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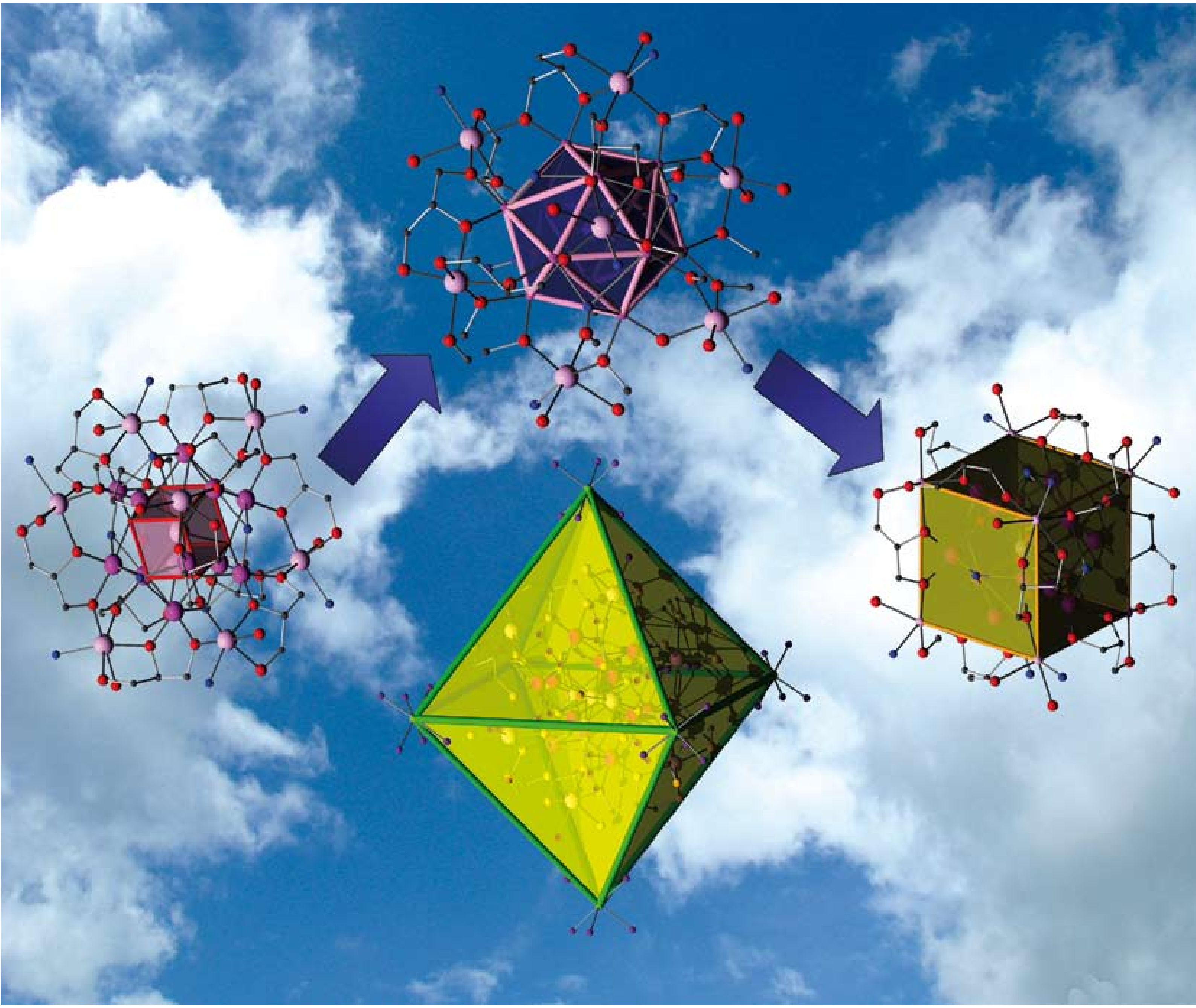

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Concentric Archimedean polyhedra: $Mn^{III}_{12}Mn^{II}_9$ aggregates linked into a cubic network†‡

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A $Mn^{III}_{12}Mn^{II}_9$ aggregate has a structure built up of concentric polyhedra with these units linked into a cubic network to give a remarkably pleasing structure isotypic with iron pyrites.

Over the past twenty years or so there has been an explosion of interest in the coordination chemistry of manganese clusters.[1] This is the result of attempts to model the tetramanganese cluster at the oxygen evolving centre of Photosystem II[2] and of the realisation that, when such clusters contain Mn^{III} centres, the Ising-type anisotropy of these can lead to interesting magnetic behaviour such as single molecule magnetism.[3] These stimuli have led to the isolation of a large number of new manganese clusters[4] most of which display topologies which, unlike the many beautiful compounds based on polyoxometallates,[5] are hard to describe in terms of any regular polyhedra. However, in the course of our investigations into synthesising high spin Mn^{II}/Mn^{III} clusters, we found that using propan-1,2,3-triol ($glycH_3$; glycerol) as a ligand with azide as co-ligand led to the formation of a manganese cluster§ in which the manganese centres describe a set of concentric Archimedean polyhedra. These clusters are linked into a 3-D network isotypic to the iron pyrites structure as explained below. Upon heating, the porous compound undergoes a subtle structural rearrangement with the loss of some lattice waters. To date, this system represents the highest nuclearity manganese cluster which is linked into a 3-D network.[6]

The structures of a fresh (as-prepared) crystal of **1** and a crystal that had been heated to 120 °C overnight (**1a**) were both determined at 100 K. **1** was formulated as $[\{Mn^{III}_{12}Mn^{II}_9(\mu_4\text{-}O)_8(glycH)_{12}(\mu\text{-}1,1\text{-}N_3)_6(OH_2)_6(N_3)_{1.5}\}\{Mn^{II}(\mu\text{-}1,3\text{-}N_3)_{4.5}(OH_2)_{1.5}\}]Cl_4\cdot ca.7.5H_2O$, where $(glycH)^{2-}$ is the dianion of propan-1,2,3-triol, resulting from double deprotonation of glycerol. The chloride anions and some lattice waters were not directly observable in the structure and are presumably heavily disordered, but could be inferred from microanalytical data, as could the complete loss of the lattice waters in **1a**.

Both the as-prepared (**1**) and heated (**1a**) samples crystallise in the cubic space group $Pa\bar{3}$.¶ For **1a** the reflections were, as expected, broader and the diffraction intensity fell away sharply at $2\theta > 45°$. The crystal quality was still sufficient for the structure to be determined and refined, albeit with significantly higher *R*-factors and some difficulties in fully resolving the ligand disorder. Generally no great differences from the structure of **1** could be found although heating the crystals causes a slight reduction in the unit cell volume, with *a* decreasing from 21.6500(7) to 21.5248(12) Å and the volume decreasing by 1.72% from 10147.8(6) to 9972.8(10) $Å^3$. The structural description given below is based on the dataset obtained for **1**.

The structure of the $Mn^{III}_{12}Mn^{II}_9$ aggregate can be regarded as a series of concentric Archimedean polyhedra (Fig. 1). At the centre is a Mn^{II} cation, Mn(1), which lies on a site of crystallographic $\bar{3}$ symmetry (Wyckoff site *a*). This is surrounded by eight oxo ligands, with Mn(1)–O = 2.333(3), 2.369(4) Å. These oxygens describe an almost perfect cube, with O···O in the range 2.700–2.709 Å and the O···O···O angles all between 89.0 and 90.8°. These oxygens are further surrounded by a slightly distorted icosahedron of twelve Mn^{III} cations (Mn(2), Mn(3) and their symmetry-equivalents), with each oxygen forming a (μ_4-O) bridge between Mn(1) and three of the Mn^{III} centres. The O–Mn^{III} distances are all in the range 1.932–1.937 Å, the Mn^{II}–O–Mn^{III} angles are 98.30(13)–99.38(11)° and the Mn^{III}–O–Mn^{III} angles are in the range 115.73(13)–120.33(14)°. These twelve Mn^{III} centres are all also linked pair-wise by six (μ-1,1-N_3) azide ligands, with Mn(2)–N(11)–Mn(3) = 127.23(17)°.

The eight triangular faces of the Mn^{III}_{12} icosahedron that are bridged by one of the oxo ligands are capped by a Mn^{II} centre (Mn(4), Mn(5) or their symmetry-equivalents), which are each linked *via* three deprotonated oxygens of ligands to the Mn^{III} centres at the vertices of the respective triangles. These eight Mn^{II} cations thus form a cube surrounding the Mn^{III}_{12} icosahedron.

Each of the twelve $(glycH)^{2-}$ ligands provides two μ_2-alkoxo bridges, with the third hydroxyl group of each ligand coordinating as a terminal ligand to a capping Mn^{II}. In the as-prepared complex, both these ligands are partly disordered as shown in Fig. 2. While two of the oxygens are fixed, as are the carbons to which they are bonded, the remaining –CH_2OH group can be attached to either of these carbons resulting in it being disordered against a terminal ligand. In the case of the ligand involving oxygens O(3) and O(4), the hydroxymethyl

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‡ Dedicated to Professor Jan Reedijk on the occasion of his 65th birthday.

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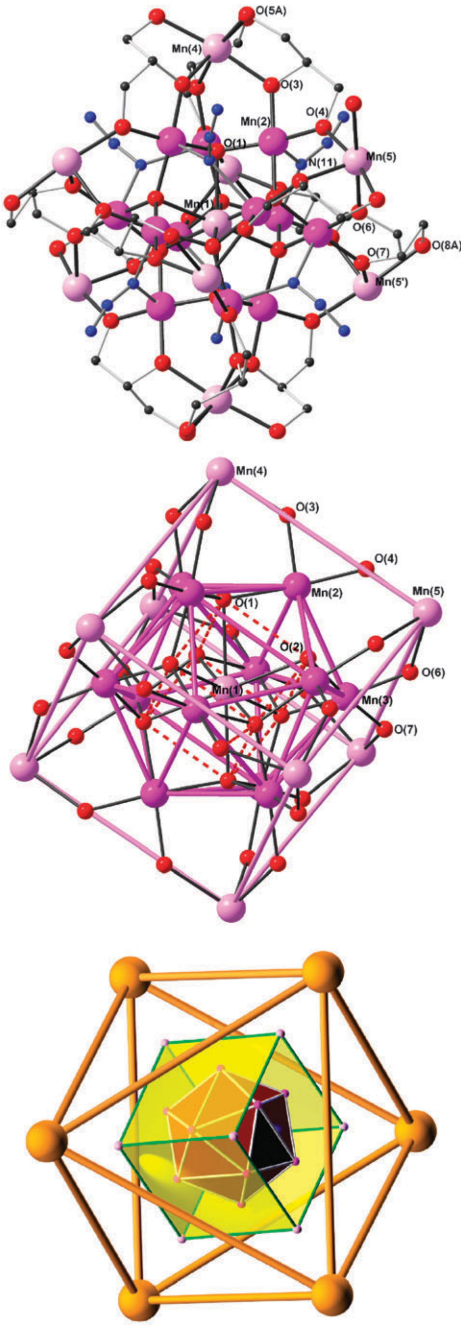

Fig. 1 The Mn_{21} aggregate (top). The core of concentric Archimedean polyhedra (middle) showing the cubic array of eight oxo ligands about Mn(1) as red dashed lines, the purple lines show the icosahedron of Mn^{III} centres and the pink lines the cube of outer Mn^{II} centres, which are inscribed into linked octahedra of Mn^{II} ions (lower) creating the cubic network.

group is coordinated to Mn(4) as the major component, 75% O(5A), while an aqua ligand O(9A) is coordinated to Mn(5). In the corresponding minor component, O(5B) is coordinated to Mn(5), while an azide is coordinated to Mn(4). This behaviour is more important with the second independent $(glycH)^{2-}$ ligand. In this case in the major (75%) component O(8A) is coordinated to Mn(5′) while the azide nitrogen N(21A) occupies a site on Mn(5). In the minor component this is reversed and O(8B) coordinates to Mn(5) and O(21B) to Mn(5′). N(23A) is coordinated to the mononuclear Mn^{II} cation Mn(6), with the azide ligand forming a (μ-1,3-N_3) bridge, but this has only 75% occupancy. The octahedral coordination sphere of Mn(6), which also lies on site of crystallographic $\bar{3}$ symmetry (Wyckoff site *b*), is completed by the aqua ligand O(23B) with 25% occupancy. Thus on average within the crystal structure $4\frac{1}{2}$ of the six coordination sites on Mn(6) are occupied by azides bridging from Mn_{21} aggregates, and $1\frac{1}{2}$ by aqua ligands.

Each cluster unit is thus further surrounded by six different Mn^{II} mononuclear units which describe the vertices of an octahedron, giving the last of our concentric polyhedra (Fig. 1 and S1 in ESI†), although it is not covalently linked to all of these because of the ligand disorder about Mn(6). With its cubic array of alternating cationic and anionic species with coordination numbers {6:6} the structure is strongly reminiscent of that of NaCl. A more appropriate structural type, however, would be that of iron pyrites (FeS_2) which derives from a symmetry-lowering of the NaCl structure to space group Pa$\bar{3}$. In the present case the Mn_{21} units in the present structure occupy the sites of $\bar{3}$ symmetry corresponding to the positions of the disulfide dianions in FeS_2 (Fig. 3).

Since the compound easily loses some lattice waters when isolated from the mother liquor, magnetic measurements were performed on a polycrystalline sample maintained in its mother liquor. For compound **1**, the χT product at room temperature is 51.4 cm^3 $Kmol^{-1}$ which is lower than the expected value (79.75 cm^3 $Kmol^{-1}$) for the presence of ten Mn^{II} metal ions (S = 5/2, g = 2: C 4.375 cm^3 $Kmol^{-1}$) and twelve Mn^{III} ions (S = 2, g = 2: C = 3 cm^3 $Kmol^{-1}$) (Fig. S3, ESI†). On lowering the temperature, the χT product at 1000 Oe steadily decreases to reach a minimum value of 9.2 cm^3 K mol^{-1} at 1.8 K, indicating dominant antiferromagnetic interactions. The χT product showed no clear plateau at low temperature. The magnetization as a function of field at low temperatures was measured up to 7 T between 1.8 and 8 K. Even at 7 T and 1.8 K, the magnetic moment, that reaches 22.2 μ_B, is not saturated. These results suggest the presence of magnetic anisotropy or a field-induced population of

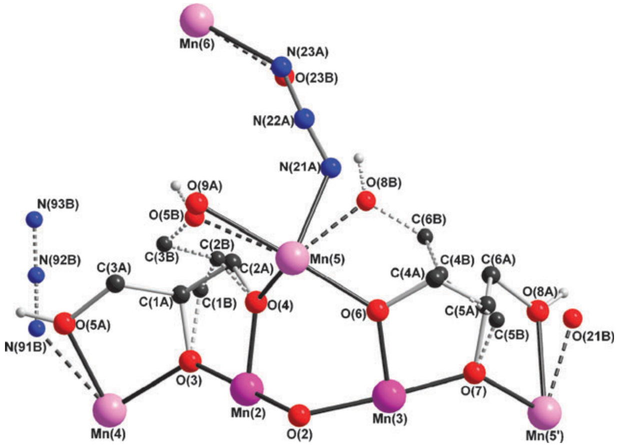

Fig. 2 The disorder of the organic and terminal ligands in the structure of **1**. Minor disorder components are shown with dotted bonds.

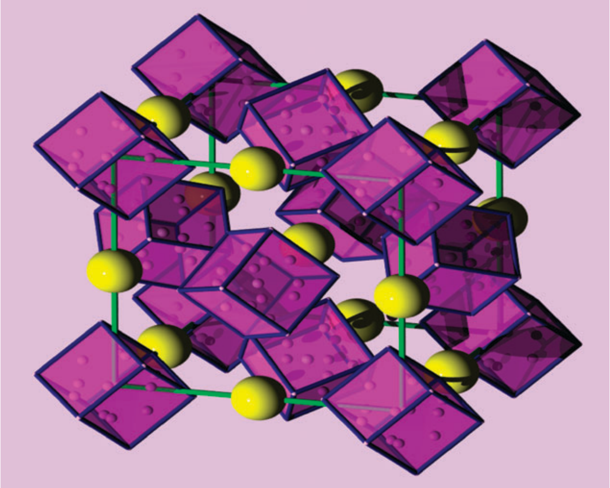

Fig. 3 A Pov-Ray representation of the cationic cluster-units (cube) and anionic Mn^{II} linkers (yellow spheres) in the 3D network which resembles iron pyrites lattice type.

low-lying excited states in the Mn_{21} units, or (most likely) a combination of these. The *M versus H*/*T* plot confirmed that these effects are relevant, as the data are not superposed on a single master-curve as would be expected for a system with isotropic and well-defined spin ground states. Antiferromagnetic interactions between the Mn_{21} aggregates and the surrounding mononuclear Mn^{II} centres through the azide bridges are also possible. Overall, the interpretation of the magnetic behaviour is complicated by these effects, although the data suggest that Mn_{21} aggregates should have non-zero ground spin states.

In summary, using simple starting components we have found a system which self-assembles into a remarkably symmetric array consisting of Mn_{21} aggregates where, unusually for open-shell 3d metals, the manganese ions are arranged in concentric Archimedean polyhedra. Thus a central Mn is surrounded by further Mn ions arranged first as an icosahedron, then a cube and finally an octahedron, the vertices of which link to further units to give an array as found in the iron pyrites structure.

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Notes and references

§ *Synthesis:* $MnCl_2 \cdot 4H_2O$ (198 mg, 1 mmol) was added with vigorous stirring to a solution of propan-1,2,3-triol (73 μL, 1 mmol) in methanol (20 mL). The resulting solution was added with stirring to a solution of sodium azide (65 mg, 1 mmol) in MeOH (5 mL). The final solution was stirred for 8 h, filtered and left undisturbed at room temperature. Slow evaporation of the solvent gave black prism shaped crystals of **1** within 3 weeks in approximately 30% yield.
Elemental analysis (%): **1** calcd for $C_{36}H_{102}Cl_4Mn_{22}N_{36}O_{59}$ C 12.97, H 3.08, N 15.12; found: C 12.74, H 3.05, N 15.25. **1a** calcd for $C_{36}H_{87}Cl_4Mn_{22}N_{36}O_{51.5}$ (corresponding to loss of all lattice waters) C 13.52, H 2.74, N 15.76; found: C 13.50, H 3.25, N 16.15%; Selected IR data (KBr disc, cm^{-1}): 3401 (b), 2928 (s), 2877 (s), 2063 (vs), 1633 (m), 1466 (m), 1348 (m), 1321 (m), 1265 (m), 1086 (vs), 1021 (s), 956 (s), 917 (m), 860 (s), 743 (vs), 593 (s).
¶ *Crystallography:* Data were measured on a Bruker SMART Apex diffractometer at 100 K. Structure solution and full-matrix least-squares refinement were carried out using the SHELXTL software package.[7] The disorder of the $(glycH)^{2-}$ ligands and associated terminal ligands was modelled using partial atoms; some geometrical and similarity restraints were used as necessary. Attempts were made to refine the structure in lower-symmetry space groups ($P2_13$, $R\bar{3}$ and Pbca) using appropriate TWIN commands,[8] to see if the disorder of the organic ligands was in fact the result of a twinning of a lower-symmetry structure. No improvement was found, and the disorder is considered genuine; it presumably goes back to the formation of the Mn_{21} units in solution, before these crystallise into the observed crystal lattice.
1: $C_{36}H_{102}Cl_4Mn_{22}N_{36}O_{59}$, 3334.02 g mol^{-1}, cubic, $Pa\bar{3}$, a = 21.6500(7) Å, V = 10147.8(6) $Å^3$, Z = 4, T = 100 K, $F(000)$ = 6640, D_c = 2.182 g cm^{-3}, μ(Mo-Kα) = 2.848 mm^{-1}. 66 744 data measured, of which 3719 unique (R_{int} = 0.0383), 292 parameters, 22 restraints, wR_2 = 0.1652, S = 1.056 (all data), R_1 = 0.0551 (3227 with $I > 2\sigma(I)$), largest final difference peak/hole +1.17/−1.54 e $Å^{-3}$.
Magnetism: The magnetic measurements were obtained using a Quantum Design SQUID magnetometer MPMS-XL between 1.8 and 400 K for dc applied fields ranging from −7 to 7 T. The ac susceptibility measurements were measured with an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz. *M vs. H* measurements were performed at 100 K to check for the presence of ferromagnetic impurities which were found to be absent. Data were corrected for the diamagnetic contribution.

1 H. J. Eppley, H. L. Tsai, N. de Vries, K. Folting, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1995, **117**, 301; G. Rajaraman, M. Murugesu, E. C. Sanudo, M. Soler, W. Wernsdorfer, M. Helliwell, C. Muryn, J. Raftery, S. J. Teat, G. Christou and E. K. Brechin, *J. Am. Chem. Soc.*, 2004, **126**, 15445; R. Sessoli, H. L. Tsai, Anna R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1993, **115**, 1804.

2 I. J. Hewitt, J. Tang, N. T. Madhu, R. Clérac, G. Buth, C. E. Anson and A. K. Powell, *Chem. Commun.*, 2006, 2650; S. Mukhopadhyay, H. J. Mok, R. J. Staples and W. H. Armstrong, *J. Am. Chem. Soc.*, 2004, **126**, 9202; A. Cua, D. H. Stewart, M. J. Reifler, G. W. Brudvig and D. F. Bocian, *J. Am. Chem. Soc.*, 2000, **122**, 2069; C. Tommos, J. McCracken, S. Styring and G. T. Babcock, *J. Am. Chem. Soc.*, 1998, **120**, 10441.

3 C.-I. Yang, W. Wernsdorfer, Y.-J. Tsai, G. Chung, T.-S. Kuo, G.-H. Lee, M. Shieh and H.-L. Tsai, *Inorg. Chem.*, 2008, **47**, 1925; A. M. Ako, V. Mereacre, I. J. Hewitt, R. Clérac, L. Lecren, C. E. Anson and A. K. Powell, *J. Mater. Chem.*, 2006, **16**, 2579; R. Bagai, K. A. Abboud and G. Christou, *Dalton Trans.*, 2006, 3306; L. M. Wittick, L. F. Jones, P. Jensen, B. Moubaraki, L. Spiccia, K. J. Berry and K. S. Murray, *Dalton Trans.*, 2006, 1534.

4 C.-H. Ge, Z.-H. Ni, C.-M. Liu, Ai-Li. Cui, D.-Q. Zhang and H.-Z. Kou, *Inorg. Chem. Commun.*, 2008, **11**, 675; J. T. Brockman, T. C. Stamatatos, W. Wernsdorfer, K. A. Abboud and G. Christou, *Inorg. Chem.*, 2007, **46**, 9160; T. Stamatatos, K. A. Abboud, W. Wernsdorfer and G. Christou, *Angew. Chem., Int. Ed.*, 2007, **46**, 884; M. Manoli, A. Prescimone, R. Bagai, A. Mishra, M. Murugesu, S. Parsons, W. Wernsdorfer, G. Christou and E. K. Brechin, *Inorg. Chem.*, 2007, **46**, 6968; A. M. Ako, I. J. Hewitt, V. Mereacre, R. Clérac, W. Wernsdorfer, C. E. Anson and A. K. Powell, *Angew. Chem., Int. Ed.*, 2006, **45**, 4296; A. M. Ako, I. J. Hewitt, V. Mereacre, R. Clérac, W. Wernsdorfer, C. E. Anson and A. K. Powell, *Angew. Chem.*, 2006, **118**, 5048–5051; M. Murugesu, W. Wernsdorfer, K. A. Abboud, E. K. Brechin and G. Christou, *Dalton Trans.*, 2006, 2285; M. Murugesu, M. Habrych, W. Wernsdorfer, K. A. Abboud and G. Christou, *J. Am. Chem. Soc.*, 2004, **126**, 4766; A. J. Tasiopoulos, A. Vinslava, W. Werndorfer, K. A. Abboud and G. Christou, *Angew. Chem., Int. Ed.*, 2004, **43**, 2117; M. Murugesu, J. Raftery, W. Wernsdorfer, G. Christou and E. K. Brechin, *Inorg. Chem.*, 2004, **43**, 4203.

5 See for example: S. Alvarez, *Dalton Trans.*, 2005, 2209; A. Müller, S. Sarkar, S. Q. N. Shah, H. Bögge, M. Schmidtmann, S. Sarkar, P. Kögerler, B. Hauptfleisch, A. X. Trautwein and V. Schünemann, *Angew. Chem., Int. Ed.*, 1999, **38**, 3238.

6 E. E. Moushi, T. C. Stamatatos, W. Wernsdorfer, V. Nastopoulos, G. Christou and A. J. Tasiopoulos, *Angew. Chem., Int. Ed.*, 2006, **45**, 7722.

7 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **A64**, 112.

8 R. Herbst-Irmer and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1998, **B54**, 443.