Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

An octanuclear iron(III) isobutyrate wheel

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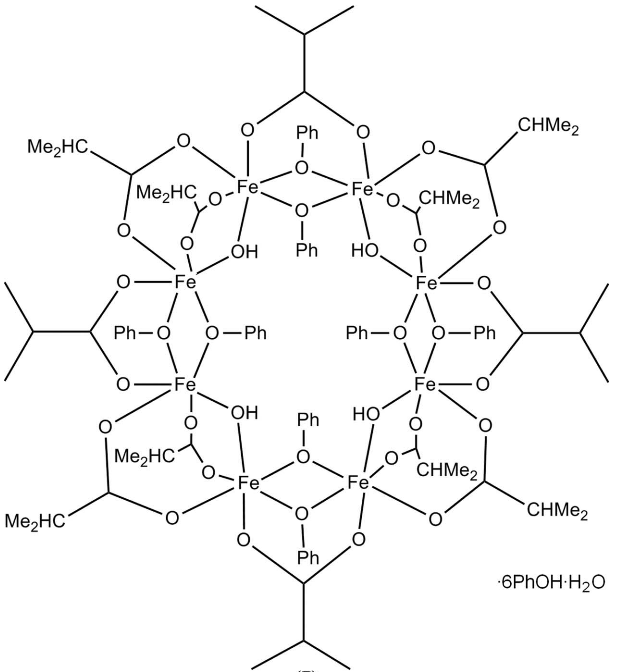
Received 26 September 2011
Accepted 24 October 2011
Online 5 November 2011

The reaction of the μ_3-oxido-centred trinuclear isobutyrate cluster $[Fe_3O(O_2CCHMe_2)_6(H_2O)_3]^+$ with an excess of phenol (PhOH) in chloroform produces a novel octanuclear Fe^{III} cluster, *cyclo*-tetra-μ_2-hydroxido-dodeca-μ_2-isobutyrato-$\kappa^{24}O$:O'-octa-μ_2-phenolato-$\kappa^{16}O$:O'-octairon(III) phenol hexasolvate monohydrate, $[Fe_8(C_4H_7O_2)_{12}(C_6H_5O)_8(OH)_4]\cdot 6C_6H_5OH\cdot H_2O$. The neutral cluster is located about a centre of inversion and consists of a planar ring of eight Fe^{III} centres with two types of bridges between adjacent Fe atoms: each Fe atom is bridged to one of its neighbours by a μ-hydroxide and two 1,3-bridging carboxylates, or by two phenolate and one 1,3-bridging isobutyrate ligand. The cavity within the $\{Fe_8\}$ wheel is occupied by a disordered water molecule. Intermolecular O—H$\cdots$O hydrogen bonds and C—H$\cdots\pi$ interactions connect the clusters and the phenol solvent molecules to form a three-dimensional network.

Comment

The design of new polynuclear iron(III) cluster complexes has garnered substantial interest due to their archetypal role as single-molecule magnets (SMMs), since initial reports on $\{Fe_8\}$ cages by Wieghardt *et al.* (1984) and Gatteschi *et al.* (2000), followed by the discovery of other ferric $\{Fe_{10}\}$ (Benelli *et al.*, 2001) and $\{Fe_{19}\}$ (Goodwin *et al.*, 2000) SMMs. Of special interest are wheel-shaped high-nuclearity iron cluster complexes, which can magnetically be regarded as chains with a finite number of spin centres. Several iron wheels, ranging from $\{Fe_6\}$ (Caneschi *et al.*, 1995; Saalfrank *et al.*, 1997; Hoshino *et al.*, 2009) to $\{Fe_8\}$ (Saalfrank *et al.*, 1997; Canada-Vilalta, O'Brien *et al.*, 2003; Canada-Vilalta, Pink & Christou, 2003; Jones *et al.*, 2006), $\{Fe_9\}$ (Yao *et al.*, 2006), $\{Fe_{10}\}$ (Taft & Lippard, 1990; Taft *et al.*, 1994; Benelli *et al.*, 1996; Liu *et al.*, 2001; Jones *et al.*, 2002), $\{Fe_{12}\}$ (Abbati *et al.*, 2000; Raptopoulou *et al.*, 2002; Abu-Nawwas *et al.*, 2004), $\{Fe_{16}\}$ (Jones *et al.*, 2002, 2006) and $\{Fe_{18}\}$ (King *et al.*, 2006), have been reported so far. Compared with other polynuclear metal clusters comprising paramagnetic metal ions, wheel-type clusters generally reveal interesting physical properties, *e.g.* soliton excitations, and can be model compounds for studying one-dimensional magnetic materials [see, for example,



(I)

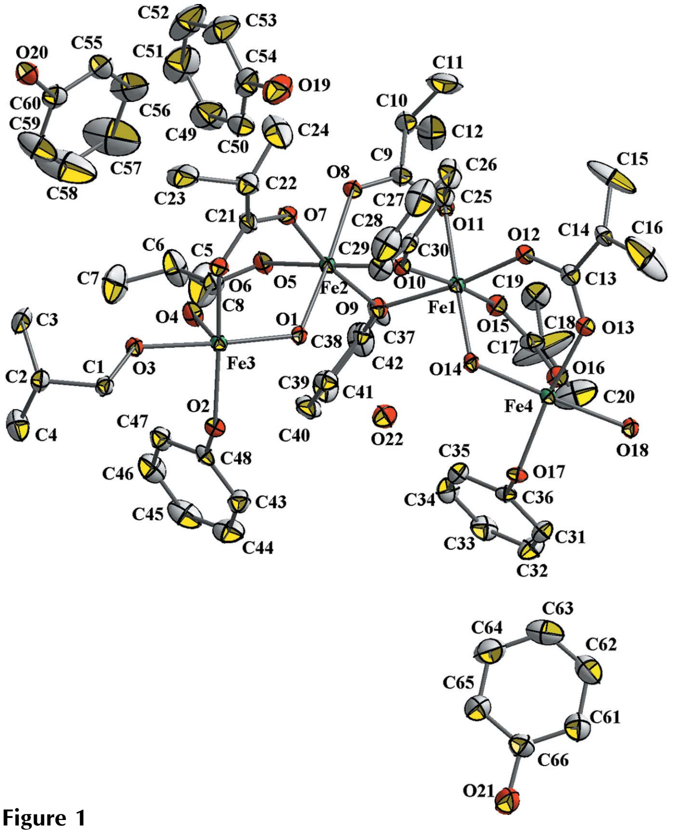


Figure 1
A displacement ellipsoid plot at the 50% probability level of the contents of the asymmetric unit of (I). Only one conformation of the disordered components is depicted.

doi:10.1107/S010827011104412X

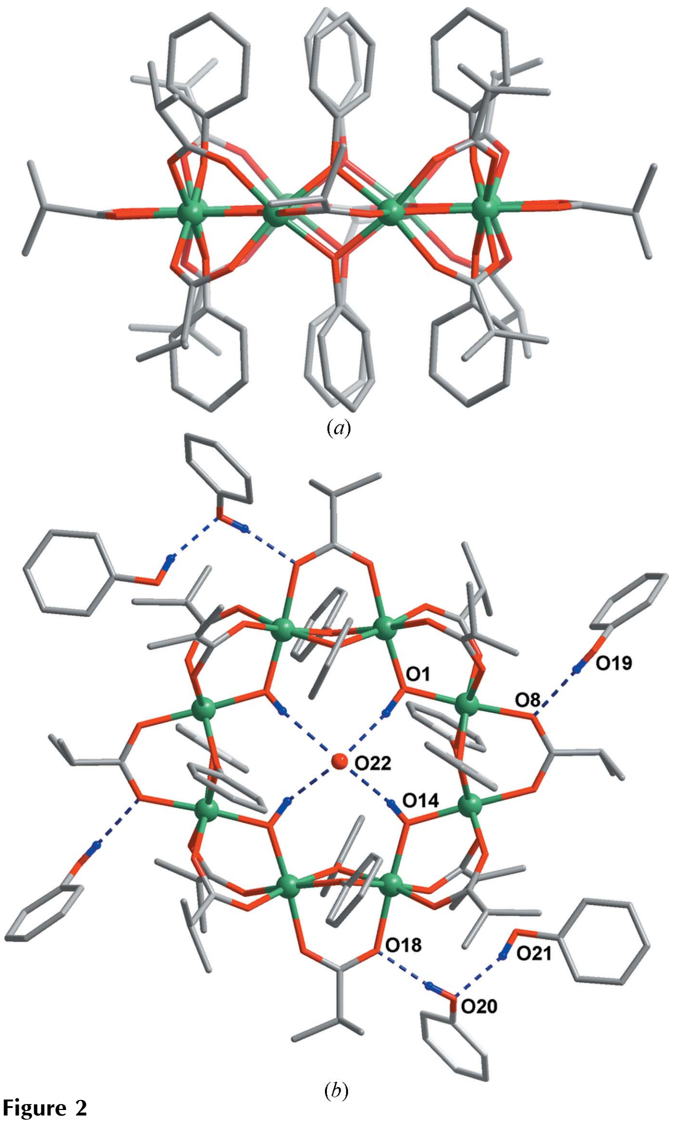


Figure 2
The molecular structure of (I), showing (*a*) a side view and (*b*) a top view, displaying the hydrogen-bonding interactions (dashed lines). H atoms, except those participating in hydrogen bonding, and disordered Me_3C groups have been omitted for clarity. [Colour scheme in the electronic version of the paper: Fe green spheres, O red sticks, C grey sticks, H blue spheres and water molecule (only one of two disordered O-atom positions is shown) red sphere.]

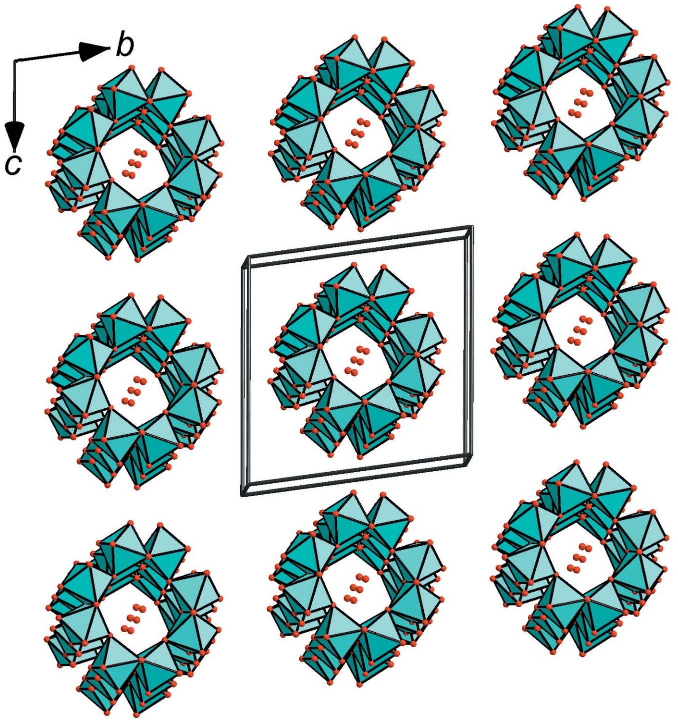


Figure 3
The stacked packing of $\{Fe_8\}$ wheels extended within the *bc* plane in the lattice of (I) (the viewing direction is approximately along *a*). Isobutyrate and phenolate ligands and phenol solvent molecules have been omitted for clarity.

Gatteschi *et al.* (2006) and Timco *et al.* (2009, 2011)]. Here, we report the title novel iron(III) isobutyrate-based wheel with phenolate (PhO) ligands, (I).

Single-crystal X-ray diffraction analysis reveals that (I) (Fig. 1) crystallizes in the triclinic space group $P\overline{1}$, and consists of a wheel-shaped centrosymmetric octanuclear $[Fe_8(OH)_4(O_2CCHMe_2)_{12}(PhO)_8]$ neutral cluster unit, six phenol solvent molecules and one disordered water molecule per formula unit (Fig. 2). The asymmetric unit of (I) contains half of the eight Fe^{III} ions, two hydroxide ions, six isobutyrate residues, four phenolate groups, three phenol molecules and one half-molecule of water. The eight Fe^{III} ions are bridged by a combination of isobutyrate, phenolate and hydroxide groups into a cyclic structure of ~8.5 Å in diameter (measured between opposite Fe^{III} ions). The isobutyrate groups link neighbouring Fe^{III} ions in the usual manner, adopting a μ_2-η^1:η^1 bridging mode. The distances between two Fe^{III} ions bridged by two phenolate groups and one isobutyrate are in the range 3.108 (6)–3.115 (6) Å, shorter than the distances of 3.426 (6)–3.435 (6) Å between Fe^{III} ions linked by a μ-hydroxide and two bridging carboxylate groups. Each Fe^{III} ion adopts a distorted octahedral arrangement formed by three O atoms from three bridging carboxylate ligands [$Fe-O_{carb}$ bond lengths 1.972 (2)–2.065 (2) Å], two O atoms from two phenolate groups [$Fe-O_{PhO}$ = 1.999 (2)–2.040 (2) Å] and one hydroxide [$Fe-O_{OH}$ = 1.959 (2)–1.977 (2) Å].

The structure of (I) is comparable with that of the $\{Fe_8\}$ rings based on pivalate or benzoate ligands (Canada-Vilalta, Pink & Christou, 2003), with small differences in the Fe—O distances: $Fe-O_{carb}$ = 1.830 (2)–2.15 (1) (pivalate) and 1.964 (6)–2.050 (6) Å (benzoate); $Fe-O_{PhO}$ = 2.007 (2)–2.015 (2) (pivalate) and 2.005 (6)–2.022 (6) Å (benzoate); and Fe—OH = 1.961 (2)–1.982 (2) (pivalate) and 1.969 (6)–1.976 (6) Å (benzoate).

The ferric isobutyrate wheel in (I) contains a cavity which can be occupied by small guest molecules. The inner rims of the wheel are geometrically constricted by the opposite aromatic phenol ligands, resulting in a distance of *ca* 5.5 Å and a depth of 10.7 Å. Disordered across a centre of inversion [the two positions are only 1.341 (2) Å apart], a single water molecule (atom O22) resides in the central cavity of (I) and forms O—H···O hydrogen bonds with μ-hydroxide groups (atoms O1 and O14) of the ring, with O···O distances of 2.977 (5) and 2.984 (5) Å (Table 1), respectively, as shown in Fig. 2(*b*). The

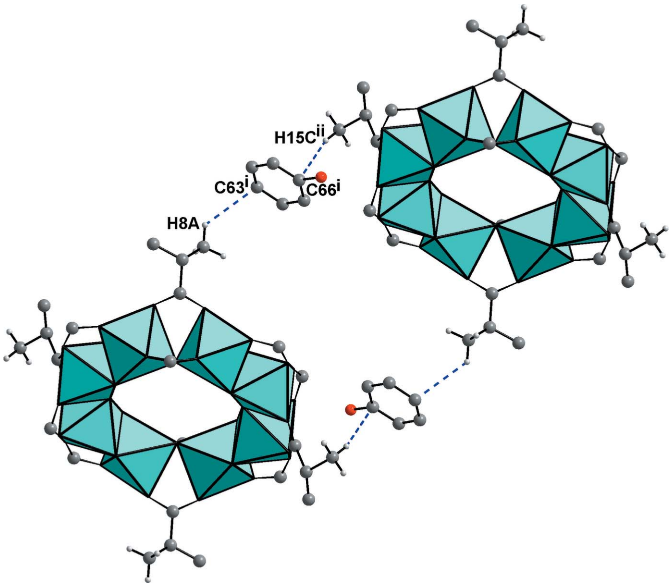


Figure 4
Intermolecular C—H$\cdots\pi$ contacts (dashed lines) between neighbouring {Fe$_8$} wheel clusters in the solid-state lattice of (I). (Colour scheme in the electronic version of the paper: O red spheres, C grey sticks and H white spheres.) C—H$\cdots\pi$ interactions are drawn and calculated according to Nishio (2004) and Suezawa *et al.* (2001). [Symmetry codes: (i) $-x + 1$, $-y + 1$, $-z + 1$; (ii) $-x$, $-y + 1$, $-z$.]

Fe^{III} wheels are stacked on top of each other to form channels along the *a* axis. The crystal packing of (I) is illustrated in Fig. 3.

All the phenol solvent molecules of (I) participate in the formation of extensive O—H$\cdots$O hydrogen bonding with the Fe^{III} clusters. Thus, phenol atoms O19 and O20 form hydrogen bonds with coordinated carboxylate atoms O8 and O18($x + 1$, $y + 1$, z) of the {Fe$_8$} ring, respectively (Table 1). Further, the oxygen site O20 accepts a hydrogen bond from atom O21 from a third phenol molecule with a shorter O$\cdots$O distance. Additionally, neighbouring {Fe$_8$} rings are associated through aliphatic–aromatic C—H$\cdots\pi$ interactions between the methyl groups (C15—H15*C* and C8—H8*A*) of the isobutyrates and a phenol solvent molecule (C61–C66/O21) to generate a hydrogen-bonded one-dimensional chain (Fig. 4). The H$\cdots\pi$ distances involved in this contact are 2.63 and 2.87 Å, respectively, shorter than the value of 3.05 Å considered to be relevant for the presence of a C—H$\cdots\pi$ interaction [see, for example, Nishio (2004) and Suezawa *et al.* (2001)].

Experimental

Solvents and reagents were obtained commercially and used without further purification. The precursor $[Fe_3O(O_2CCHMe_2)_6(H_2O)_3]NO_3$ was prepared according to a previously reported procedure (Malaestean *et al.*, 2010). Phenol (0.40 g, 4.25 mmol) was added to a chloroform solution (10 ml) of $[Fe_3O(O_2CCHMe_2)_6(H_2O)_3]NO_3$ (0.168 g, 0.204 mmol). The reaction mixture was stirred for 10 min at room temperature and then filtered. Red crystals of (I) suitable for X-ray diffraction analysis were obtained within a week by slow evaporation of the reaction solution.

Crystal data

$[Fe_8(C_4H_7O_2)_{12}(C_6H_5O)_8(OH)_4]\cdot 6C_6H_6O\cdot H_2O$	$\beta = 110.485 (1)^\circ$
$M_r = 2887.45$	$\gamma = 108.261 (1)^\circ$
Triclinic, $P\overline{1}$	$V = 3435.5 (3)$ Å^3
$a = 13.2648 (7)$ Å	$Z = 1$
$b = 16.6182 (9)$ Å	Mo $K\alpha$ radiation
$c = 17.679 (1)$ Å	$\mu = 0.90$ mm^{-1}
$\alpha = 90.557 (1)^\circ$	$T = 153$ K
	$0.27 \times 0.11 \times 0.08$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer	27326 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	12041 independent reflections
$T_{min} = 0.161$, $T_{max} = 0.931$	9628 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	59 restraints
$wR(F^2) = 0.108$	H-atom parameters constrained
$S = 1.14$	$\Delta\rho_{max} = 1.03$ e Å^{-3}
12041 reflections	$\Delta\rho_{min} = -1.05$ e Å^{-3}
867 parameters	

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
O1—H1*A*$\cdots$O22	0.92	2.08	2.977 (6)	166
O1—H1*A*$\cdots$O22^{i}	0.92	2.18	3.025 (6)	152
O14—H14*A*$\cdots$O22	0.80	2.20	2.983 (6)	168
O14—H14*A*$\cdots$O22^{i}	0.80	2.36	3.094 (6)	153
O19—H19*D*$\cdots$O8	0.84	2.11	2.946 (4)	179
O20—H20*D*$\cdots$O18^{ii}	0.84	1.96	2.795 (3)	172
O21—H21*A*$\cdots$O20^{iii}	0.84	1.97	2.771 (4)	159

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x + 1, y + 1, z$; (iii) $x, y - 1, z + 1$.

Some of the isobutyrate ligands showed evidence of disorder and two positions were defined for the atoms of three out of the five structurally independent isobutyrate ligands. A common site-occupation factor was refined for each disordered group and the major conformations have occupation factors of 0.570 (5). The significant disorder in large metal coordination clusters with light polydentate ligands is very common and it is difficult to identify an appropriate model for an ideal description, therefore a reasonable compromise would be to accept quite large anisotropic displacement parameters for atoms of terminal groups.

A total of 59 similarity restraints (C—C distances and displacement parameters for disordered atoms) were used to model the disordered isobutyrate groups. H atoms of the hydroxy groups were located from difference Fourier maps. The H atoms of the main cluster were treated using a riding model, with fixed distances of O—H = 0.80–0.92 Å and C—H = 0.95 (aromatic), 0.98 (methyl) or 1.00 Å (methine), and with $U_{iso}(H) = 1.5U_{eq}(C_{methyl},O)$ or $1.2U_{eq}(C)$ otherwise. The H atoms of the disordered (*via* the inversion centre) water molecule were not located or included in the refinement. However, they were taken into account for the final formula to obtain true metric data.

Data collection: *APEX2* (Bruker, 2010); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Financial support of this work was provided by the German Federal Ministry of Education and Research (grant No. MDA 08/022) and the Academy of Sciences of Moldova (grant No. 09.820.05.10 GF). The authors thank the European Commission for an IIF Marie Curie Fellowship (POLYMAG, contract No. 252984). The Ames Laboratory is operated for the US Department of Energy by Iowa State University under Contract 40 No. DE-AC02-07CH11358.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: YF3006). Services for accessing these data are described at the back of the journal.

References

Abbati, G. L., Caneschi, A., Cornia, A., Fabretti, A. C. & Gatteschi, D. (2000). *Inorg. Chim. Acta*, **297**, 291–300.

Abu-Nawwas, A.-A. H., Cano, J., Christian, P., Mallah, T., Rajaramm, G., Teat, S. J., Winpenny, R. E. P. & Yukawa, Y. (2004). *Chem. Commun.* pp. 314–315.

Benelli, C., Cano, J., Journaux, Y., Sessoli, R., Solan, G. A. & Winpenny, R. E. P. (2001). *Inorg. Chem.* **40**, 188–189.

Benelli, C., Parson, S., Solan, G. A. & Winpenny, R. E. P. (1996). *Angew. Chem. Int. Ed.* **35**, 1825–1828.

Bruker (2008). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2010). *APEX2*. Suite Version 11/3. Bruker AXS Inc., Madison, Wisconsin, USA.

Canada-Vilalta, C., O'Brien, T. A., Pink, M., Davidson, E. R. & Christou, G. (2003). *Inorg. Chem.* **42**, 7819–7829.

Canada-Vilalta, C., Pink, M. & Christou, G. (2003). *Chem. Commun.* pp. 1240–1241.

Caneschi, A., Cornia, A. & Lippard, S. J. (1995). *Angew. Chem. Int. Ed.* **34**, 467–469.

Gatteschi, D., Sessoli, R. & Cornia, A. (2000). *Chem. Commun.* pp. 725–732.

Gatteschi, D., Sessoli, R. & Villain, J. (2006). In *Molecular Nanomagnets*. New York: Oxford University Press Inc.

Goodwin, J. C., Sessoli, R., Gatteschi, D., Wernsdorfer, W., Powell, A. K. & Heath, S. L. (2000). *J. Chem. Soc. Dalton Trans.* pp. 1835–1840.

Hoshino, N., Ako, A. M., Powell, A. K. & Oshio, H. (2009). *Inorg. Chem.* **48**, 3396–3407.

Jones, L. F., Batsanov, A., Brechin, E. K., Collison, D., Helliwell, M., Mallah, T., McInnes, E. J. L. & Piligkos, S. (2002). *Angew. Chem. Int. Ed.* **41**, 4318–4321.

Jones, L. F., Low, D. M., Helliwell, M., Raftery, J., Collison, D., Aromi, G., Cano, J., Mallah, T., Wernsdorfer, W., Brechin, E. K. & McInnes, E. J. L. (2006). *Polyhedron*, **25**, 325–333.

King, P., Stamatatos, T. C., Abboud, K. A. & Christou, G. (2006). *Angew. Chem. Int. Ed.* **45**, 7379–7383.

Liu, S.-X., Lin, S., Lin, B.-Z., Lin, C.-C. & Huang, J.-Q. (2001). *Angew. Chem. Int. Ed.* **40**, 1084–1087.

Malaestean, I. L., Speldrich, M., Ellern, A., Baca, S. G. & Kögerler, P. (2010). *Polyhedron*, **29**, 1990–1997.

Nishio, M. (2004). *CrystEngComm*, **6**, 130–158.

Raptopoulou, C. P., Tangoulis, V. & Devlin, E. (2002). *Angew. Chem. Int. Ed.* **41**, 2386–2389.

Saalfrank, R. W., Bernt, I., Uller, E. & Hampel, F. (1997). *Angew. Chem. Int. Ed.* **36**, 2482–2485.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Suezawa, H., Yoshida, T., Hirota, M., Takahashi, H., Umezawa, Y., Honda, K., Tsuboyama, S. & Nishio, M. (2001). *J. Chem. Soc. Perkin Trans. 2*, pp. 2053–2058.

Taft, K. L., Delfs, C. D., Papaefthymiou, G. C., Foner, S., Gatteschi, D. & Lippard, S. J. (1994). *J. Am. Chem. Soc.* **116**, 823–832.

Taft, K. L. & Lippard, S. J. (1990). *J. Am. Chem. Soc.* **112**, 9629–9630.

Timco, G. A., Carretta, S., Troiani, F., Tuna, F., Prichard, R. J., Muryn, C. A., McInnes, E. J. L., Ghirri, A., Candini, A., Santini, P., Amoretti, G., Affronte, M. & Winpenny, R. E. P. (2009). *Nat. Nanotechnol.* **4**, 173–178.

Timco, T. A., Faust, T. B., Tuna, F. & Winpenny, R. E. P. (2011). *Chem. Soc. Rev.* **40**, 3067–3075.

Wieghardt, K., Pohl, K., Jibril, I. & Huttner, G. (1984). *Angew. Chem. Int. Ed.* **23**, 77–78.

Yao, H.-C., Wang, J.-J., Ma, Y.-S., Waldmann, O., Du, W.-X., Song, Y., Li, Y.-Z., Zheng, L.-M., Decurtins, S. & Xin, X.-Q. (2006). *Chem. Commun.* pp. 1745–1747.