High-Spin Iron Wheels

High-Spin Wheel of a Heptanuclear Mixed-Valent $Fe^{II,III}$ Complex**

Hiroki Oshio, Norihisa Hoshino, Tasuku Ito,
Motohiro Nakano, Franz Renz, and
Philipp Gütlich*

Iron and manganese clusters with oxygen atoms acting as bridging ligands possess a variety of structures and are of current interest in materials and bioinorganic chemistry. For example, nanosized molecules with a high-spin ground state afford single-domain magnets,[1] which may display hysteresis,[2] slow magnetic relaxation,[3] and spin-quantum tunneling characteristics of a purely molecular origin.[4] The iron-storage protein ferritin and manganese clusters have been extensively studied as a biological prototype in the inorganic systems,[5] and as models of the water-oxidizing complex in photosystem II,[6] respectively. The development of synthetic routes to metal clusters has resulted in remarkable achievements in spin chemistry and biochemistry. Among organic bridging ligands, alkoxo groups have been employed extensively for constructing metal clusters because of their versatile bridging modes (μ_2 and μ_3). Subtle changes in reaction conditions have resulted in the formation of unexpected and beautiful structures, such as cyclic polymetallic clusters.[7] Previously, we have described an alkoxo-bridged iron(II) cube, $[Fe_4(sae)_4(MeOH)_4]$ (H_2sae = 2-salicylideneamino-1-ethanol), which exhibited superparamagnetic behavior with a blocking temperature of 1.1 K.[7g] In the course of exploring the versatility of Schiff base ligands, we found that complexes with higher spin multiplicities could be synthesized from reactions involving iron(II or III) chloride and the tridentate Schiff base ligand 3-methoxy-2-salicylideneamino-1-ethanol (H_2L). Alkoxo-bridged cluster molecules with core structures of $[Fe^{II}_3Fe^{III}]$, $[Fe^{II}Fe^{III}_6]$, and $[Fe^{III}Fe^{II}_6]$ were prepared by varying the amount of oxidant used. In this communication, we report the synthesis and magnetic properties of a heptanuclear iron(II, III) wheel with the highest spin ground state in this series.

A stoichiometric amount of $[(tBu_4N)MnO_4]$ was added to a mixture of $FeCl_2{\cdot}4H_2O$ and H_2L in methanol. After 1–2 weeks, dark-red hexagonal blocks of $[Fe^{III}Fe^{II}_6(MeO)_6(HL)_6]Cl_3$ (**1**-Cl_3) were obtained in 50% yield. **1**-Cl_3 crystallizes in the trigonal $P\bar{3}c1$ space group,[8] in which the $\mathbf{1}^{3+}$ ion is situated on a $\bar{3}$ inversion axis. The cyclic structure is composed of seven coplanar iron ions; the core can, therefore, be regarded as a wheel with crystallographically imposed S_6 symmetry. The molecular structure of the $\mathbf{1}^{3+}$ ion, viewed perpendicular to the ring plane, is shown in Figure 1.

The Schiff base ligand (H_2L) has four possible coordination sites, namely, the methoxy, phenoxy, imino, and alcohol moieties. X-ray structural analysis showed that the alcohol groups are uncoordinated and have positional disorder. Therefore, the ligand acts as a tridentate monoanion (HL^-). In the wheel, six μ_2-phenoxo groups bridge the iron ions on the rim, which themselves are linked to the central ion through six μ_3-bridging methoxy groups that act as "spokes" to form the wheel structure. Each iron ion on the rim (Fe2) adopts an N_1O_5 configuration through coordination to the Schiff base and methoxide groups; a Jahn–Teller distortion for the Fe2 ions was observed. Coordination bond lengths about the Fe2 ions are in the range of 2.042(4)–2.362(5) Å. The coordination geometry of the central iron ion (Fe1) is octahedral with bond lengths of 2.150(4) Å (Fe1−O4 (meth-

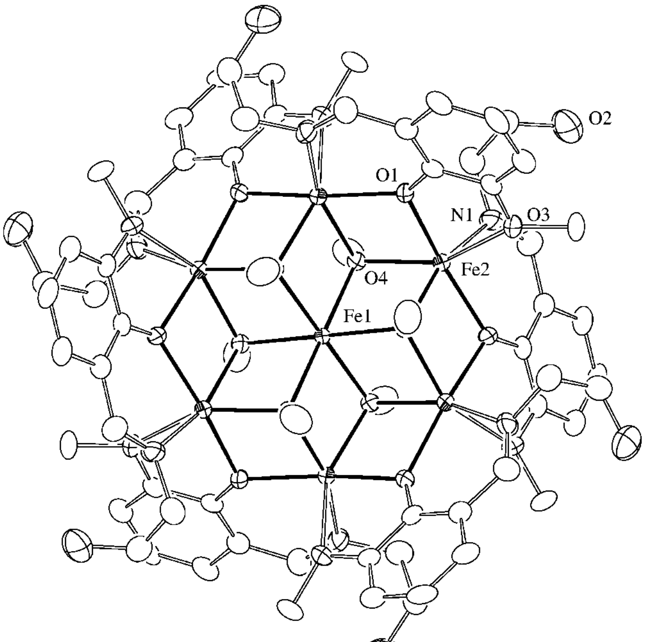

Figure 1. ORTEP diagram of the $\mathbf{1}^{3+}$ ion. Selected bond lengths [Å] and angles [°]: Fe1-O4 2.153(3), Fe2-O1A 2.041(3), Fe2-O4 2.079(3), Fe2-O1 2.092(4), Fe2-N1 2.125(5), Fe2-O4A 2.181(3), Fe2-O3 2.367(4); O4A-Fe2-O3 96.52(15), Fe2B-O1-Fe2 103.51(15), Fe2-O4-Fe1 98.43(14), Fe2-O4-Fe2B 99.28(13), Fe1-O4-Fe2B 95.37(13). Symmetry operations: A: $x-y, x-1, -z$; B: $y+1, -x+y+1, -z$.

---

[*] Prof. H. Oshio
Department of Chemistry
University of Tsukuba
Tennodai 1-1-1, Tsukuba 305-8571 (Japan)
Fax: (+81) 298-4238
E-mail: oshio@chem.tsukuba.ac.jp

N. Hoshino, Prof. T. Ito
Department of Chemistry
Graduate School of Science, Tohoku University
Aoba-ku, Sendai 980-8578 (Japan)

Dr. M. Nakano
Department of Molecular Chemistry
Graduate School of Engineering, Osaka University
1-16 Machikaneyama, Toyonaka, Osaka 560-0043 (Japan)

Dr. F. Renz, Prof. P. Gütlich
Institut für Anorganische Chemie und Analytische Chemie
Johannes Gutenberg Universität Mainz
Staudinger Weg 9, 55099 Mainz (Germany)

[**] This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

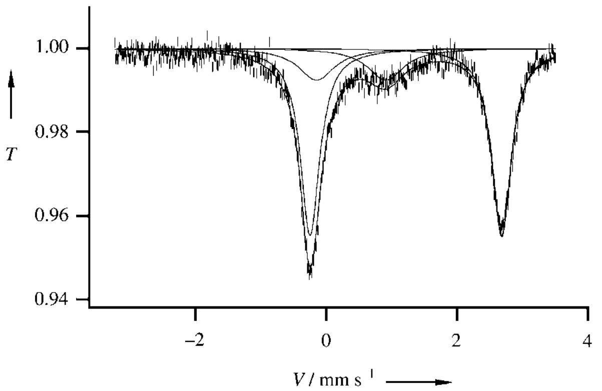

Figure 2. Mössbauer spectrum of **1**-Cl_3. The velocity scale was calibrated relative to α-iron.

oxide)). The iron ions on the rim (Fe2) and at the center (Fe1) were, therefore, assigned to be Fe^{II} and Fe^{III} ions, respectively, based on both the valence sum calculation and the presence of a Jahn–Teller distortion. This assignment was also confirmed by Mössbauer spectroscopy. The bond angles for Fe^{III}-O-Fe^{II} (95.33(15) and 98.61(16)°) are more acute than those of Fe^{II}-O-Fe^{II} (99.23(15) and 103.45(18)°).

The Mössbauer spectrum at 20 K exhibits two doublets (Figure 2). One doublet ($\delta = 0.38\,mm\,s^{-1}$ and $\Delta E_Q = 1.02\,mm\,s^{-1}$; the velocity was calibrated relative to α-iron) is characteristic of a high-spin Fe^{3+} ion, while the other ($\delta = 1.22\,mm\,s^{-1}$ and $\Delta E_Q = 2.93\,mm\,s^{-1}$) is characteristic of high-spin Fe^{2+} ion. Assuming that the Mössbauer–Lamb factors for the Fe^{3+} and Fe^{2+} ions have similar values, the Fe^{3+}/Fe^{2+} ratio calculated from the peak areas is 0.18:0.82, which is in good agreement with the ratio of 1:6 (approximately 0.14:0.86) determined from the chemical formula.

The temperature dependence of the magnetic susceptibilities was measured down to 1.8 K and is shown in Figure 3, together with a plot of magnetization versus field strength at 1.8 K (inset). The $\chi_m T$ value at 300 K is 25.2 emu mol^{-1} K, and this value increased gradually as the temperature was lowered, reaching a maximum value of 73.8 emu mol^{-1} K at 5.5 K. This magnetic behavior is characteristic of the occurrence of ferromagnetic interactions, and suggests an $S = 29/2$ spin ground state for **1**-Cl_3. The sudden decrease in the $\chi_m T$ value below 5.5 K results from magnetic anisotropy and/or through-space antiferromagnetic interactions.[9]

Magnetization data were collected as a function of the applied field up to 5 T at 1.8 K. The $M/N\mu_B$ values increased with increasing magnetic field strength, and did not show saturation up to 5 T. The $M/N\mu_B$ versus H/T data at 1.8 K were fitted assuming only that the ground state is populated. The spin-Hamiltonian was constructed using the sum of the isotropic Zeeman and axial zero-field splitting (ZFS) terms,[10] and the 30 × 30 matrix elements ($= (2S+1)^2$) were diagonalized to yield magnetization curves following a powder average procedure.[11] Least-squares calculations gave a best-fit parameter of $D = +0.53(2)\,cm^{-1}$, with a fixed g_{av} value of 2.046.[12] It should be noted that the calculation assuming a $S = 27/2$ ground state gave $D = +0.42(2)\,cm^{-1}$, while that for a ground state of $S = 25/2$ was divergent.

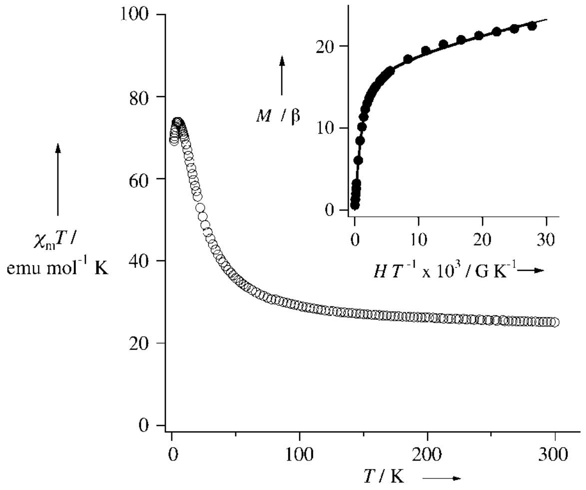

Figure 3. The $\chi_m T$ versus temperature and magnetization (M) versus field strength (H/T, inset) plots for **1**-Cl_3. The solid line results from a least-squares fit using the parameters and the equation described in the text.

Measurements of ac magnetic susceptibility were also performed in the temperature range of 1.8–4.0 K with a 3 G ac field oscillating at 250–1000 Hz, but no out-of-phase signal was observed. This is understandable, as a result of the positive D value of this compound.

In summary, we have prepared a mixed-valent high-spin wheel with a spin ground state of $S = 29/2$. The emphasis of further studies will be to prepare a high-spin wheel with a negative D value by modifying the Schiff base ligands.

Experimental Section

All synthetic procedures were carried out in Schlenk-type vessels under a nitrogen atmosphere, with solvents that were degassed prior to use. A solution of $FeCl_2 \cdot 4H_2O$ (232 mg, 1.17 mmol) in methanol (40 mL) was added to a mixture of 3-methoxysalicylaldehyde (152 mg, 1 mmol), 2-amino-1-ethanol (61 mg, 1 mmol), and Et_3N (101 mg, 1 mmol). After adding [(tBu$_4$N)MnO$_4$] (15 mg, 0.13 mmol), the resulting mixture was stored for 1–2 weeks, in which time dark-red hexagonal blocks had formed, which were collected by filtration. No manganese ions were detected by optical emission spectroscopy (Shimadzu ICPS-7000). Elemental analysis (%) calculated for $C_{66}H_{90}Cl_3Fe_7N_6O_{24}$: C 42.88, H 4.91, N 4.55, Fe 21.14; found: C 43.12, H 4.49, N 4.70, Fe 21.47.

Received: September 2, 2002 [Z50080]

---

[1] a) S. M. J. Aubin, M. W. Wemple, D. M. Adams, H.-L. Tsai, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1996**, *118*, 7746; b) J. Yoo, A. Yamaguchi, M. Nakano, J. Krzystek, W. E. Streib, L.-C. Brunel, H. Ishimoto, G. Christou, D. N. Hendrickson, *Inorg. Chem.* **2001**, *40*, 4604; c) A. L. Barra, D. Gatteschi, R. Sessoli, *Chem. Eur. J.* **2000**, *6*, 1608; d) A. L. Barra, A. Caneschi, A. Cornia, F. Fabrizi de Biani, D. Gatteschi, C. Sangregorio, R. Sessoli, L. Sorace, *J. Am. Chem. Soc.* **1999**, *121*, 5302; e) S. Ferlay, T. Mallah, R. Ouahes, P. Veillet, M. Verdaguer, *Inorg. Chem.* **1999**, *38*, 229; f) A. Cornia, D. Gatteschi, R. Sessoli, *Coord. Chem. Rev.* **2001**, *219*, 573; g) *Magnetism: Molecules to Materials III* (Eds.: J. S. Miller, M. Drillon), Wiley, VCH, **2002**.

[2] a) R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, *365*, 141; b) A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vingigni, A. Rettori, M. G. Pini, M. A. Novak, *Angew. Chem.* **2001**, *113*, 1810; *Angew. Chem. Int. Ed.* **2001**, *40*, 1760; c) A. L. Barra, A. Caneschi, D. Gatteschi, D. P. Goldberg, R. Sessoli, *Solid State Chem.* **1999**, *451*, 484.

[3] a) A. L. Barra, D. Gatteschi, R. Sessoli, *Chem. Eur. J.* **2000**, *6*, 1608; b) L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, A. L. Barra, *Nature* **1996**, *383*, 145; c) J. R. Friedman, M. Sarachik, J. Tejada, R. Ziolo, *Phys. Rev. Lett.* **1996**, *76*, 3830.

[4] a) A. Yamaguchi, H. Ishimoto, K. Awaga, J. S. Yoo, M. Nakano, D. N. Hendrickson, E. K. Brechin, G. Christou, *Phys. B* **2000**, *284*–288, 1225; b) D. Gatteschi, A. Caneschi, L. Pardi, R. Sessoli, *Science* **1994**, *265*, 1054; c) A. Müller, F. Peters, M. T. Pope, D. Gatteschi, *Chem. Rev.* **1998**, *98*, 239.

[5] a) K. L. Taft, C. D. Delfs, G. C. Papaefthymiou, S. Foner, D. Gatteschi, S. J. Lippard, *J. Am. Chem. Soc.* **1994**, *116*, 823; b) R. R. Crichton, *Angew. Chem.* **1973**, *85*, 53; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 57; c) K. L. Taft, G. C. Papaefthymiou, S. J. Lippard, *Science* **1993**, *259*, 1302.

[6] a) K. Wieghardt, *Angew. Chem.* **1994**, *106*, 765; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 725; b) R. J. Debus, *Biochim. Biophys. Acta* **1992**, *1102*, 269; c) G. W. Bruvig, H. H. Thorp, R. H. Crabtree, *Acc. Chem. Res.* **1991**, *24*, 311; d) G. Christou, *Acc. Chem. Res.* **1989**, *22*, 328.

[7] a) A. Caneschi, A. Cornia, S. J. Lippard, *Angew. Chem.* **1995**, *107*, 511; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 467; b) S. P. Watton, P. Fuhrmann, L. E. Pence, A. Caneschi, A. Cornia, G. L. Abbati, S. J. Lippard, *Angew. Chem.* **1997**, *109*, 2917; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2774; c) R. W. Saalfrank, I. Bernt, E. Uller, F. Hampel, *Angew. Chem.* **1997**, *109*, 2596; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2482; d) G. L. Abbati, A. Cornia, A. C. Fabretti, A. Caneschi, D. Gatteschi, *Inorg. Chem.* **1998**, *37*, 3759; e) O. Waldmann, R. Koch, S. Schromm, J. Schülein, P. Müller, I. Bernt, R. W. Saalfrank, F. Hampel, E. Balthes, *Inorg. Chem.* **2001**, *40*, 2986; f) A. L. Dearden, S. Parsons, R. E. P. Winpenny, *Angew. Chem.* **2001**, *113*, 155; *Angew. Chem. Int. Ed.* **2001**, *40*, 151; g) H. Oshio, N. Hoshino, T. Ito, *J. Am. Chem. Soc.* **2000**, *122*, 12602.

[8] Crystal data for **1**-Cl$_3$ ($C_{66}H_{90}Cl_3Fe_7N_6O_{24}$): dark-red block (0.2x0.2x0.3 mm^3), $M = 1848.75$, trigonal, space group $P\bar{3}c1$ (No. 165), $a = 14.5632(15)$, $c = 22.374(3)$ Å, $V = 4109.4(9)$ Å^3, $Z = 2$, $T = -70$°C; A total of 22130 (R(int) = 0.0807) unique reflections ($3° < 2\theta < 50°$) were measured. Nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. Full-matrix least-squares refinement on F^2 (194 variables) converged to $R1 = 0.0650$, $wR2 = 0.1785$ ($I > 2\sigma(I)$). CCDC-192326 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit @ccdc.cam.ac.uk).

[9] An iron ion has unquenched orbital momentum and the spin-Hamiltonian should include the anisotropic term. Analysis of the magnetic data has not been performed.

[10] a) G. Armoi, M. J. Knapp, J.-O. Claude, J. C. Huffman, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* **1999**, *121*, 5489; b) H. J. Eppley, H.-L. Tsai, N. de Vries, K. Folting, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1995**, *117*, 301.

[11] V. R. Marath, S. Mitra, *Chem. Phys. Lett.* **1974**, *27*, 103.

[12] The average g value was estimated by the Curie plot of the χ_m values in the temperature range of 200–300 K.

Carborane Cages

Beyond the Icosahedron: The First 13-Vertex Carborane[**]

Anthony Burke, David Ellis, Barry T. Giles,
Bruce E. Hodson, Stuart A. Macgregor,
Georgina M. Rosair, and Alan J. Welch[*]

The chemistry of carboranes and heterocarboranes is dominated by the 12-vertex icosahedron. The first carborane reported[1] was 1-$C(CH_3)CH_2$-1,2-*closo*-$C_2B_{10}H_{11}$ and there are now literally thousands of heterocarboranes known based on the icosahedral geometry. The field of subicosahedral heterocarboranes is also well developed, which reflects the existence of carboranes from $C_2B_3H_5$ to $C_2B_9H_{11}$.

In contrast, the area of supraicosahedral heterocarboranes is relatively unexplored. Although the first 13-vertex metallacarborane was reported over 30 years ago,[2] there are only about a hundred such compounds currently known. The first supraicosahedral p-block metallacarborane was described only last year.[3] We are aware of only a handful of 14-vertex metallacarboranes,[4,5] and no such species of greater cluster size. Crucially, there are no reports of carboranes which extend the homologous family $C_2B_nH_{2+n}$ beyond $n = 10$ nor any reports of the parent borane ions $[B_nH_n]^{2-}$ for $n > 12$. This situation is unfortunate since several of the current applications of boron-cluster compounds, for example, in catalysis as "least-coordinating anions"[6] and in boron–neutron-capture therapy of tumors,[7] would benefit from the existence of carboranes with larger numbers of B atoms.

The most recent computational study of supraicosahedral boranes[8] concluded that a) $[B_{13}H_{13}]^{2-}$, $[B_{14}H_{14}]^{2-}$, and $[B_{15}H_{15}]^{2-}$ ions are thermodynamically unstable with respect to $[B_{12}H_{12}]^{2-}$, and b) the $[B_{12}H_{12}]^{2-} \rightarrow [B_{13}H_{13}]^{2-}$ step is particularly unfavorable and represents a synthetic bottleneck. Tantalizingly, the higher boranes $[B_{16}H_{16}]^{2-}$ and $[B_{17}H_{17}]^{2-}$ are predicted to be progressively more stable than $[B_{15}H_{15}]^{2-}$. In a separate study,[9] other workers have predicted stable, spherical, geometries for $B_{20}H_{20}$, $B_{32}H_{32}$, $B_{42}H_{42}$, and $B_{92}H_{92}$ clusters. Although similar calculations have not been performed on closo carboranes, the results of these computational studies suggest that several stable, large, carboranes could be viable synthetic targets as long as the 12-vertex→13-vertex barrier is overcome. We now report that breakthrough.

---

[*] Prof. A. J. Welch, A. Burke, Dr. D. Ellis, B. T. Giles, Dr. B. E. Hodson, Dr. S. A. Macgregor, Dr. G. M. Rosair
Department of Chemistry
Heriot-Watt University
Edinburgh EH14 4AS (UK)
Fax: (+44) 131-451-3180
E-mail: a.j.welch@hw.ac.uk

[**] We thank D. Ferrer, M. A. Laguna, and F. Schmidt for preliminary experiments. We acknowledge the EPSRC and the Leverhulme Trust for support of this work. We also thank A. S. F. Boyd for NMR spectra, R. Ferguson for mass spectra and G. Evans for microanalyses. A.J.W is the recipient of a Royal Society Leverhulme Trust Senior Research Fellowship.