A self-assembled hexadecanuclear 4 × [2 × 2] Mn(II)$_{16}$ square grid from a pyridazine bis(hydrazone) ligand: synthesis, structure and magnetism†

Subrata K. Dey, Laurence K. Thompson* and Louise N. Dawe

Received (in Cambridge, UK) 4th August 2006, Accepted 26th September 2006
First published as an Advance Article on the web 12th October 2006
DOI: 10.1039/b611267f

A compartmentalized {4 × [2 × 2]} Mn(II)$_{16}$ antiferromagnetically coupled square grid results from the self-assembly reaction of a tetratopic pyridazine bis(hydrazone) ligand and Mn(II).

Ditopic and tritopic picolinic hydrazone based ligands (Fig. S1†) have proven to be powerful precursors for the self-assembly of high nuclearity square [2 × 2] M$_4$ (M = Mn, Co, Ni, Cu, Zn),[1–3] and [3 × 3] M$_9$ (M = Mn, Fe, Co, Ni, Cu, Zn)[4–9] grids, M$_5$ (M = Mn, Co, Zn)[10] trigonal bipyramidal clusters, Cu$_8$ pinwheels,[11] and a Cu$_{36}$ spheroidal cluster.[12] Examples of both antiferromagnetic (Mn(II)) and ferromagnetic (Cu(II)) systems are observed, suggesting that polynuclear systems based on larger ligands in this class would display interesting magnetic properties, possibly with large ground state spins. A recent review[13] focuses on examples of square [2 × 2], [3 × 3] and [4 × 4] self-assembled grid-like metal ion arrays formed from a series of ditopic, tritopic and tetratopic ligands, with an emphasis on their potential importance as nanoscale platforms for possible molecular information storage and processing. Important attributes in this context include redox, optical and magnetic properties. It is of interest to note that magnetic square [4 × 4] systems have not yet been reported.

The tetratopic bis(hydrazone) ligand L1 (Fig. 1, R = H) has two pairs of coordination pockets, arranged on either side of a central pyridazine group, which can in principle bind to four metal ions. It is synthesized readily from the precursor pyridazine dimethylester by reaction with hydrazine, followed by reaction with pyridine-2-carboxaldehyde. The projected bend in the subunit shown in Fig. 1 was considered to be a possible impediment for self-assembly to form a [4 × 4] M$_{16}$ grid. This was also suggested by previous reports of an incomplete Cu(II)$_{12}$ grid-like assembly,[14] and a linear helical trinuclear Ni(II) complex with a coordination site occupied by water instead of a metal ion,[15] with L2 (R = NH$_2$).

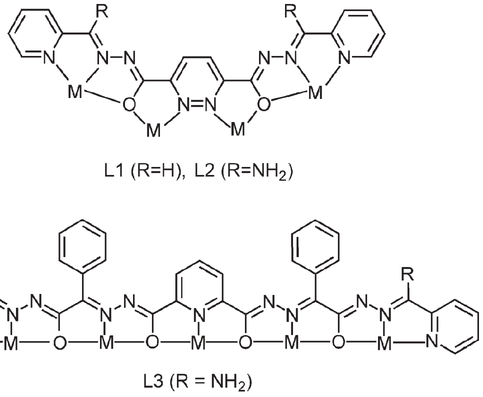

Fig. 1 Tetratopic and pentatopic hydrazone ligands.

Reaction of L1 with Mn(II) salts in the presence of air produced orange coloured products, with the deep red-orange crystalline material [Mn$_{16}$(L1)$_8$(OH)$_8$](NO$_3$)$_8$(H$_2$O)$_{29}$ (**1**) resulting from the reaction with Mn(NO$_3$)$_2$·6H$_2$O in MeOH–CH$_3$CN.‡ Such colours are typical of the [2 × 2] and [3 × 3] Mn(II) grids,[4,9] while [3 × 3] manganese grids containing mixed spin states, *e.g.* [Mn(III)$_4$Mn(II)$_5$(2poap)$_6$](ClO$_4$)$_{10}$ (**2**) (2poap = tritopic picolinic bis(hydrazone) ligand; see ESI†), produced by electrochemical or chemical oxidation (*e.g.* with Cl$_2$) of the Mn(II)$_9$ precursor, are dark brown, and have a moderately intense visible absorption (700 nm) in solution (CH$_3$CN), which is associated with intervalence charge transfer.[16] No such absorption is observed for **1**, indicating the presence of Mn(II).

A single crystal diffraction study shows that **1** is the square Mn$_{16}$ grid [Mn$_{16}$(L1)$_8$(OH)$_8$](NO$_3$)$_8$ (**1**).§ The structure of the hexadecanuclear cation is shown in Fig. 2, and the core structure involving just the metal ions and the immediate ligand donor atoms is shown in Fig. 3. The cation has crystallographically imposed two-fold symmetry. During the refinement process only one nitrate was located in the asymmetric unit, but elemental analysis‡ clearly indicates that eight are present. The PLATON Squeeze[17] procedure was employed to account for disordered

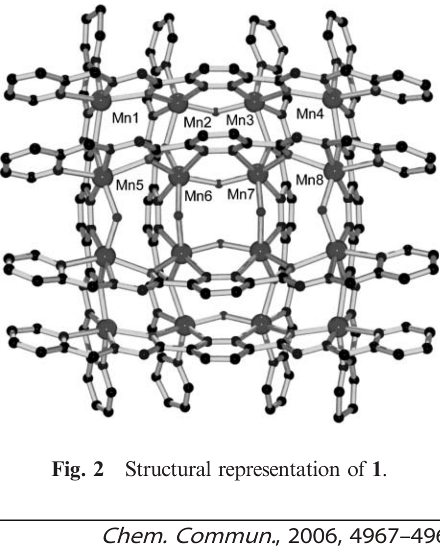

Fig. 2 Structural representation of **1**.

Dept of Chemistry, Memorial University, St. John's, Newfoundland, Canada A1B 3X7. E-mail: lthomp@mun.ca; Fax: 01-709-737-3702; Tel: 01-709-737-8750

† Electronic supplementary information (ESI) available: Synthetic details for the ligand L1 and Fig. S1. See DOI: 10.1039/b611267f

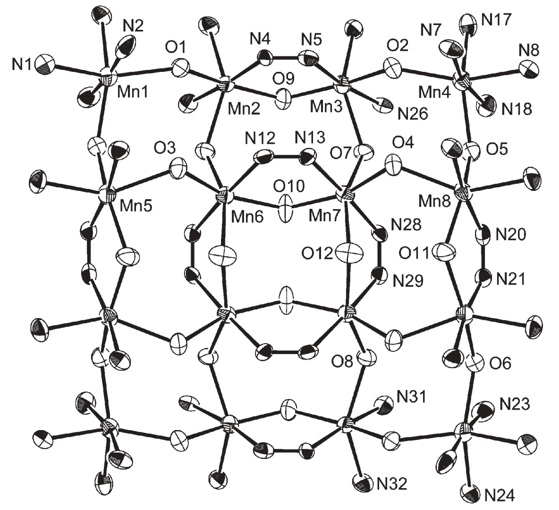

Fig. 3 Core structure of **1**.

solvent waters for which a good point atom model could not be achieved. The missing nitrates are presumed to be present in the disordered solvent waters. The application of Squeeze gave a significant improvement in the data statistics. Sixteen pseudo-octahedral Mn ions are arranged in a square array (Fig. 3), bound to eight ligands which are arranged in two roughly parallel groups of four above and four below the metal pseudo plane. A sideways view of the grid (Fig. 4) shows that, in fact, the sixteen metal ion arrangement is not strictly planar, but has a puckered structure, in keeping with the predicted bent ligand conformation (Fig. 1). The grid can be divided into four [2 × 2] [$Mn_4(\mu\text{-}O)_4$] subunits, resulting from the congruence of the tridentate end pockets of the ligands, with the metals bridged by deprotonated hydrazone oxygen atoms. Therefore, technically, the overall structure is best described as a 4 × [2 × 2] 'grid of grids'. Each [2 × 2] subunit is then joined to its neighbours by a pyridazine bridge. Metal–ligand distances (2.179–2.207 Å on average) indicate that all manganese ions are Mn(II). In a previous study on the mixed oxidation state Mn(II)/Mn(III) grid **2**, average Mn(III)–L distances were <2.07 Å, with Mn(II)–L distances in the range 2.20–2.23 Å.[16]

Since the inner ligand pockets are only bidentate, an extra donor is necessary to satisfy the six-coordinate requirement of the inner Mn(II) centres. On the basis of the Mn–L distances and the elemental analysis, it is reasonable to assume that adventitious hydroxide ions fill the breach, and end up providing μ-OH connections between remaining pairs of metal ions, in addition to the pyridazine bridges. Eight hydroxide ions are therefore required, and are presumed to come from residual water in the solvent mixture under basic conditions.

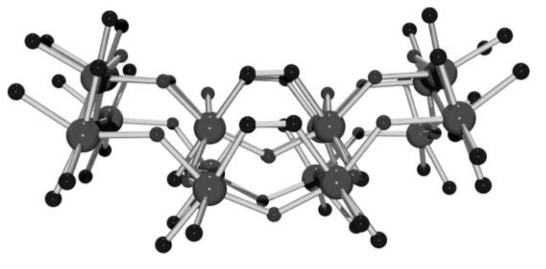

Fig. 4 Sideways projection of the core in **1** (Mn = large spheres).

Within each [$Mn_4(\mu\text{-}O)_4$] square, Mn–Mn distances fall in the range 3.82–4.00 Å, and Mn–O–Mn angles fall in the range 119.7–128.8°. These values differ slightly from those observed in the comparable [2 × 2] square grids,[1–3] but this is to be expected based on the presence of the hydroxide and pyridazine bridges connecting the [2 × 2] subunits. Mn–Mn distances involving the pyridazine bridges fall in the range 3.63–3.70 Å, which is typical for dinuclear complexes involving tetradentate and hexadentate pyridazine ligands.[18] Hydroxide bridge angles fall in the range 118.8–126.5°, again typical of the simpler dinuclear systems.

The dimensions of the Mn_4 oxygen bridged subunits would suggest that the magnetic properties of these grid components are likely to be dominated by antiferromagnetic exchange interactions, and the connectivity between them *via* the combined $\mu\text{-}N_2/\mu\text{-}OH$ bridges would also lead to antiferromagnetic exchange. Magnetic data for **1** were obtained in the temperature range 2–300 K, and the plots of susceptibility and moment (per mole) as a function of temperature are shown in Fig. 5. The maximum in the χ_{mol} *vs.* T profile at ~6 K signifies the presence of intramolecular antiferromagnetic exchange, and this is confirmed by a drop in moment from 21.2 μ_B at 300 K to 3.3 μ_B at 2 K. The room temperature moment is slightly lower than the spin only value for sixteen Mn(II) centers (23.6 μ_B), which would be expected. Low temperature moments for the $Mn(II)_9$ [3 × 3] grids are around 6 μ_B, close to the value expected for one residual Mn(II) centre in the low temperature antiferromagnetic limit for an odd numbered symmetric [$n \times n$] grid.[8,9,16] The even number of spin centres in **1** would suggest a low temperature moment approaching zero, which is consistent with the observed value at 2 K. No attempt has been made at this time to carry out a full analysis of the exchange interactions in this grid, in large measure because of the enormity of the matrix calculations required to determine the spin state/energy spectrum. However, on the basis of the similarity between the [2 × 2] $Mn(II)_4$ subunits in **1** and [2 × 2] and [3 × 3] Mn(II) grids already reported, with related ditopic and tritopic picolinic hydrazone ligands, J values in the range −2 to −5 cm^{-1} might be anticipated for the hydrazone oxygen bridging connections.[2,8,9,16,19]

One other example of a 4 × [2 × 2] M_{16} grid has been reported, with a pyrimidine based hydrazone ligand and Pb(II),[20] but [4 × 4] Pb_{16} grids have been reported with tetratopic ligands based on multiple pyrimidine fragments.[21,22] However, **1** appears to be the first magnetically coupled paramagnetic example in this class, and

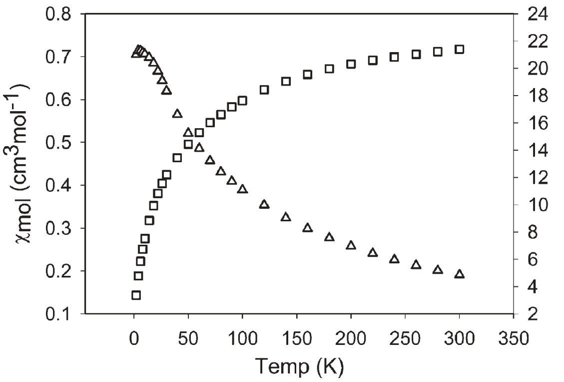

Fig. 5 Variable temperature magnetic properties (χ_{mol} △, and μ_{mol} □) of **1**.

opens the way to other magnetic grids with different transition metal ions. Extending this type of ligand to higher polytopic order can be achieved by connecting repeating components so that an approximately linear array of coordination pockets is established. This has been done with multiple 3,6-disubstituted pyridazine subunits terminated with pyridine rings, and a linear pentatopic ligand was created. Complexation with Ag(I) was shown to form a 2 × [2 × 5] grid array, rather than a [5 × 5] grid, because of the lack of rotational rigidity in the ligand backbone.[23] Hydrazone ligands have the advantage of undergoing significant tautomeric charge delocalization along the hydrazone backbone, particularly when deprotonated, and consequently adopt flatter ligand conformations. Larger pentatopic ligands, *e.g.* L3 (Fig. 1), have this structural attribute, and are currently under study. They have the potential to produce [5 × 5] self-assembled M_{25} grids, highlighting the important strategy of extending the ligand with repeating hydrazone functional groups, and the importance of ligand rigidity in assisting in the self-assembly process. The prospect of organizing large numbers of paramagnetic metal ions, *e.g.* M_{16}, M_{25}, in a predictable manner in a small region of 'nanospace' presents exciting possibilities for the production of systems with novel magnetic and electronic properties, and, based on our previous experience with [3 × 3] $Mn(II)_9$ grids, the potential also for surface applications (*e.g.* on HOPG (highly ordered pyrolytic graphite)), and device behaviour.[24] A recent review, highlighting advances in techniques of addressing individual metal ions in grid and cluster supramolecular metal ion assemblies, shows the power of STS/CITS (scanning tunneling spectroscopy/current induced tunneling spectroscopy) imaging on HOPG, and paves the way forward for the possible direct spectroscopic imaging of single metal centres.[25]

Notes and references

‡ *Synthesis of **1***: $Mn(NO_3)_2\cdot 6H_2O$ (3.5 mmol) was added to a stirred suspension of L1 (1.5 mmol) (synthesis included in ESI†) in MeOH–CH_3CN (1 : 1, 30 mL), with the addition of a few drops of NEt_3 (pH ∼7). A red-orange solution formed, which was heated with stirring at 75 °C for 35 min, and then was allowed to stand at room temperature. A deep orange crystalline solid formed after two weeks (yield 55%), which was dissolved in DMSO–MeOH (3 : 2, 20 mL), and the volume was reduced, giving orange-red crystals, suitable for a structural determination, on standing. Elemental analysis. Calc. (%) for $Mn_{16}(C_{18}H_{12}N_8O_2)_8(OH)_8(NO_3)_8(H_2O)_{29}$: C, 34.51; H, 3.26; N, 20.12. Found (%): C, 34.31; H, 2.83; N, 20.09.

§ *Crystal data for **1***: $C_{144}H_{96}Mn_{16}N_{66}O_{30}$, $M = 4109.77$, monoclinic, $a = 40.32(2)$, $b = 12.990(6)$, $c = 22.830(12)$ Å, $\alpha = 90$, $\beta = 117.670(8)$, $\gamma = 90°$, $U = 10\,590(9)$ Å^3, $T = 153(2)$ K, space group $C2$, $Z = 2$, μ(Mo-Kα) = 9.88 cm^{-1}, 35 421 reflections measured, 16 847 unique ($R_{int} = 0.060$), used in the calculations, $R1 = 0.0868$, w$R2 = 0.2330$ ($I > 2\sigma(I)$). CCDC 616858. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611267f

1 C. J. Matthews, K. Avery, Z. Xu, L. K. Thompson, L. Zhao, D. O. Miller, K. Biradha, K. Poirier, M. J. Zaworotko, C. Wilson, A. E. Goeta and J. A. K. Howard, *Inorg. Chem.*, 1999, **38**, 5266.
2 L. K. Thompson, C. J. Matthews, L. Zhao, Z. Xu, D. O. Miller, C. Wilson, M. A. Leech, J. A. K. Howard, S. L. Heath, A. G. Whittaker and R. E. P. Winpenny, *J. Solid State Chem.*, 2001, **159**, 308.
3 Z. Xu, L. K. Thompson, C. J. Matthews, D. O. Miller, A. E. Goeta and J. A. K. Howard, *Inorg. Chem.*, 2001, **40**, 2446.
4 L. Zhao, C. J. Matthews, L. K. Thompson and S. L. Heath, *Chem. Commun.*, 2000, 265.
5 L. Zhao, Z. Xu, L. K. Thompson, S. L. Heath, D. O. Miller and M. Ohba, *Angew. Chem., Int. Ed.*, 2000, **39**, 3114.
6 O. Waldmann, R. Koch, S. Schromm, P. Müller, L. Zhao and L. K. Thompson, *Chem. Phys. Lett.*, 2000, **332**, 73.
7 O. Waldmann, L. Zhao and L. K. Thompson, *Phys. Rev. Lett.*, 2002, **88**, 066401.
8 L. Zhao, Z. Xu, L. K. Thompson and D. O. Miller, *Polyhedron*, 2001, **20**, 1359.
9 L. K. Thompson, L. Zhao, Z. Xu, D. O. Miller and W. M. Reiff, *Inorg. Chem.*, 2003, **42**, 128.
10 C. J. Matthews, L. K. Thompson, S. R. Parsons, Z. Xu, D. O. Miller and S. L. Heath, *Inorg. Chem.*, 2001, **40**, 4448.
11 V. A. Milway, V. Niel, T. S. M. Abedin, Z. Xu, L. K. Thompson, H. Grove, D. O. Miller and S. R. Parsons, *Inorg. Chem.*, 2004, **43**, 1874.
12 T. S. M. Abedin, L. K. Thompson, D. O. Miller and E. Krupicka, *Chem. Commun.*, 2003, 708.
13 M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine and J.-M. Lehn, *Angew. Chem., Int. Ed.*, 2004, **43**, 3644.
14 C. J. Matthews, S. T. Onions, G. Morata, M. B. Salvia, M. R. Elsegood and D. J. Price, *Chem. Commun.*, 2003, 320.
15 L. K. Thompson, C. J. Matthews, L. Zhao, C. Wilson, M. A. Leech and J. A. K. Howard, *J. Chem. Soc., Dalton Trans.*, 2001, 2258.
16 L. K. Thompson, T. L. Kelly, L. N. Dawe, H. Grove, M. T. Lemaire, J. A. K. Howard, E. Spencer, C. J. Matthews, S. T. Onions, S. J. Coles, P. N. Horton, M. B. Hursthouse and M. E. Light, *Inorg. Chem.*, 2004, **43**, 7605.
17 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
18 S. S. Tandon, L. K. Thompson, M. E. Manuel and J. N. Bridson, *Inorg. Chem.*, 1994, **33**, 5555.
19 O. Waldmann, H. U. Güdel, T. L. Kelly and L. K. Thompson, *Inorg. Chem.*, 2006, **45**, 3295.
20 S. T. Onions, A. M. Frankin, P. N. Horton, M. B. Hursthouse and C. J. Matthews, *Chem. Commun.*, 2003, 2864.
21 A. M. Garcia, F. J. Romero-Salguero, D. M. Bassani, J.-M. Lehn, G. Baum and D. Fenske, *Chem.–Eur. J.*, 1999, **5**, 1803.
22 M. Barboiu, G. Vaughan, R. Graff and J.-M. Lehn, *J. Am. Chem. Soc.*, 2003, **125**, 10257.
23 P. N. W. Baxter, J.-M. Lehn, G. Baum and D. Fenske, *Chem.–Eur. J.*, 2000, **6**, 4510.
24 V. A. Milway, S. M. T. Abedin, V. Niel, T. L. Kelly, L. N. Dawe, S. K. Dey, D. W. Thompson, D. O. Miller, M. S. Alam, P. Müller and L. K. Thompson, *Dalton Trans.*, 2006, 2835.
25 M. Ruben, J.-M. Lehn and P. Müller, *Chem. Soc. Rev.*, 2006, **35**, DOI: 10.1039/b517267p.