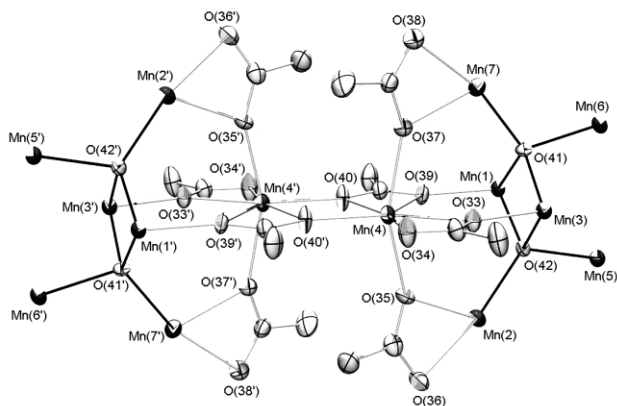


Fig. 2 A simplified view of **1** emphasizing the $[Mn_6(\mu_4-O)_2]^{10+}$ sub-cores, the attachment of Mn(4) and Mn(4') to these units and the dimerization of the {Mn7} fragment.

collected in the field range -5 to 5 T. It was not possible to obtain a good fit for these data assuming that only the ground state is populated at this temperature. There is a linear dependence of the magnetization upon the applied field indicating that several energy levels are close to the ground state and are populated even at 2 K.²⁷ The low-spin ground state indicated for **1** is not surprising given its structural relationship to the family of hexanuclear compounds containing the $[Mn_4^{II}Mn_2^{III}(\mu_4-O)_2]^{10+}$ core,¹² which have been found to have $S = 0$. Low-spin ground states are not uncommon in large Mn_x clusters ($x > 12$).^{8, 18–21}

Treatment of a stirred colourless solution of $Mn(O_2CPh)_2 \cdot 2H_2O$ (0.166 g, 0.50 mmol) in EtOH/MeCN (15 mL, 2:1 v/v) with $NBu_4^+MnO_4^-$ (0.060 g, 0.16 mmol) resulted in a dark brown solution. To this was slowly added solid (ph)(2-py)CNOH (0.100 g, 0.50 mmol) which was soon dissolved to give a solution of essentially the same colour. The solvents were then evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (25 mL), filtered and the filtrate layered with Et₂O/n-hexane (50 mL, 1:1 v/v) to give X-ray quality, dark brown crystals of $[Mn_8O_2(OH)_2(O_2CPh)_{10}\{(ph)(2-py)CNO\}_4] \cdot 4CH_2Cl_2 \cdot 2 \cdot 4CH_2Cl_2$ in ca. 55% yield. The dried sample analysed as solvent free. † The molecule of **2** (Fig. 3) ‡ lies on an inversion centre and has a novel $[Mn_8(\mu_4-O)_2(\mu_3-OH)_2]^{14+}$ core with peripheral ligation provided by two monodentate and eight bridging (four 2.11 and four 3.21)¹³ $PhCO_2^-$ groups, and four 2.111 (Scheme 1) (ph)(2-py)CNO⁻ ligands. Mn(1) and Mn(3) are bound to an O_4N_2 set of donor atoms, while Mn(2) and Mn(4) to an O_6 set. Charge considerations indicate a $4Mn^{II}, 4Mn^{III}$ oxidation level description. Mn(2) and Mn(3) [and their symmetry related Mn(2') and Mn(3')] are assigned as Mn^{II} ions on the basis of the longer Mn–O bond lengths at these ions (no individual value shorter than 2.07 Å) compared with those for the other metal ions, and the clear presence of a JT axial elongation at Mn(1) and Mn(4) (and their symmetry related partners). The JT axes are O(21)–Mn(1)–N(11) and O(42)–Mn(4)–O(51'). BVS calculations were also performed and the obtained values of 3.21, 2.12, 1.75 and 3.20 for Mn(1), Mn(2), Mn(3) and Mn(4), respectively, are in agreement with the above assignments. The core of the molecule (Fig. 4) may be conveniently described as two $[Mn_2^{II}Mn_2^{III}(\mu_3-O)(\mu_3-OH)]^{7+}$ units [atoms Mn(1)–Mn(4) and their symmetry related partners] linked *via* one μ_3-O^{2-} ion in each unit converting to a μ_4 mode and thus providing the two 'inter-fragment' bonds, Mn(4)–O(21') and Mn(4')–O(21). The four metal ions in each unit are nearly coplanar. Although tetranuclear complexes containing the $[Mn_4(\mu_3-O)_2]$ core, where the metals are arranged in either planar or nonplanar ('butterfly') fashion and the metal oxidation states are $Mn_2^{II}Mn_2^{III}$, $Mn^{II}Mn_3^{III}$ or Mn_4^{III} , have been reported,²⁸ compounds with the $[Mn_4(\mu_3-O)(\mu_3-OH)]$ core are unknown.

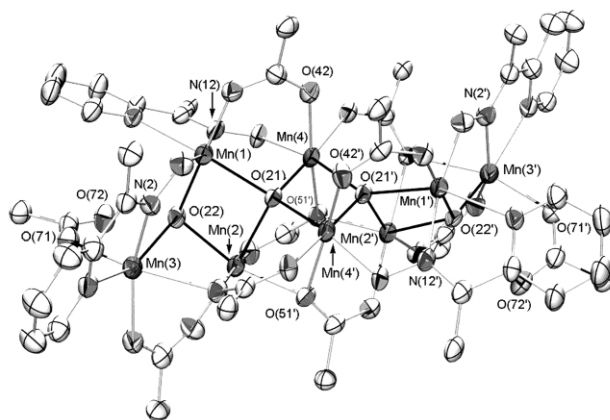


Fig. 3 ORTEP representation of **2**. Thermal ellipsoids are at the 30% probability level. Primed and unprimed atoms are related by the crystallographic inversion centre. Only the *ipso* carbon atoms of the phenyl groups of the benzoate and oximate ligands are shown.

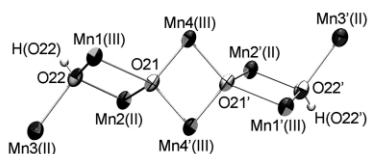


Fig. 4 ORTEP representation of the $[\text{Mn}_4^{\text{II}}\text{Mn}_4^{\text{III}}(\mu_4\text{-O})_2(\mu_3\text{-OH})_2]^{14+}$ core of **2** emphasizing the linked-tetranuclear structure.

The value of $\chi_{\text{M}}T$ per $\{\text{Mn}8\}$ decreases from $25.2 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at room temperature to $0.82 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2.0 K. The value at room temperature is smaller than the expected for an uncoupled $\{\text{Mn}_4^{\text{II}}\text{Mn}_4^{\text{III}}\}$ system with $g = 2$ ($29.5 \text{ cm}^3 \text{ K mol}^{-1}$). A well defined maximum of χ_{M} appears at 16 K. The drop of $\chi_{\text{M}}T$ with decreasing temperature reflects the presence of strong antiferromagnetic interactions within the cluster, presumably leading to a spin ground state of $S = 0$.²⁷ Since typically $\text{Mn}^{\text{II}} \cdots \text{Mn}^{\text{II}}$ and $\text{Mn}^{\text{II}} \cdots \text{Mn}^{\text{III}}$ exchange interactions are weak and antiferromagnetic,⁵ the apparent $S = 0$ spin ground state of **2** seems to be a consequence of the well established¹² strong antiferromagnetic coupling at the central $[\text{Mn}_2^{\text{III}}\text{O}_2]$ unit of the molecule; this strong, dominating coupling will give an $S = 0$ ground state for the complete molecule.⁵

In summary, the use of the $\text{RCO}_2^-/(2\text{-py})_2\text{CO}$ and $\text{RCO}_2^-/(\text{ph})(2\text{-py})\text{CNOH}$ 'blends' in Mn chemistry has provided access to the first members of the $\text{Mn}_{10}^{\text{II}}\text{Mn}_4^{\text{III}}$ and $\text{Mn}_4^{\text{II}}\text{Mn}_4^{\text{III}}$ subfamilies of complexes. Manganese carboxylate chemistry continues to surprise with the structural variety and aesthetic beauty of its molecular complexes.

We thank Professor D. Gatteschi (Florence) for permitting us to collect the magnetic data of **1** at his laboratory and for helpful discussions.

Notes and references

† Satisfactory analyses (C, H, N) were obtained for **1** and **2**. Crystals of both complexes were mounted in capillary to avoid solvent loss.

‡ Crystal data for $\text{C}_{90.8}\text{H}_{111.2}\text{Mn}_{14}\text{N}_{11.4}\text{O}_{54.5}$, **1**: $3.4\text{MeCN} \cdot 2.5\text{H}_2\text{O}$: $M = 3003.45$, monoclinic, space group $P2_1/c$, $a = 11.792(6)$, $b = 23.62(1)$, $c = 23.85(1)$ Å, $\beta = 96.30(2)^\circ$, $V = 6604(5)$ Å³, $T = 298$ K, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 1.375 \text{ mm}^{-1}$, 9045 reflections collected, 8760 unique ($R_{\text{int}} = 0.0651$), $R1 = 0.0699$ for 5426 reflections with $I > 2\sigma(I)$. For $\text{C}_{122}\text{H}_{96}\text{Cl}_8\text{Mn}_8\text{N}_8\text{O}_{28}$, **2**: $4\text{CH}_2\text{Cl}_2$: $M = 2845.19$ monoclinic, space group $C2/c$, $a = 32.889(8)$, $b = 16.543(4)$, $c = 33.206(8)$ Å, $\beta = 136.09(1)^\circ$, $V = 12530(5)$ Å³, $T = 298$ K, $Z = 4$, $\mu(\text{Cu-K}\alpha) = 8.544 \text{ mm}^{-1}$, 6602 reflections collected, 6462 unique ($R_{\text{int}} = 0.0220$), $R1 = 0.0650$ for 4495 reflections with $I > 2\sigma(I)$. Structure solution and refinement were performed using programs SHELXS-86 and SHELXL-97. CCDC 195208 (**1**: $3.4\text{MeCN} \cdot 2.5\text{H}_2\text{O}$) and 195209 (**2**: $4\text{CH}_2\text{Cl}_2$). See <http://www.rsc.org/suppdata/cc/b3/b300986f/> for crystallographic data in CIF or other electronic format.

- G. Christou, D. Gatteschi, D. N. Hendrickson and R. Sessoli, *MRS Bull.*, 2000, **25**, 725.
- S. S. Mukhopadhyay, R. J. Staples and W. W. Armstrong, *Chem. Commun.*, 2002, 864.
- R. E. P. Winpenny, *Adv. Inorg. Chem.*, 2001, **52**, 1.
- For example, see: R. W. Saalfrank, N. Löw, B. Demleitner, D. Stalke and M. Teichert, *Chem. Eur. J.*, 1998, **4**, 1305.

- C. Boskovic, W. Wernsdorfer, K. Folting, J. C. Huffman, D. N. Hendrickson and G. Christou, *Inorg. Chem.*, 2002, **41**, 5107.
- M. W. Wemple, H.-L. Tsai, S. Wang, J. P. Claude, W. E. Streib, J. C. Huffman, D. N. Hendrickson and G. Christou, *Inorg. Chem.*, 1996, **35**, 6437.
- E. Libby, K. Folting, C. J. Huffman, J. C. Huffman and G. Christou, *Inorg. Chem.*, 1993, **32**, 2549; H.-L. Tsai, S. Wang, K. Folting, W. E. Streib, D. N. Hendrickson and G. Christou, *J. Am. Chem. Soc.*, 1995, **117**, 2503; S. Wang, H.-L. Tsai, K. Folting, J. D. Martin, D. N. Hendrickson and G. Christou, *J. Chem. Soc., Chem. Commun.*, 1994, 671; V. A. Grillo, M. J. Knapp, J. C. Bollinger, D. N. Hendrickson and G. Christou, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1818.
- G. Aromi, A. Bell, S. J. Teat, A. G. Whittaker and R. Winpenny, *Chem. Commun.*, 2002, 1896.
- For example, see: M.-L. Tong, S.-L. Zheng, J.-X. Shi, Y. Tong, H. K. Lee and X.-M. Chen, *J. Chem. Soc., Dalton Trans.*, 2002, 1727; M. G. Barandika, Z. Serna, R. Cortes, L. Lezana, M. K. Uriaga, M. I. Arriortua and T. Rojo, *Chem. Commun.*, 2001, 45.
- For example, see: G. S. Papaefstathiou, A. Escuer, R. Vicente, M. Font-Bardia, X. Solans and S. P. Perlepes, *Chem. Commun.*, 2001, 2414; G. S. Papaefstathiou, S. P. Perlepes, A. Escuer, R. Vicente, M. Font-Bardia and X. Solans, *Angew. Chem., Int. Ed.*, 2001, **40**, 884; G. S. Papaefstathiou and S. P. Perlepes, *Comments Inorg. Chem.*, 2002, **23**, 249.
- C. J. Milios, C. P. Raptopoulou, A. Terzis, R. Vicente, A. Escuer and S. P. Perlepes, manuscript in preparation.
- A. R. Schake, J. B. Vincent, Q. Li, P. D. W. Boyd, K. Folting, J. C. Huffman, D. N. Hendrickson and G. Christou, *Inorg. Chem.*, 1989, **28**, 1915.
- R. A. Coxall, S. G. Harris, D. K. Henderson, S. Parsons, P. A. Tasker and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 2001, 2349.
- J. B. Vincent, C. Christmas, H.-R. Chang, Q. Li, P. D. W. Boyd, J. C. Huffman, D. N. Hendrickson and G. Christou, *J. Am. Chem.*, 1989, **111**, 2086.
- Z. Sun, P. K. Gantzel and D. N. Hendrickson, *Inorg. Chem.*, 1996, **35**, 6640.
- D. J. Price, S. R. Batten, B. Moubaraki and K. S. Murray, *Chem. Commun.*, 2002, 762.
- E. K. Brechin, C. Boskovic, W. Wernsdorfer, J. Yoo, A. Yamaguchi, E. C. Sañudo, T. R. Concolino, A. L. Rheingold, H. Ishimoto, D. N. Hendrickson and G. Christou, *J. Am. Chem.*, 2002, **124**, 9710.
- E. K. Brechin, W. Clegg, M. Murrie, S. Parsons, S. J. Teat and P. Winpenny, *J. Am. Chem. Soc.*, 1998, **120**, 7365.
- R. C. Squire, S. M. J. Aubin, K. Folting, W. E. Streib, G. Christou and D. N. Hendrickson, *Inorg. Chem.*, 1995, **34**, 6463.
- H. J. Eppley, N. deVries, S. Wang, S. M. Aubin, H.-L. Tsai, K. Folting, D. N. Hendrickson and G. Christou, *Inorg. Chim. Acta*, 1997, **263**, 323.
- L. A. M. Pohl, L. G. Westin and M. Kritikos, *Chem. Eur. J.*, 2001, **7**, 3439.
- J. T. Brockman, J. C. Huffman and G. Christou, *Angew. Chem., Int. Ed.*, 2002, **41**, 2506.
- For example, see: A.-L. Barra, D. Gatteschi, L. Pardi, A. Müller and J. Döring, *J. Am. Chem. Soc.*, 1992, **114**, 8509.
- For example, see: H. J. Schugar, C.-C. Ou, J. A. Thich, Potenza, T. R. Felthouse, M. S. Haddad, D. N. Hendrickson, W. Furey Jr. and R. A. Lalancette, *Inorg. Chem.*, 1980, **19**, 543.
- A. Eichhofer, O. Fenske and W. Holstein, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 242.
- J. Burger and P. Klüfers, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 776.
- Detailed magnetic studies will be reported in the full paper.
- B. Albelá, M. S. El Fallah, J. Ribas, K. Folting, G. Christou and N. Hendrickson, *Inorg. Chem.*, 2001, **40**, 1037 and refs. therein.