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# Crystal structure and synthesis of a novel tetranuclear iron(III) complex with a defective double-cubane core†

**Hui Li,**[a] **Zhuang Jin Zhong,***[,a] **Wei Chen**[b] **and Xiao-Zeng You**[a]

[a] *Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, P. R. China*
[b] *Department of Chemistry, University of Malaya, Lambah Pautai, 59100 Kuala, Malaysia*

A novel tetranuclear iron(III) complex $[Fe_4(OCH_3)_6(acac)_4(N_3)_2]$ (acac = acetylacetonate) has been synthesized and shown by X-ray crystallography to contain an unusual defective double-cubane core connected by $\mu$-$OCH_3$ and $\mu_3$-$OCH_3$ bridges; it also shows an antiferromagnetic interaction.

One-dimensional magnetic compounds as important precursors of molecular magnets have aroused wide interest.[1–3] The azide group is a versatile bridging ligand and useful for generating this kind of system. A series of one- and two-dimensional $\mu$-azide nickel(II) complexes has been synthesized and characterized.[4–6] A few manganese(III) chain complexes have also been synthesized.[7] However, no $\mu$-azide $Fe^{III}$ chain complexes have been reported until now. To obtain such a complex we have attempted the reaction of $[Fe(acac)_2NO_3]$ with $NaN_3$ in methanol. To our surprise, a methoxo-bridged tetranuclear iron(III) complex $[Fe_4(OCH_3)_6(acac)_4(N_3)_2]$ (acac = acetylacetonate) was obtained instead in which the azide ion acts as a terminal ligand. There has been a growing interest in the synthesis of polynuclear iron complexes due to the discovery that the catalytic sites of a number of non-haem iron proteins contain oxo- or hydroxo-bridged diiron units and the relevance of large polyiron(II,III)–oxo aggregates to the ferritin core.[8–10] And a large number of polynuclear oxo-, hydroxo- and alkoxo-bridged iron complexes have been synthesized and characterized so far.[11–14] However, no tetranuclear $[Fe^{III}{}_4(OR)_6]^{6+}$ complex has been reported. In this view, $[Fe_4(OCH_3)_6(acac)_4(N_3)_2]$ is a novel example. In this communication, the synthesis, crystal structure and magnetic properties of this tetranuclear iron(III) complex are presented.

The complex $[Fe_4(OCH_3)_6(acac)_4(N_3)_2]$ was prepared by the reaction of equimolar amounts of $[Fe(acac)_2NO_3]$[15] (0.315 g, 1 mmol) and $NaN_3$ (0.065 g, 1 mmol) in methanol and acetone (1 : 2; 30 cm$^3$) with stirring for 0.5 h at room temperature. A red crystalline solid suitable for X-ray structure analysis was obtained after slow evaporation of this solution (Found: C, 34.90; H, 5.45; N, 9.75. Calc. for $C_{26}H_{46}Fe_4N_6O_{14}$: C, 35.10; H, 5.20; N, 9.45%). The structure of the entire molecule is illustrated in Fig. 1.‡

The structure consists of a centrosymmetric tetranuclear $Fe^{III}$ complex. The four Fe atoms are located at four corners of a defective double cubane and bridged by four $\mu$-$OCH_3$ and two $\mu_3$-$OCH_3$ groups. The intramolecular Fe · · · Fe distances range from 3.193(6) [Fe(1) · · · Fe(2′)] to 5.514(5) Å [Fe(1) · · · Fe(1′)]. The asymmetric unit consists of $Fe_2(acac)_2N_3(OCH_3)_3$. Within the asymmetric unit, the geometrical environment of Fe(1) and Fe(2) are roughly similar. Atom Fe(1) has a $NO_5$ distorted octahedral ligand donor set in which the O-donor atoms are supplied by an acac ligand [O(1), O(2)], two $\mu$-$OCH_3$ [O(6), O(7′)] and a $\mu_3$-$OCH_3$ [O(5)]. The N-donor atom comes from a terminal azide. However, Fe(2) has an $O_6$ donor set in a distorted octahedron, where five of the oxygen-donor atoms are the same as those of Fe(1) and the remainder is supplied by another $\mu_3$-$OCH_3$ [O(5′)]. The average Fe–$\mu$-OR bond length in $[Fe_4(OCH_3)_6(acac)_4(N_3)_2]$ (1.99 Å) is close to those in other $\mu$-alkoxo iron(III) complexes [2.06 Å].[12] The longest bond distance is Fe(1)–O(5) [2.196(5) Å], the $\mu_3$-$OCH_3$ ligand bridge being slightly asymmetric. The Fe(2)–O(5) bond distance [2.100(5) and 2.077(5) Å] is slightly shorter than Fe(1)–O(5) [2.196(5) Å] and the Fe(2′)–O(5)–Fe(2) bond angle [100.6(2)°] is slightly larger than those of Fe(2)–O(5)–Fe(1) [96.8(2)°] and Fe(2′)–O(5)–Fe(1) [96.7(2)°]. This is the first example of a structurally characterized tetranuclear iron(III) complex with a defective double cubane to our knowledge, although a pentanuclear one has been reported.[18]

The effective magnetic moment per iron ion in $[Fe_4(OCH_3)_6(acac)_4(N_3)_2]$ varies gradually from 4.26 $\mu_B$ at 300 K down to 2.75 $\mu_B$ at 80 K, indicative of an antiferromagnetic interaction between the metal ions. This behaviour is similar to another tetranuclear iron(III) complex, $[Fe_4O_2(O_2CCH_3)_7(bipy)_2][ClO_4]$ (bipy = 2,2′-bipyridine).[13] Further investigation into the magnetic behaviour of $[Fe_4(OCH_3)_6(acac)_4(N_3)_2]$ is in progress.

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† *Non-SI unit employed*: $\mu_B \approx 9.274 \times 10^{-24}$ J T$^{-1}$.

‡ Crystal data. $C_{26}H_{46}Fe_4N_6O_{14}$, red cubic crystal of dimension 0.25 × 0.14 × 0.05 mm, $M = 890.08$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 11.500(1)$, $b = 8.515(1)$, $c = 20.385(2)$ Å, $\beta = 99.26(1)°$, $U = 1970.1$ Å$^3$, $D_c = 1.500$ g cm$^{-3}$, $T = 300(2)$ K, $F(000) = 920$, Mo-K$\alpha$ radiation ($\lambda = 0.710\,73$ Å), $\mu = 1.509$ mm$^{-1}$. The structure was solved by the direct methods and refined by full-matrix least-squares methods using 3445 observed reflections. Absorption correction was not applied owing to the small size of the crystal. A total of 3617 unique data were measured on a four-circle Enraf-Nonius CAD4 diffractometer using $\omega$–2$\theta$ scans. The final $R1$ and $wR2$ values were 0.0697 and 0.1488 respectively for 226 parameters and $[\sigma^2(F_o)]^{-1}$ weights, goodness of fit = 0.871 on $F^2$ for all data. All non-H atoms were refined with anisotropic displacement parameters, whereas H atoms were located from the difference map.[16,17] Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/394.

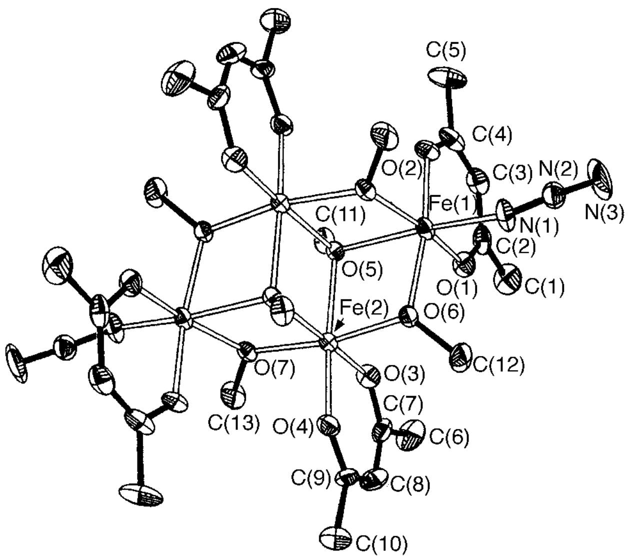

**Fig. 1** Structure of $[Fe_4(OCH_3)_6(acac)_4(N_3)_2]$. Selected bond lengths (Å) and angles (°): Fe(1)···Fe(1′) 5.514(5), Fe(2)···Fe(1) 3.212(5), Fe(1)···Fe(2′) 3.193(6), Fe(2)···Fe(2′) 3.214(5), Fe(1)–O(7′) 1.974(5). Fe(1)–O(2) 1.986(5), Fe(1)–O(6) 1.993(5), Fe(1)–O(1) 1.997(6), Fe(1)–N(1) 1.986(8), Fe(1)–O(5) 2.196(5), Fe(2)–O(3) 1.949(6), Fe(2)–O(7) 1.973(5), Fe(2)–O(6) 1.968(5), Fe(2)–O(4) 1.980(5), Fe(2)–O(5′) 2.077(5), Fe(2)–O(5) 2.100(5), O(5)–Fe(2′) 2.077(5), O(7)–Fe(1′) 1.974(5), N(1)–N(2) 1.175(1), N(2)–N(3) 1.116(1); O(7′)–Fe(1)–O(2) 89.6(2), O(7′)–Fe(1)–O(6) 92.1(2), O(2)–Fe(1)–O(6) 167.1(2), O(7′)–Fe(1)–O(1) 165.9(2), O(2)–Fe(1)–O(1) 86.2(2), O(6)–Fe(1)–O(1) 89.1(2), O(7′)–Fe(1)–N(1) 97.1(3), O(2)–Fe(1)–N(1) 97.0(3), O(6)–Fe(1)–N(1) 95.5(3), O(1)–Fe(1)–N(1) 96.8(3), O(7′)–Fe(1)–O(5) 76.1(2), O(2)–Fe(1)–O(5) 92.0(2), O(6)–Fe(1)–N(5) 76.0(2), O(1)–Fe(1)–O(5) 90.5(2), N(1)–Fe(1)–O(5) 168.7(3), O(3)–Fe(2)–O(7) 93.5(2), O(3)–Fe(2)–O(6) 93.4(2), O(7)–Fe(2)–O(6) 169.6(2), O(3)–Fe(2)–O(4) 89.7(3), O(7)–Fe(2)–O(4) 94.5(2), O(6)–Fe(2)–O(4) 93.4(2), O(3)–Fe(2)–O(5′) 170.9(2), O(7)–Fe(2)–O(5′) 79.0(2), O(6)–Fe(2)–O(5′) 93.4(2), O(4)–Fe(2)–O(5′) 95.9(2), O(3)–Fe(2)–O(5) 96.0(2), O(7)–Fe(2)–O(5) 92.7, O(6)–Fe(2)–O(5) 78.8(2), O(4)–Fe(2)–O(5) 170.5(2), O(5′)–Fe(2)–O(5) 79.4(2), Fe(2′)–O(5)–Fe(2) 100.6(2), Fe(2′)–O(5)–Fe(1) 96.7(2), Fe(2)–O(5)–Fe(1) 96.8(2), Fe(2)–O(6)–Fe(1) 108.4(2), Fe(1′)–O(7)–Fe(2) 108.0(2)

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