Synthesis, Structure and Magnetic Property of a Tetranuclear Iron(Ⅲ) Complex of "Face-to-Face" Type

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A tetranuclear iron(Ⅲ) complex $[\{Fe_2(L)(AcO)\}_2(O)_2](PF_6)_2$ of the macrocyclic dinucleating ligand (L^{2-}) derived from the [2 + 2] condensation between 2,6-diformyl-4-methylphenol and 1,3-diaminopropane has a "face-to-face" structure, comprising two dinuclear $\{Fe_2(L)(AcO)\}^{3+}$ units connected by two oxo bridges.

There are considerable studies on polynuclear oxoiron complexes as the relevance to some biological systems[1] and three types of tetranuclear oxoiron(Ⅲ) complexes have been obtained: (a) adamantane type of Fe_4O_6 core,[2] (b) butterfly type of Fe_4O_2 core[3] and (c) tetragon type of Fe_4O_4 core[4–6] (Fig. 1). We report here the first tetranuclear oxoiron(Ⅲ) complex of "face-to-face" type (Fig. 1, d) with Fe_4O_6 core.

$[\{Fe_2(L)(AcO)\}_2(O)_2](PF_6)_2$ has been obtained using a macrocyclic ligand (L^{2-}) derived from the [2 + 2] condensation between 2,6-diformyl-4-methylphenol and 1,3-diaminopropane. An ORTEP view of the complex is shown in Fig. 2.

The crystal consists of two dinuclear $\{Fe_2(L)(AcO)\}$ units, two oxo ligands and two PF_6^- ions. In each dinuclear unit the macrocyclic ligand accommodates two Fe(Ⅲ) ions in the Fe(1)···Fe(1*) separation of 3.078(1) Å. An acetate group in the *syn,syn* mode bridges the two Fe atoms. The in-plane Fe-to-donor bond distances range from 2.052(2) Å to 2.121(3) Å. Two $\{Fe_2(L)(AcO)\}$ units are combined by oxide ions, producing a tetranuclear core of a "face-to-face" type. The Fe(1)–O(3) bond distance (1.784(1) Å) is typical of Fe^{III}–O–Fe^{III} bond.[7] The Fe(1)–O(3)–Fe(1′) angle is 156.3(2)°. The O(3)···O(3*) separation is 3.810(4) Å.

The powdered sample of the complex has a subnormal magnetic moment of 1.84 BM at room temperature and the moment decreases with lowering temperature to reach a plateau value of 0.53 BM near 30 K (Fig. 3). Below 10 K the moment shows a second decrease to 0.42 BM at 2.0 K.

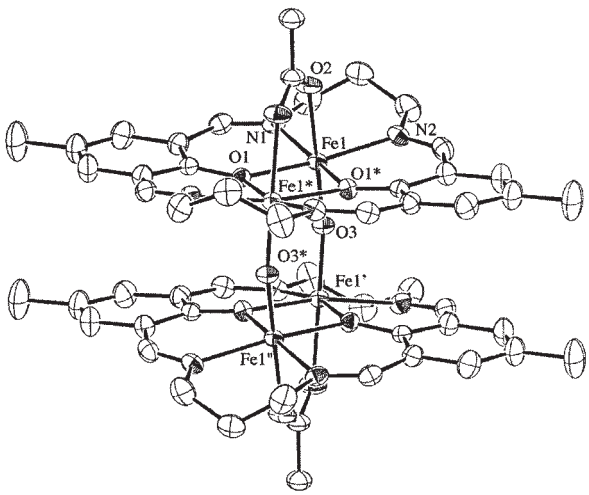

Fig. 2. An ORTEP view of $[\{Fe_2(L)(AcO)\}_2(O)_2](PF_6)_2$ with the atom numbering scheme. Selected bond distances and angles: Fe(1)–O(1) 2.052(2), Fe(1)–O(1*) 2.046(2), Fe(1)–O(2) 2.121(3), Fe(1)–O(3) 1.7840(7), Fe(1)–N(1) 2.084(3), Fe(1)–N(2) 2.089(3) Å; Fe(1)–O(1)–Fe(1*) 97.37(9), Fe(1)–O(3)–Fe(1′) 156.3(2), O(2)–Fe(1)–O(3) 179.0(1)°.

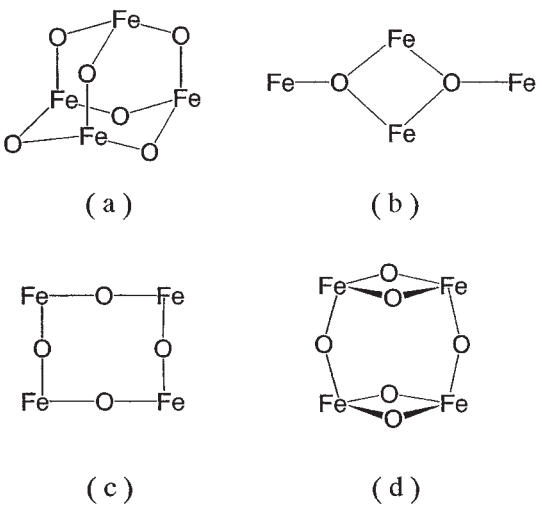

Fig. 1. Tetranuclear oxoiron(Ⅲ) core structures.

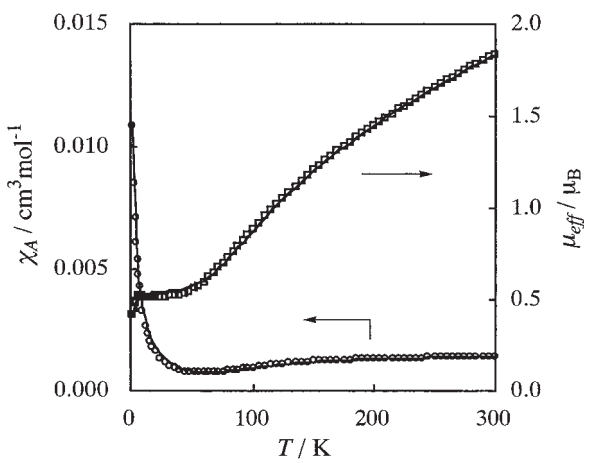

Fig. 3. Temperature-dependence of magnetic susceptibility and magnetic moment of $[\{Fe_2(L)(AcO)\}_2(O)_2](PF_6)_2$.

The spin Hamiltonian for the system is given by $\boldsymbol{H} = -2J'(S_1S_2 + S_3S_4) - 2J(S_2S_3 + S_1S_4)$ where J' is the exchange integral in the dinuclear unit (Fe1–Fe1* and Fe1′–Fe1″ of Fig. 2) and J is the exchange integral between the dinuclear units (Fe1–Fe1′ and Fe1*–Fe1″). Magnetic analyses have been carried out using the magnetic susceptibility expression based on the molecular field approximation:[8]

$$\chi_A = (1-\rho)\frac{Ng^2\beta^2}{kT-2JF}F + \rho\frac{35Ng^2\beta^2}{12k(T-\theta)} \quad (1)$$

where $F = \{x + 5x^3 + 14x^6 + 30x^{10} + 55x^{15}\}/\{1 + 3x + 5x^3 + 7x^6 + 9x^{10} + 11x^{15}\}$ with $x = \exp(2J/kT)$. In this expression ρ is the fraction of paramagnetic impurity, θ is the correction term for magnetic interaction of the paramagnetic impurity, and the remaining symbols have their usual physical meanings.

As indicated in Fig. 3 the cryomagnetic property of the complex is well reproduced using $J = -101$ cm^{-1}, $J' = -11$ cm^{-1}, $g = 2.0$, $\rho = 0.0090$ and $\theta = -1.52$ K. The large negative exchange integral in the Fe–O–Fe unit ($J = -101$ cm^{-1}) is common for μ-oxodiiron(Ⅲ) complexes[9] and the exchange integral in the dinuclear unit ($J' = -11$ cm^{-1}) is also common for di(μ-alkoxo)- and di(μ-hydroxo)diiron(Ⅲ) complexes.[9–12] The second drop in magnetic moment below 10 K, associated with the negative θ, arises from an antiferromagnetic interaction of the paramagnetic impurity.

Experimental

Preparation. $[\{Fe_2(L)(AcO)\}_2(O)_2](PF_6)_2$ was obtained as dark brown crystals by the reaction of 2,6-diformyl-4-methylphenol (100 mg), 1,3-diaminopropane (46 mg), iron(Ⅲ) acetate (146 mg) and NH_4PF_6 (194 mg) in ethanol. Found: C, 42.62; H, 4.03; N, 7.67%. Calcd for $C_{52}H_{58}F_{12}Fe_4N_8O_{10}P_2$: C, 42.53; H, 3.98; N, 7.63%.

Crystallography. Crystal data for $[\{Fe_2(L)(AcO)\}_2(O)_2](PF_6)_2$ were obtained on a Rigaku RAXIS-RAPID Imaging Plate diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å); $C_{52}H_{58}F_{12}Fe_4N_8O_{10}P_2$, MW = 1468.37; orthorhombic, space group *Cmca* (No. 64), $a = 15.1981(9)$, $b = 22.637(1)$, $c = 16.9249(5)$ Å, $Z = 4$, $V = 5822.9(5)$ Å^3, $D_c = 1.682$ g cm^{-3}; No. of reflections 3457. Intensity data were corrected for Lorentz and polarization effects.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 196163.

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