

COMMUNICATION

A triple-triangle cluster derived from a simple tridentate ligand

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The heptanuclear ferric cluster, [Fe^{III}7(O)6(HL)5(H2L)(H2O)8](BF4)4 (H2L = 2,6-bis(1,5-diphenyl-1H-pyrazol-3-yl)pyridine), was synthesized by the reaction of the planar tridentate ligand H2L with iron(II) tetrafluoroborate hexahydrate. The cluster has a corner-shared triple-triangle core structure connected by three μ -O atoms, and it has a spin-frustrated ferrimagnetic spin ground state of $S = 19/2$.

Multinuclear iron complexes have been intensively studied in the fields of biological and materials chemistry, and various iron compounds based on coordination complexes or nanoparticles with interesting structures and electronic states have been developed and investigated as a result of continuous explorations of new compounds motivated by the ubiquitous presence of iron as an element.¹

Focusing on molecule-based magnetic materials, the [Fe₈] cluster [Fe^{III}8O2(OH)12(tacn)6]Br8(H2O)9 (tacn = 1,4,7-triazacyclononane) is a representative example of a single-molecule magnet with an $S = 10$ spin ground state.² It is noted that this [Fe₈] cluster displays a spin-frustrated property. An Fe(II) ion has a large magnetic anisotropy compared with an Fe(III) ion; consequently, the Fe(II) ion is an appropriate candidate for constructing single-molecule magnets. For example, a single-molecule magnet containing an iron(II) cube, [Fe₄(sae)₄(MeOH)₄] (H₂sae = 2-(salicylideneamino)ethanol), has been reported, and the cluster has an $S = 8$ spin ground state which is due to the accidental orthogonal magnetic orbitals.³ To construct multinuclear iron complexes that show high-performance single-molecule magnetic behaviour, appropriate bridging/capping ligands have to be developed and the synthetic conditions should be optimized.⁴

Ring- and wheel-type clusters consisting of iron ions form another class of interesting magnetic materials.⁵ The [Fe₁₀] antiferromagnetic ring, [Fe₁₀(OCH₃)₂₀(C₂H₂O₂Cl)₁₀], showed a distinct stepwise magnetization originating from the level crossing of spin ground states at low temperatures.⁶ Recently, magnetocaloric properties of polynuclear complexes containing Fe(III) ions have been investigated.⁷ Some iron(III) clusters with isotropic magnetic centers turned out to be promising as magnetic coolants. On the other hand, Christou and co-workers have reported two heptanuclear iron wheels, [Fe₇O₃(OMe)₃(heen)₃Cl_{4.5}(MeOH)(H₂O)_{1.5}]Cl_{1.25}[FeCl₄]_{1/4} (heenH₂ = *N,N'*-bis(2-hydroxyethyl)ethylenediamine) and [Fe₇O₃(OH)₃Cl(paeo)₆](Cl)(ClO₄)₄ (paeoH = 2-[(pyridin-2-ylmethyl)amino]ethanol).⁸ The detailed magnetic studies revealed that their spin ground states of $S = 15/2$ and $21/2$, respectively, were stabilized by strong anti-ferromagnetic-exchange interactions between inner and outer iron ions with spin frustration. Powell and co-workers investigated the [Fe₇] wheel complex, [Fe^{III}7(Cl)(MeOH)₆(μ -O)₃(μ -OMe)₆(O₂CPh)₆]Cl₂, with the spin ground states of $S = 7/2$ or $9/2$, and discussed the relationship between magnetic-exchange interactions and spin ground states.⁹ Most [Fe₇] wheel complexes have an $S = 5/2$ spin ground state because the presence of dominant antiferromagnetic interactions between neighbouring outer iron ions results in the existence of residual central Fe(III) spin.¹⁰ When the [Fe₇] wheel has strong antiferromagnetic interactions between the central and outer iron ions, a maximum spin ground state is $S = 25/2$, however, various spin states appear in spin frustrated and canting systems. To date, we have reported several magnetic clusters with the wheel-shaped structures containing alkoxo-type and rigid bridging ligands,¹¹ and the planar multidentate ligand afforded to synthesize various polynuclear complexes.¹² To extend our research, we report here the synthesis and magnetic properties of the unprecedented heptanuclear ferric cluster, [Fe^{III}7(O)6(HL)5(H2L)(H2O)8](BF4)₄ (**1**) (H₂L = 2,6-bis(1,5-diphenyl-1H-pyrazol-3-yl)pyridine), with a corner-shared triple-triangle core structure, derived from the simple tridentate ligand H₂L.

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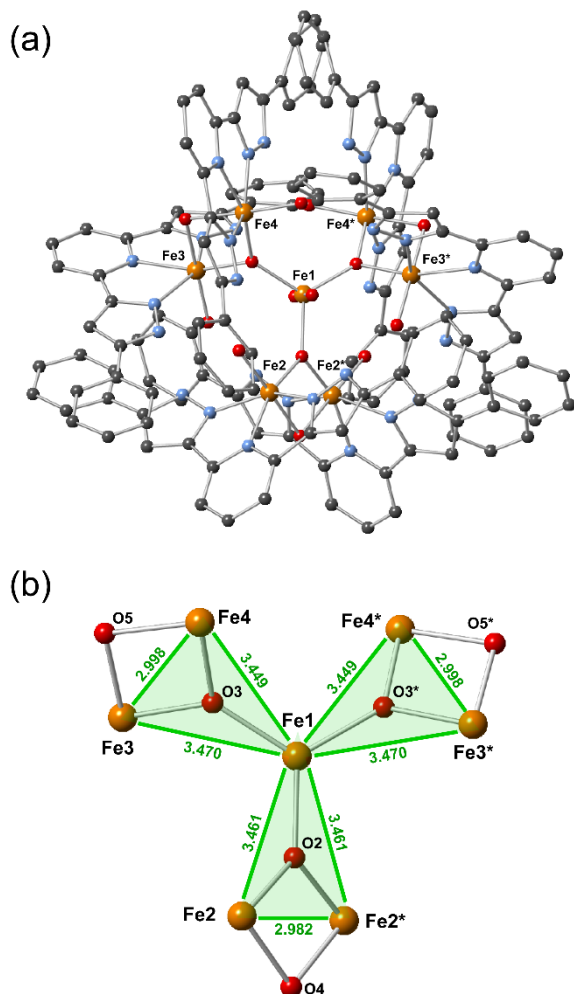


Fig. 1. Molecular structure of **1** determined at 100 K. (a) Top view and (b) core structure [showing metal–metal separations (Å)]. Hydrogen atoms, solvent molecules, and counteranions are omitted for clarity. Colour code: iron, orange; carbon, grey; nitrogen, blue; oxygen red. Symmetry operation * : $1 - x, +y, 1/2 - z$.

The heptanuclear ferric complex **1** was synthesized by the reaction of $\text{Fe}^{\text{III}}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ with H_2L in butyronitrile.[†] **1** crystallizes in the monoclinic space group $C2/c$. X-ray structural analysis revealed that the heptanuclear complex consists of seven iron(III) ions, five monodeprotonated ligands, one protonated ligand, six bridging oxygen atoms, and eight coordinated water molecules, forming a corner-shared triple-triangle core structure shaped like a three-leaf clover (Figure 1).[§] The asymmetric unit is half the heptanuclear cluster, and the molecule has a two-fold axis of symmetry passing through the Fe1, O2, and O4 atoms. There are four kinds of crystallographically independent iron ions. The Fe1 ion is located at centre of the molecule and has a trigonal bipyramidal geometry with three μ_3 -O atoms and two axially coordinated water molecules. Fe2, Fe3, and Fe4 ions are located in the outer portion of the molecule and form three binuclear units (Fe2–Fe2*, Fe3–Fe4, and Fe3*–Fe4*) with two bridging oxygen atoms. The iron ions of the binuclear units have an octahedral coordination geometry with three nitrogen atoms from the ligand, two oxygen atoms of two bridging oxido ions, and one coordinated water molecule. This coordinated water molecule

interacts with a nitrogen atom of a neighbouring ligand through a hydrogen bond, stabilizing the cyclic triangle structure. In addition, π – π stacking is present between pyrazole moieties of neighbouring ligands (Figure S1).

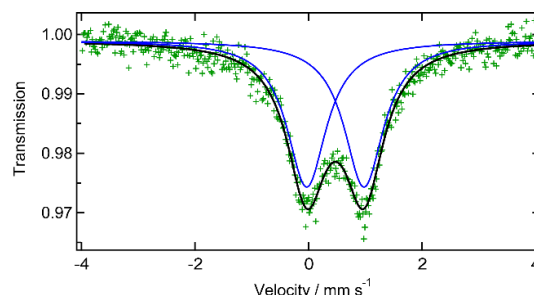


Fig. 2. Mössbauer spectrum of **1** at 20 K. The fitting parameters are given in the text.

On the basis of the coordination bond lengths and bond valence sum (BVS) calculations, all iron ions can be assigned to high-spin trivalent iron ions.^{§§} To confirm the electronic state of the iron ions, we measured the Mössbauer spectrum of **1** at 20 K (Figure 2) and this showed a slightly broadened one-quadrupole doublet. The obtained fitting parameters for the doublet are $\delta_{\text{IS}} = 0.474 \text{ mm}\cdot\text{s}^{-1}$ and $\Delta E_{\text{Q}} = 1.009 \text{ mm}\cdot\text{s}^{-1}$, characteristic of high spin Fe(III) ions. The broad doublet might be due to the similar coordination atomspheres of the four iron ions.

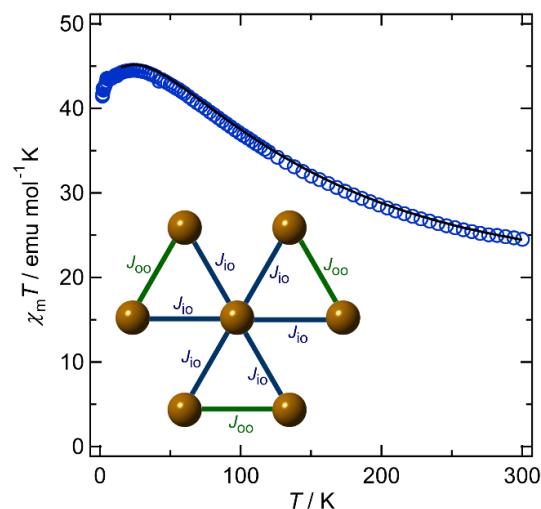


Fig. 3. The $\chi_{\text{m}}T$ versus T plot for **1**. The solid line represents the fitting curve (see text). Inset: Schematic representation of the spin model used in the fitting procedure.

The magnetic susceptibility of **1** was measured in the temperature range of 1.8–300 K with an applied magnetic field of 500 Oe (Figure 3). The $\chi_{\text{m}}T$ value for **1** increased from $24.5 \text{ emu}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ at 300 K to the maximum value of $44.5 \text{ emu}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ at 24 K, and then decreased to $41.4 \text{ emu}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ at 1.8 K. Exchange paths can be modelled by using two kinds of magnetic-exchange coupling constants, J_{IO} (inner–outer iron ions) and J_{OO} (outer–outer iron ions), with the spin Hamiltonian $H = 2J_{\text{IO}}(\mathbf{S}_{\text{Fe1}}\cdot\mathbf{S}_{\text{Fe2}}+\mathbf{S}_{\text{Fe1}}\cdot\mathbf{S}_{\text{Fe3}}+\mathbf{S}_{\text{Fe1}}\cdot\mathbf{S}_{\text{Fe4}}+\mathbf{S}_{\text{Fe1}}\cdot\mathbf{S}_{\text{Fe2}^*}+\mathbf{S}_{\text{Fe1}}\cdot\mathbf{S}_{\text{Fe3}^*}+\mathbf{S}_{\text{Fe1}}\cdot\mathbf{S}_{\text{Fe4}^*}) - 2J_{\text{OO}}(\mathbf{S}_{\text{Fe2}}\cdot\mathbf{S}_{\text{Fe2}^*}+\mathbf{S}_{\text{Fe3}}\cdot\mathbf{S}_{\text{Fe4}}+\mathbf{S}_{\text{Fe3}^*}\cdot\mathbf{S}_{\text{Fe4}^*})$ (a schematic representation is shown in the inset to Figure 3). By using the MAGPACK

program¹³ to fit the data above 15 K, the following parameters were obtained: $g_{\text{Fe}} = 2.00$, $J_{\text{io}} = -35.0$ K, and $J_{\text{oo}} = -20.5$ K. Magnetization experiments for **1** were carried out, and the reduced magnetization versus H/T plots are shown in Figure 4. The magnetization of **1** saturated with a value of $17.93 N\beta$ when the magnetic field exceeded 5.0 T at 1.8 K. The reduced magnetization data in the 1.8–2.8 K and 1–5 T ranges were fitted by assuming an $S = 19/2$ spin ground state with $g = 2.00$ (fixed) and $D/k_{\text{B}} = +0.41$ K. For the ac magnetic susceptibilities, there was no out-of-phase response, suggesting the absence of single-molecule magnet behaviour, which is associated with a positive D value.

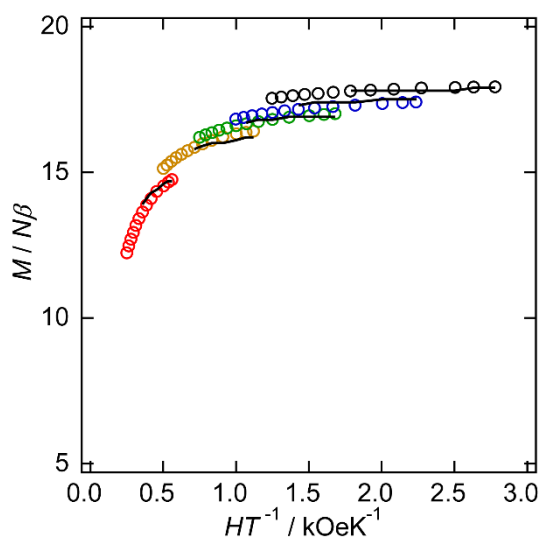


Fig. 4. Reduced magnetization $M/N\beta$ versus H/T plots for **1** at 1–5 T. The solid lines are the fits; see the text for the fitting parameters.

In summary, the heptanuclear ferric cluster $[\text{Fe}^{\text{III}}_7(\text{O})_6(\text{HL})_5(\text{H}_2\text{L})(\text{H}_2\text{O})_8](\text{BF}_4)_4$ (**1**) with a corner-shared triple-triangle core structure was synthesized by using a simple tridentate ligand, and its structural and magnetic properties were investigated. The analyses of the magnetic data revealed that the strong antiferromagnetic interactions among the iron ions stabilized the $S = 19/2$ spin ground state at low temperature, a rare case of high-spin state among the reported heptanuclear iron(III) compounds. This result demonstrates that a simple tridentate ligand can form oxo-bridged polynuclear complexes through hydrogen bonds and π - π stacking interactions. Such stabilization effects by hydrogen bonds are sometimes found in supramolecular architectures.¹⁴ Furthermore, an unusual spin ground state was built up by spin frustration with strong magnetic exchange interactions between inner and outer iron ions. The present work will shed light on the development of high-spin ground state magnetic materials such as single molecule magnets and magnetic coolants, and might lead to novel molecular designs for polynuclear cluster compounds.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

‡ Synthesis of **1**: To a suspension of 2,6-bis(1,5-diphenyl-1H-pyrazol-3-yl)pyridine (H_2L) (147.0 mg, 0.40 mmol) in butyronitrile (45 mL) was added a solution of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (72.8 mg, 0.22 mmol) in butyronitrile (15 mL). The stirred mixture changed from an orange suspension to a dark reddish-orange solution. This was filtered and diffused with butan-2-ol to give orange crystals of **1** suitable for X-ray structural analysis, which were collected by filtration and air dried. Yield: 34.29 mg (33%). Anal.: Found: C, 52.14; H, 4.23; N, 12.01%. Calc. for $\text{C}_{150}\text{H}_{151}\text{B}_4\text{F}_{16}\text{Fe}_7\text{N}_{30}\text{O}_{21}$ [$1 \cdot 3(2\text{-BuOH}) \cdot 4\text{H}_2\text{O}$]: C, 52.25; H, 4.41; N, 12.19%. IR (KBr pellets; $\nu_{\text{max}}/\text{cm}^{-1}$): 1454, 1083, 765.

§ Crystal data for **1** ($\text{C}_{138}\text{H}_{97}\text{B}_4\text{F}_{16}\text{Fe}_7\text{N}_{30}\text{O}_{14}$): $M = 3137.64$; monoclinic, $C2/c$, $T = 100(2)$ K, $a = 31.366(2)$ Å, $b = 21.3000(16)$ Å, $c = 25.0526(19)$ Å, $\beta = 100.3570(10)^\circ$, $V = 16465(2)$ Å³, $Z = 4$, $D_c = 1.266$ g·cm⁻³, 47723 reflections measured, 18763 unique ($R_{\text{int}} = 0.0502$), $\text{GOF} = 1.027$, $R[I] > 2\sigma(I) = 0.0691$, $wR(F_o^2) = 0.1859$, CCDC 1944640.†

§§ BVS calculations gave values of 3.051, 3.134, 3.081 and 3.113 for Fe1, Fe2, Fe3 and Fe4, respectively, assuming Fe(III).

- R. H. Holm and W. Lo, *Chem. Rev.*, 2016, **116**, 13685; N. V. S. Vallabani and S. Singh, *3 Biotech*, 2018, **8**, 279; S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L. Vander Elst and R. N. Muller, *Chem. Rev.*, 2008, **108**, 2064; C. Papatriantafyllopoulou, E. E. Moushi, G. Christou and A. J. Tasiopoulos, *Chem. Soc. Rev.*, 2016, **45**, 1597; T. Liu, Y.-J. Zhang, Z.-M. Wang and S. Gao, *J. Am. Chem. Soc.*, 2008, **130**, 10500; C. M. Beavers, A. V. Prosser, J. D. Cashion, K. R. Dunbar and A. F. Richards, *Inorg. Chem.*, 2013, **52**, 1670; Y.-F. Zeng, X. Hu, L. Xue, S.-J. Liu, T.-L. Hu and X.-H. Bu, *Inorg. Chem.*, 2012, **51**, 9571.
- [Fe₈] cluster: A.-L. Barra, P. Debrunner, D. Gatteschi, C. E. Schulz and E. Sessoli, *Europhys. Lett.*, 1996, **35**, 133.
- H. Oshio, N. Hoshino, T. Ito, M. Nakano, *J. Am. Chem. Soc.*, 2004, **126**, 8805; H. Oshio, N. Hoshino, T. Ito, *J. Am. Chem. Soc.*, 2000, **122**, 12602.
- A. L. Barra, A. Caneschi, A. Cornia, F. Fabrizi de Biani, D. Gatteschi, C. Sangregorio, R. Sessoli and L. Sorace, *J. Am. Chem. Soc.*, 1999, **121**, 5302; S. Parsons, G. A. Solan, R. E. P. Winpenney and C. Benelli, *Angew. Chem. Int. Ed.*, 1999, **35**, 1825; L. F. Jones, E. K. Brechin, D. Collison, M. Helliwell, T. Mallah, S. Piligkos, G. Rajaraman and W. Wernsdorfer, *Inorg. Chem.*, 2003, **42**, 6601; A. K. Boudalis, B. Donnadieu, V. Nastopoulos, J. M. Clemente-Juan, A. Mari, Y. Sanakis, J.-P. Tuchagues and S. P. Perlepes, *Angew. Chem. Int. Ed.*, 2004, **43**, 2266.
- A. Caneschi, A. Cornia, A. C. Fabretti, S. Foner, D. Gatteschi, R. Grandi and L. Schenetti, *Chem. Eur. J.*, 1996, **2**, 1379; M. Affronte, J. C. Lasjaunias and A. Cornia, *Eur. Phys. J. B*, 2000, **15**, 633; M. Affronte, J. C. Lasjaunias and A. Cornia, *Physica B*, 2000, **284–288**, 1233; M. Affronte, A. Cornia, A. Lascialfari, F. Borsa, D. Gatteschi, J. Hinderer, M. Horvatić, A. G. M. Jansen and M.-H. Julien, *Phys. Rev. Lett.*, 2002, **88**, 167201.
- M. Affronte, J. C. Lasjaunias, A. Cornia and A. Caneschi, *Phys. Rev. B*, 1999, **60**, 1161.

- 7 X. X. Zhang, H. L. Wei, Z. Q. Zhang and L. Zhang, *Phys. Rev. Lett.*, 2001, **87**, 157203; M. Evangelisti, A. Candini, A. Ghirri, M. Affronte, S. Piligkos, E. K. Brechin and E. J. L. McInnes, *Polyhedron*, 2005, **24**, 2573; M. Evangelisti, A. Candini, A. Ghirri, M. Affronte, E. K. Brechin, and E. J. L. McInnes, *Appl. Phys. Lett.*, 2005, **87**, 072504; R. Shaw, R. H. Laye, L. F. Jones, D. M. Low, C. Talbot-Eckelaers, Q. Wei, C. J. Milios, S. Teat, M. Helliwell, J. Raftery, M. Evangelisti, M. Affronte, D. Collison, E. K. Brechin and E. J. L. McInnes, *Inorg. Chem.*, 2007, **46**, 4968; I. A. Gass, E. K. Brechin and M. Evangelisti, *Polyhedron*, 2013, **52**, 1177.
- 8 S. Mukherjee, R. Bagai, K. A. Abboud and G. Christou, *Inorg. Chem.*, 2011, **50**, 3849.
- 9 K. C. Mondal, V. Mereacre, G. E. Kostakis, Y. Lan, C. E. Anson, I. Proseccaru, O. Waldmann, A. K. Powell, *Chem. Eur. J.*, 2015, **21**, 10835.
- 10 [Fe^{III}] wheels with an $S = 5/2$ spin ground state: S. Shova, M. Cazacu, G. Novitchi, G. Zoppellaro, C. Train and V. B. Arion, *Dalton Trans.*, 2017, **46**, 1789; M. Menelaou, E. Vournari, V. Psycharis, C. P. Raptopoulou, A. Terzis, V. Tangoulis, Y. Sanakis, C. Mateescu and A. Salifoglou, *Inorg. Chem.*, 2013, **52**, 13849; S. Datta, A. Betancur-Rodriguez, S. C. Lee, S. Hill, D. Foguet-Albiol, R. Bagai, G. Christou, *Polyhedron*, 2007, **26**, 2243; A. M. Ako, O. Waldmann, V. Mereacre, F. Klöwer, I. J. Hewitt, C. E. Anson, H. U. Güdel, A. K. Powell, *Inorg. Chem.*, 2007, **46**, 756; L. F. Jones, P. Jensen, B. Moubaraki, K. J. Berry, J. F. Boas, J. R. Pilbrow, K. S. Murray, *J. Mater. Chem.*, 2006, **16**, 2690.
- 11 S. Koizumi, M. Nihei, T. Shiga, M. Nakano, H. Nojiri, R. Bircher, O. Waldmann, H. U. Güdel, H. Oshio, *Chem. Eur. J.*, 2007, **13**, 8445; R. Saiki, N. Yoshida, G. N. Newton, T. Shiga and H. Oshio, *Chem. Lett.*, 2017, **46**, 1197.
- 12 H. Sato, L. Miya, K. Mitsumoto, T. Matsumoto, T. Shiga, G. N. Newton and H. Oshio, *Inorg. Chem.*, 2013, **52**, 9714; T. Shiga, T. Matsumoto, M. Noguchi, T. Onuki, N. Hoshino, G. N. Newton, M. Nakano and H. Oshio, *Chem. Asian J.*, 2009, **4**, 1660; T. Shiga, M. Noguchi, H. Sato, T. Matsumoto, G. N. Newton and H. Oshio, *Dalton Trans.*, 2013, **42**, 16185; T. Shiga, G. N. Newton and H. Oshio, *Dalton Trans.*, 2018, **47**, 7384.
- 13 MAGPACK: J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado, B. S. Tsukerblat, *J. Comput. Chem.*, 2001, **22**, 985.
- 14 M. Tadokoro, H. Kanno, T. Kitajima, H. Shimana-Umemoto, N. Nakanishi, K. Isobe and K. Nakasuji, *PNAS*, 2002, **99**, 4950; A. Burkhardt, E.T. Spielberg, S. Simon, H. Górls, A. Buchholz and W. Plass, *Chem. Eur. J.*, 2009, **15**, 1261; B. Schneider, S. Demeshko, S. Dechert and F. Meyer, *Inorg. Chem.*, 2012, **51**, 4912.