# Microwave-Assisted Synthesis of a Ferrimagnetic Dodecanuclear Iron(III) Complex with a Fe$_4$(OH)$_4$ Cubane Core

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**S** *Supporting Information*

**ABSTRACT:** The microwave-assisted reaction of Fe-(ClO$_4$)$_2$ with NaN$_3$, NaO$_2$CPh, and 1,3-di(2-pyridyl)-1,3-propanedione gave a ferrimagnetic dodecanuclear iron(III) complex that shows magnetization relaxation behavior.

The synthesis of polynuclear transition-metal complexes has become the focus of intense research activities in the last few decades, not only because of their fascinating chemical and physical properties but also because of the architectural beauty of their structures.[1,2] To this end, synthetic efforts to prepare model complexes of iron proteins have yielded several interesting and unexpected polyiron complexes.[3] In contrast to the abundant Fe$_x$S$_y$ system, the corresponding iron oxo clusters are few in nature, but the design and preparation of polynuclear oxido-, hydroxido-, and alkoxido-bridged iron clusters have received considerable interest for four reasons: First, such coordination complexes may serve as biomimetic models;[3a−c] second, high-nuclearity iron complexes may exhibit interesting magnetic properties, e.g., single-molecule-magnet (SMM) behavior;[3d−g] third, some polyiron complexes show electrochemical bistability;[3h,i] fourth, a few complexes with a Fe$_2$O core show interesting catalytic properties.[3j]

To date, a number of coordination complexes in which iron ions are bridged by $\mu_n$-O(H) have been reported that involve the Fe$_2$O (V shape), Fe$_3$O (triangle), Fe$_4$O (square[4] or tetrahedron[3g,5]) and Fe$_4$O$_4$ (cubane) cores,[3g,h,5,6] in which the Fe$_4$O$_4$ cubic core built from most frequently $\mu_3$-O(H) bridges associated with other O-bridging moieties (carboxylato, carbonato, alkoxo, phenoxo, etc.) has been found in some Fe$_4$ and Fe$_8$ complexes. From the magnetic point of view, [Fe$_4$O$_4$]-containing complexes are particularly interesting because they often show ferromagnetic exchanges within the core.[3g,h,5,6]

On the other hand, microwave heating is an increasingly common tool for cluster synthesis.[5,7] As a preparative method, it may improve the yields and hasten the reaction rates. Moreover, it may lead to novel products by stabilizing different energy minima in a reaction system than the conventional methods of heating. Here, we report the microwave-assisted synthesis, crystal structure, and magnetic properties of a dodecanuclear iron(III) complex (**1**) with a cubic [Fe$_4$(OH)$_4$] core. It should be mentioned that, although several dodecanuclear iron(III) complexes have been reported,[8] complex **1** is the first one with the [Fe$_4$(OH)$_4$] core.

A microwave-assisted reaction (50 psi and 30 W) of Fe-(ClO$_4$)$_2$, NaO$_2$CPh, and NaN$_3$ with 1,3-di(2-pyridyl)-1,3-propanedione (dppo) in a MeOH−MeCN (1:5) solution at 70 °C for 10 min gave rodlike red crystals of [Fe$_{12}$O$_4$(OH)$_{12}$-(C$_7$H$_5$O$_2$)$_8$(C$_{13}$H$_9$N$_2$O$_2$)$_4$](ClO$_4$)$_4$·$x$MeCN·$y$H$_2$O (**1**·$x$Me-CN·$y$H$_2$O).[9] It should be mentioned that synthesis in the absence of sodium azide could give the complex but in low yield, and solvothermal synthesis without microwaves also gave the complex but in a longer time (2 weeks) and with a lower yield. The crystals lost guest solvents in air and then gave stable crystals of **1**·16H$_2$O after 2 weeks, which were used for X-ray and magnetic studies.

Single-crystal X-ray structural analysis[10] of **1**·16H$_2$O revealed that the crystals crystallized in the tetragonal space group $I4_1/a$, and the molecular structure is shown in Figure 1a. All iron ions in complex **1** are obviously iron(III), based on the charge balance and valence bond calculation (Supporting Information). The whole entity of the Fe$_{12}$ cluster has a 4/$m$ point group, and the cluster can be viewed as a [Fe$_4$(OH)$_4$] cubane connected to eight peripheral iron(III) ions through $\mu_3$-O$^{2−}$, $\mu_2$-OH$^−$, and $\eta^1$:$\eta^1$-$\mu_2$-O$_2$CPh$^−$ bridges, respectively. The ligand dppo$^−$ coordinates to iron(III) ions in a $\eta^1$:$\eta^1$:$\eta^1$:$\eta^1$-$\mu_2$ mode, as shown in Scheme 1, whereas the ligand PhCO$_2$$^−$ coordinates to iron(III) ions in a $\eta^1$:$\eta^1$-$\mu_2$ mode that connects peripheral−peripheral iron(III) ions (Fe1 and Fe2) and peripheral−internal iron(III) ions (Fe2 and Fe3), respectively. In the [Fe$_4$(OH)$_4$] core (Figure 1b), the Fe3 atom locates in an octahedron with O8, O8B, and O8C atoms from the core, O9 from $\mu_3$-O$^{2−}$, O10C from $\mu_2$-OH$^−$, and O6 from the benzoate ligand, respectively. Both Fe1 and Fe2 atoms are coordinated by one N atom and five O atoms to form coordination octahedra, in which O3 and O4 atoms belonging to one benzoate connect Fe1 and Fe2, which are also connected by the outside O7 atom and the inside O9 atom, respectively. The O1 and N1 atoms coordinated to Fe1 come from a dppo$^−$ ligand, the O2A and N2A atoms coordinated to Fe2 come from another one. The Fe1 and Fe2 atoms are connected to the [Fe$_4$(OH)$_4$] core in a slightly different way, where Fe1 is connected to Fe3 and Fe3A via $\mu_3$-O9 and $\mu_2$-O10 atoms, while Fe2 is connected to Fe3 via $\mu_3$-O9 and the benzoate group (O5 and O6). The four iron(III) (Fe3, Fe3A, Fe3B, and Fe3C) atoms in the [Fe$_4$(OH)$_4$] cubane are bridged by four $\mu_3$-OH$^−$ groups with Fe−O−Fe bond angles of 100.94°, 101.28°, and 103.73°, respectively. Also, each iron(III) ion of the [Fe$_4$(OH)$_4$] core is bridged to two peripheral iron(III) atoms by both oxygen ($\mu_3$-O$^{2−}$ and
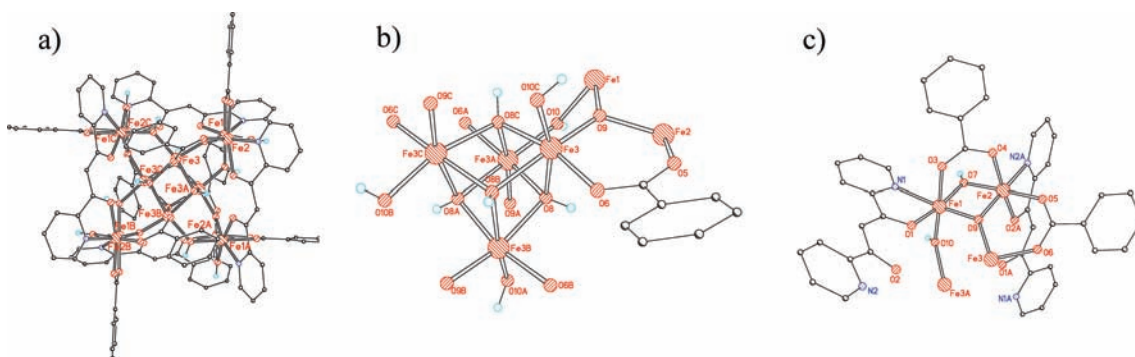
**Figure 1.** Perspective view of **1** with atom labels and a "metallic skeleton" of the new type $Fe_{12}$ showing the $[Fe_4O_4]$ cubane. Selected bond distances (Å) and angles (deg): Fe3−O8 2.083(5), Fe3−O8A 2.093(5), Fe3−O8C 2.057(5), Fe3−O9 1.868(5), Fe3−O10C 1.957(6), Fe3−O6 1.961(5), Fe2−O9 1.902(5), Fe2−O4 1.947(7), Fe2−O5 1.981(6), Fe2−O2A 2.007(6), Fe2−O7 2.102(6), Fe2−N2A 2.137(7), Fe1−O9 1.920(5), Fe1−O10 1.937(6), Fe1−O7 1.958(6), Fe1−O1 1.987(6), Fe1−O3 2.090(6), Fe1−N1 2.137(8); Fe3−O8−Fe3A 103.7(2), Fe3−O8−Fe3B 101.3(2), Fe3A−O8−Fe3B 100.9(2), Fe3−O9−Fe2 125.2(3), Fe3−O9−Fe1 130.7(3), Fe1−O10−Fe3A 130.3(3), Fe1−O9−Fe2 98.5(3), Fe1−O7−Fe2 90.9(2). Symmetry codes: A, $-x$, $-y + \frac{1}{2}$, $z$; B, $-y + \frac{1}{4}$, $x + \frac{1}{4}$, $-z + \frac{1}{4}$; C, $y - \frac{1}{4}$, $-x + \frac{1}{4}$, $-z + \frac{1}{4}$.

**Scheme 1. Deprotonation and Coordination Modes of Ligand dppo in 1**





**Figure 3.** In-phase ($\chi'$) and out-of-phase ($\chi''$) magnetic susceptibilities versus temperature in a 3.0 Oe ac field oscillating at the indicated frequencies and dc fields of 0 Oe for **1**.



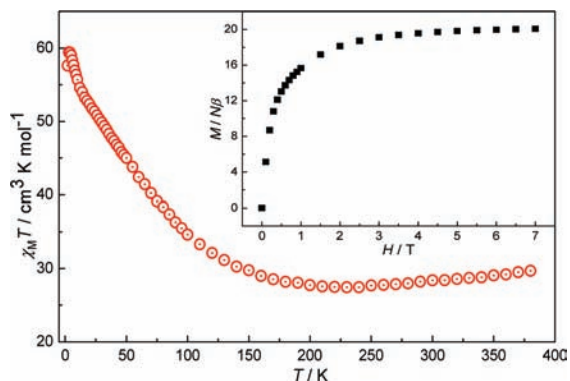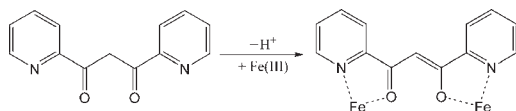**Figure 2.** Temperature-dependent susceptibilities of **1** under an applied field of 1000 Oe. Inset: Magnetization at 2 K.

$\mu_2$-OH$^-$) and benzoate groups with Fe−O−Fe bond angles of 125.20°, 130.65°, and 130.31°, respectively. Among the eight peripheral iron(III) ions, every two iron(III) ions are bridged together by both oxygen ($\mu_3$-O$^{2-}$ and $\mu_2$-OH$^-$) and benzoate groups with Fe−O−Fe bond angles of 98.52° and 90.92°, respectively (Figure 1c). The Fe−O−Fe bond angles between internal−peripheral iron(III) ions are larger than those within the $[Fe_4(OH)_4]$ core and peripheral−peripheral iron ions.

The direct-current (dc) magnetic susceptibilities of **1** were measured in the temperature range of 2−380 K (Figure 2). The $\chi_M T$ value is 29.69 cm$^3$ K mol$^{-1}$ at 380 K, which is much smaller than the theoretical one (52.5 cm$^3$ K mol$^{-1}$) for 12 uncoupled iron(III) ions ($S = \frac{5}{2}$ and $g = 2$). Upon cooling, the $\chi_M T$ value slowly decreases to a minimum value (27.45 cm$^3$ K mol$^{-1}$) at 230 K, and when the temperature continues to decrease from 230 K, the $\chi_M T$ value smoothly increases to reach a maximum of
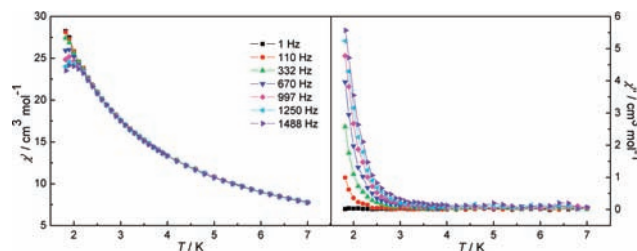
59.43 cm$^3$ K mol$^{-1}$ at 3 K, indicating the presence of intramolecular ferrimagnetic interactions within the $Fe_{12}$ cluster. Finally, the $\chi_M T$ value suddenly decreases upon cooling to reach a value of 57.62 cm$^3$ K mol$^{-1}$ at 2 K, which may be due to magnetization saturation and/or zero-field splitting. The $M$ vs $H$ plots at 2 K (Figure 2, inset) also confirm the observed ferrimagnetism. The magnetization value at 7 T is 20.04 $\mu_B$, which is similar to that (20 $\mu_B$) for a ferrimagnetic $Fe_{12}$ cluster with ground state $S_T = 10$ ($8 \times \frac{5}{2} - 4 \times \frac{5}{2}$, $g = 2$). Generally, iron(III) oxo complexes show antiferromagnetic properties when the Fe−O−Fe angles are larger than 110°. A further investigation of the core structure of **1** reveals that the average Fe−O−Fe angle between the peripheral and cubane iron(III) ions is 128.8°, and the average Fe−O−Fe angles within the $[Fe_4(OH)_4]$ core and between the peripheral and peripheral iron(III) ions are 101.9° and 94.7°, respectively, which imply that ferromagnetic exchanges exist within the $[Fe_4(OH)_4]$ core and among the peripheral iron(III) ions, while antiferromagnetic exchanges are present between the $[Fe_4(OH)_4]$ core and the peripheral iron(III) ions.

The alternating-current (ac) susceptibilities (Figure 3) of **1** show obvious frequency-dependent behavior although without a maximum in the out-of-phase signal until 1.8 K; meanwhile, the out-of-phase signal intensity increases with an increase in the frequency, which indicates that complex **1** may behave as a SMM, showing magnetization relaxation. On the other hand, the reduced magnetization (1−5 T; Figure 4) at a temperature range of 2−4 K shows that the $M \sim H/T$ lines are far from superposition, which further confirms the possible SMM behavior of **1** with significant anisotropy.
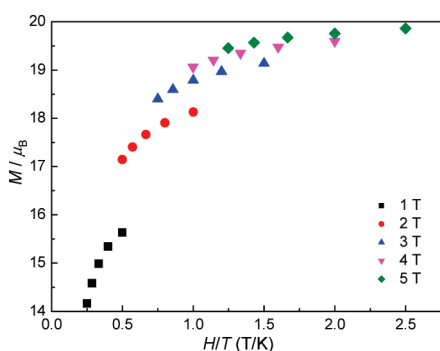
**Figure 4.** Magnetization in applied fields from 1 to 5 T at a temperature between 2 and 4 K.

In conclusion, we have synthesized a new dodecanuclear iron(III) complex with a $[Fe_4(OH)_4]$ core. Magnetic studies have revealed ferromagnetic interactions within the $[Fe_4(OH)_4]$ core and among the eight peripheral iron(III) ions as well as antiferromagnetic interactions between the $[Fe_4(OH)_4]$ core and the peripheral iron(III) ions, thus resulting in a ferrimagnetic cluster with ground state $S_T = 10$. Further studies on the ac susceptibilities and reduced magnetization show that complex **1** may be a SMM with magnetization relaxation.

## ■ ASSOCIATED CONTENT

**ⓢ Supporting Information.** Crystallographic information in CIF format, synthesis of **1**·16H$_2$O, bond valence calculations, XRPD pattern, a "metallic skeleton", and zero-field-cooled/field-cooled plots and IR spectrum of complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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## ■ ACKNOWLEDGMENT

## ■ REFERENCES

(1) (a) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141. (b) Stamatatos, T. C.; Foguet-Albiol, D.; Lee, S.-C.; Stoumpos, C. C.; Raptopoulou, C. P.; Terzis, A.; Wernsdorfer, W.; Hill, S. O.; Perlepes, S. P.; Christou, G. *J. Am. Chem. Soc.* **2007**, *129*, 9484. (c) Hu, K.-L.; Kurmoo, M.; Wang, Z.-M.; Gao, S. *Chem.—Eur. J.* **2009**, *15*, 12050. (d) Muller, A.; Peters, F.; Pope, M. T.; Gatteschi, D. *Chem. Rev.* **1998**, *98*, 239.

(2) (a) Liu, T.; Zhang, Y.-J.; Wang, Z.-M.; Gao, S. *J. Am. Chem. Soc.* **2008**, *130*, 10500. (b) Bai, Y.-L.; Tangoulis, V.; Huang, R.-B.; Zheng, L.-S.; Tao, J. *Chem.—Eur. J.* **2009**, *15*, 2377. (c) Bi, Y.-F.; Xu, G.-C.; Liao, W.-P.; Du, S.-C.; Wang, X.-W.; Deng, R.-P.; Zhang, H.-J.; Gao, S. *Chem. Commun.* **2010**, *46*, 6362. (d) Kong, X.-J.; Ren, Y.-P.; Chen, W.-X.; Long, L.-S.; Huang, R.-B.; Zheng, L.-S. *Angew. Chem., Int. Ed.* **2008**, *47*, 2398. (e) Kong, X.-J.; Long, L.-S.; Zheng, Z.-P.; Huang, R.-B.; Zheng, L.-S. *Acc. Chem. Res.* **2010**, *43*, 201. (f) Vlahopoulou, G. C.; Stamatatos,

T. C.; Psycharis, V.; Perlepes, S. P.; Christou, G. *Dalton Trans.* **2009**, *38*, 3646.

(3) (a) Wallar, B. J.; Lioscomb, J. D. *Chem. Rev.* **1996**, *96*, 2625. (b) Solomon, E. I.; Brunold, T. C.; Davis, M. I.; Kemsley, J. N.; Lee, S.-K.; Lehnert, N.; Neese, F.; Skulan, A. J.; Yang, Y.-S.; Zhou, J. *Chem. Rev.* **2000**, *100*, 235. (c) Johansson, A. J.; Noack, H.; Siegbahn, P. M.; Xue, G.-Q.; Que, L. *Dalton Trans.* **2009**, *38*, 6741. (d) Sangregorio, C.; Ohm, T.; Paulsen, C.; Sessoli, R.; Gatteschi, D. *Phys. Rev. Lett.* **1997**, *78*, 4645. (e) Ako, A. M.; Mereacre, V.; Lan, Y.-H.; Wernsdorfer, W.; Clerac, R.; Anson, C. E.; Powell, A. K. *Inorg. Chem.* **2010**, *49*, 1. (f) Miao, Y.-L.; Liu, J.-L.; Lin, Z.-J.; Ou, Y.-C.; Leng, J.-D.; Tong, M.-L. *Dalton Trans.* **2010**, *39*, 4893. (g) Lu, J.-W.; Lin, Y.-W.; Takahashi, M.; Wei, H.-H. *Inorg. Chem. Commun.* **2008**, *11*, 388. (h) Raptis, R. G.; Georgakaki, I. P.; Hockless, D. R. *Angew. Chem., Int. Ed.* **1999**, *38*, 1632. (i) Baran, P.; Boca, R.; Chakraborty, I.; Giapintzakis, J.; Herchel, R.; Huang, Q.; McGrady, J. E.; Raptis, R. G.; Sanakis, Y.; Simopoulos, A. *Inorg. Chem.* **2008**, *47*, 645. (j) Visvaganesan, K.; Suresh, E.; Palaniandavar, M. *Dalton Trans.* **2009**, *38*, 3814.

(4) Murali, M.; Nayak, S.; Costa, J. S.; Ribas, J.; Mutikainen, I.; Turpeinen, U.; Clemancey, M.; Garcia-Serres, R.; Latour, J.-M.; Gamez, P.; Blondin, G.; Reedijk, J. *Inorg. Chem.* **2010**, *49*, 2427.

(5) Gass, I. A.; Milios, C. J.; Whittaker, A. G.; Fabiani, F. P. A.; Parsons, S.; Murrie, M.; Perlepes, S. P.; Brechin, E. K. *Inorg. Chem.* **2006**, *45*, 5281.

(6) (a) Oshio, H.; Hoshino, N.; Ito, T.; Nakano, M. *J. Am. Chem. Soc.* **2004**, *126*, 8805. (b) Clemente-Juan, J. M.; Mackiewicz, C.; Verelst, M.; Dahan, F.; Bousseksou, A.; Sanakis, Y.; Tuchagues, J.-P. *Inorg. Chem.* **2002**, *41*, 1478.

(7) (a) Milios, C. J.; Vinslava, A.; Whittaker, A. G.; Parsons, S.; Wernsdorfer, W.; Christou, G.; Perlepes, S. P.; Brechin, E. K. *Inorg. Chem.* **2006**, *45*, 5272. (b) Milios, C. J.; Prescimone, A.; Sanchez-Benitez, J.; Parsons, S.; Murrie, M.; Brechin, E. K. *Inorg. Chem.* **2006**, *45*, 7053.

(8) (a) Stamatatos, T. C.; Christou, A. G.; Jones, C. M.; O'Callaghan, B. J.; Abboud, K. A.; O'Brien, T. A.; Christou, G. *J. Am. Chem. Soc.* **2007**, *129*, 9840. (b) Caneschi, A.; Cornia, A.; Fabretti, A. C.; Gatteschi, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 1295. (c) Abu-Nawwas, A. H.; Cano, J.; Christian, P.; Mallah, T.; Rajaraman, G.; Teat, S. J.; Winpenny, R. E. P.; Yukawa, Y. *Chem. Commun.* **2004**, *40*, 314. (d) Bagai, R.; Daniels, M. R.; Abboud, K. A.; Christou, G. *Inorg. Chem.* **2008**, *47*, 3318. (e) Boskovic, C.; Gudel, H. U.; Labat, G.; Neels, A.; Wernsdorfer, W.; Moubaraki, B.; Murray, K. S. *Inorg. Chem.* **2005**, *44*, 3181. (f) Konar, S.; Clearfield, A. *Inorg. Chem.* **2008**, *47*, 5573. (g) Murugesu, M.; Abboud, K. A.; Christou, G. *Polyhedron* **2004**, *23*, 2779.

(9) Synthesis: Fe(ClO$_4$)$_2$ (183 mg, 0.5 mmol), dppo (45 mg, 0.2 mmol), NaN$_3$ (13 mg, 0.2 mmol), NaO$_2$CPh (58 mg, 0.4 mmol), and MeOH/MeCN (1 mL/5 mL) were placed in a sealed glass tube and stirred for 20 min, which was then placed in a microwave reactor. The reaction mixture was maintained at 70 °C and 50 psi with microwave power 30 W for 10 min. After cooling, the solution was filtered and then slowly evaporated. Large rod-shaped red crystals of **1**·$x$MeCN·$y$H$_2$O were collected in 5 days. The crystals were exposed to air for 2 weeks to give stable crystals **1**·16H$_2$O. Yield: 35% (based on dppo). Elem anal. Calcd (found): C, 37.12 (37.17); H, 3.46 (3.50); N, 3.21 (3.58). IR data (cm$^{-1}$): 3424(s), 2924(w), 2853(w), 1633(w), 1539(m), 1450(m), 1398(s), 1271(w), 1121(s), 1025(m), 527(w), 469(w).

(10) Crystal data for **1**: C$_{108}$H$_{88}$N$_8$O$_{56}$Cl$_4$Fe$_{12}$, $M_r$ = 3205.86, tetragonal, space group $I4_1/a$, $a$ = 31.981(1) Å, $b$ = 31.981(1) Å, $c$ = 14.657(3) Å, $V$ = 14991. (3) Å$^3$, $Z$ = 4, $T$ = 293(2), $D_c$ = 1.420 g cm$^{-3}$, $\mu$ = 1.277, GOF = 0.988, R1 = 0.0954, and wR2 = 0.2887. The structure without distorted water molecules was refined with the *PLATON*[11] SQUEEZE procedure.

(11) Spek, A. L. *PLATON*; Utrecht University: Utrecht, The Netherlands, 1998.