An Octanuclear Fe^{III} Compound Featuring a New Type of Double Butterfly Iron–Oxo Core[**]

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Iron–oxo clusters are of interest both as models for the biomineralization of iron[1, 2] and as magnetic materials with high-spin ground states.[3] "Basic" iron carboxylates, such as **1**,

$[Fe_3(\mu_3\text{-}O)(O_2CPh)_6(H_2O)_3](O_2CPh)$ **1**

have been utilized as starting reagents to prepare a number of such species, for example Fe$_{10}$ [4, 5] and Fe$_{11}$ compounds,[6] although the mechanism involved is still unclear.

In the course of studies concerned with the preparation of mixed Fe-metal-carboxylate-alkoxy derivatives for possible sol–gel processing to mixed metal oxides, we have been investigating the interaction between the benzoate **1** and various metal alkoxides. Reaction of **1** with Ti(O*n*Pr)$_4$ in boiling *n*-propanol gave a sparingly soluble precipitate containing the bulk of the Fe. This precipitate was recrystallized from THF to give crystals identified by an X-ray diffraction study as the THF solvate of the known polynuclear Fe$_{11}$ compound $[Fe_{11}(\mu_3\text{-}O)_6(\mu_3\text{-}OH)_6(O_2CPh)_{15}]$.[6] The decanuclear "ferric wheel" compounds $[Fe(OR)_2(O_2CR')]_{10}$[4, 5] resulted from comparable reactions of basic iron carboxylates (**1**[4] and $[Fe_3(\mu_3\text{-}O)(O_2CCH_3)_6(H_2O)_3](Cl)$[5]) with specific alcohols in the presence of additional Fe^{3+} ions [4] or pyridone.[5] Therefore, it was thought highly likely in the present reaction that an initial complex, containing both alkoxide and carboxylate residues, may have formed by direct reaction between **1** and propanol, possibly also involving some group exchange between the Fe and Ti precursors. Hydrolysis by adventitious water during recrystallization could then have produced the Fe$_{11}$ compound. A related reaction between $[Fe_3(\mu_3\text{-}O)(O_2CPh)_6(H_2O)(py)_2](O_2CPh)$ (py = pyridyl) and Ti(O*n*Pr)$_4$ in toluene in the presence of the bulky alcohol neopentanol gave $[Ti_6(\mu_3\text{-}O)_6(O_2CPh)_6\{OCH_2C(C(CH_3)_3)\}_6]$, a product with a $[Ti_6O_6]^{12+}$ core similar to that recently found in $[Ti_6(\mu_3\text{-}O)_6(O_2CC_6H_4OPh)_6(OEt)_6]$,[7] together with an Fe-only alkoxy–carboxylate complex which unfortunately could not be obtained in a crystalline form suitable for X-ray structural analysis.

However, direct reaction between **1** and neopentanol in toluene did produce a suitably crystalline product that was found by X-ray crystallography[8] to be the Fe$_8$ derivative **2**,

$[Fe_8(\mu_3\text{-}O)_2(\mu_4\text{-}O)_2(\mu\text{-}OCH_2t\text{Bu})_2(\mu\text{-}O_2CC_6H_5)_{12}(O_2CC_6H_5)_2(HOCH_2t\text{Bu})_2]\cdot 4\,C_6H_5CH_3$ **2**

isolated as the tetratoluene adduct (Figure 1). Compound **2** contains discrete molecules of the centrosymmetric octanuclear complex with the eight Fe^{III} atoms linked in a chainlike fashion by 12 carboxylato, two alkoxo, two μ_3-oxo, and two μ_4-oxo bridging groups. Monodentate carboxylate and alkoxide groups are attached to the end Fe atoms (Fe1, Fe1*). Overall two Fe atoms are five-coordinate and the remainder six-coordinate. The two bridging alkoxo groups link pairs of Fe atoms (Fe3, Fe4*) associated with the two central Fe$_4$(μ_4-O) units.

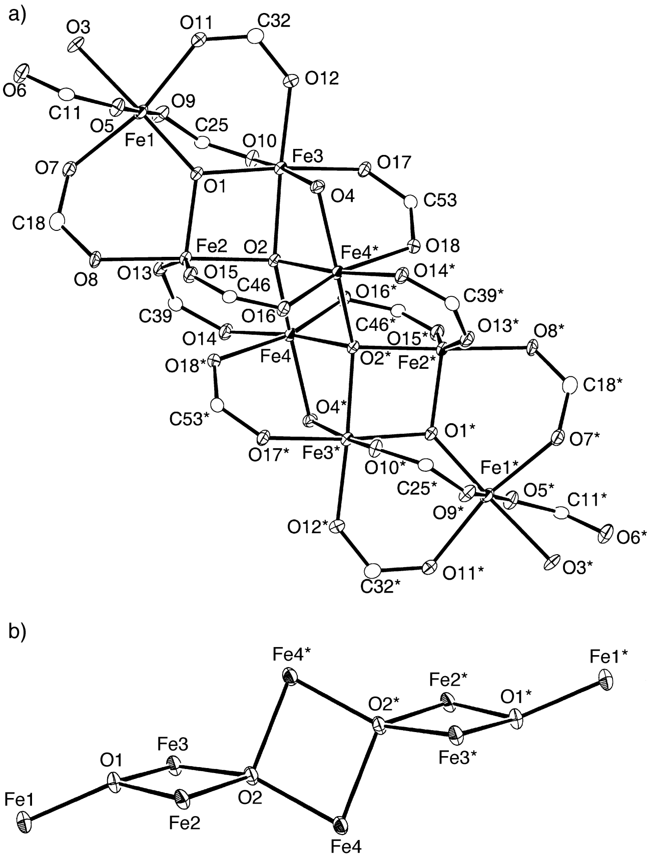

Figure 1. a) ORTEP plot of the molecular structure of **2** (30% probability ellipsoids). Phenyl groups have been omitted for clarity. b) View of the double-butterfly $[Fe_8(\mu_3\text{-}O)_2(\mu_4\text{-}O)_2]^{16+}$ core of **2**. Selected bond distances [Å] and angles [°]: μ_3-O1–Fe1 1.872(2), μ_3-O1–Fe2 1.871(2), μ_3-O1–Fe3 1.938(2), μ_4-O2–Fe2 2.018(2), μ_4-O2–Fe3 2.024(2), μ_4-O2–Fe4 1.978(2), μ_4-O2–Fe4* 2.029(2), Fe1–O5$_{carbox}$ 1.979(3), Fe1–O7$_{carbox}$ 2.048(2), Fe1–O9$_{carbox}$ 2.023(3), Fe1–O3$_{alkox}$ 2.082(2), Fe2–O13$_{carbox}$ 2.002(3), Fe3–O17$_{carbox}$ 2.015(2), Fe3–O4$_{alkox}$ 2.028(2); Fe3-O4$_{alkox}$-Fe4* 98.60(9), O3-Fe1-O5 85.7(1), O3-Fe1-O7 83.65(9), O1-Fe1-O3 176.7(1), O1-Fe1-O5 91.4(1), O1-Fe1-O9 92.0(1), O1-Fe2-O13 99.6(1), O1-Fe2-O15 98.71(10), O1-Fe3-O4 96.40(10), O1-Fe3-O10 89.06(10), O1-Fe3-O12 98.09(9), O2-Fe2-O8 173.78(10), O13-Fe2-O15 158.92(9), Fe1-O1-Fe2 129.0(1), Fe1-O1-Fe3 121.5(1), Fe2-O1-Fe3 100.6(1), Fe2-O2-Fe3 92.94(9), Fe2-O2-Fe4 108.00(9), Fe2-O2-Fe4* 120.3(1), Fe3-O2-Fe4 143.4(1), Fe3-O2-Fe4* 96.25(8), Fe4-O2-Fe4* 98.32(9).

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The Fe_8O_4 core may be viewed as a "double-butterfly" arrangement (Figure 1 b). Within each Fe_4O_2 unit the O-Fe-O and Fe-O-Fe angles are close to corresponding angles in reported butterfly Fe_4O_2 cores.[9] The dihedral angle between the planes defined by Fe1/Fe2/Fe3 and Fe2/Fe3/Fe4 is 152.8°. Within each Fe_4O_2 unit the associated μ-O atoms lie out of the planes of the Fe_3 sets. Thus, O1 (a μ_3-O atom) lies 0.32 Å above the Fe1/Fe2/Fe3 plane, while O2 (a μ_4-O atom) is 0.42 Å above the Fe2/Fe3/Fe4 plane. The centrosymmetric geometry of the Fe_8 molecule requires that the corresponding oxo groups in the other Fe_4O_2 unit lie below the appropriate Fe_3 planes. This displacement of a μ_3-O atom from the Fe_3 plane is similar to that in other $[Fe_4O_2]$ cores.[10]

The short O–O distance between the noncoordinated oxygen atom of a terminal carboxylate and the neighboring alkoxo oxygen atom (O6–O3 2.58 Å) indicates the existence of a hydrogen bond between them. In keeping with this, the C–O distance of the monodentate carboxylate group bound to Fe1 (C11–O5 1.285 Å) is longer than that involving the noncoordinated oxygen atom (C11–O6 1.249 Å), and therefore possesses greater single-bond character than the latter. The average C–O distance for bridging carboxylates in the rest of the molecule is 1.265 ± 0.007 Å. The distance from an iron center to the O_{alkoxo} atom (Fe1–O3 2.082 Å) is longer than to a bridging O_{alkoxo} atom (Fe3–O4 and Fe4–O4 av 1.991 Å), and comparable to that for MeOH bound to Fe^{III} in a basic carboxylate.[11] It is therefore concluded that an alcohol molecule is coordinated to Fe1 and hydrogen bonded to a monodentate carboxylate.

The Fe–O distances to the carboxylate, alkoxo, and oxo groups are comparable to those found in other basic Fe_3 carboxylates and polynuclear Fe-alkoxo-carboxylate complexes. The bond angles in the Fe_3 and Fe_4 arrays, however, diverge considerably from the ideal values (see the legend to Figure 1).

The solid-state Mössbauer spectrum of **2** measured at 81 K exhibits two broad lines, the sum of several unresolved quadrupole split doublets which were fitted with Lorentzian lines as the sum of four doublets. The doublets are centered at an isomer shift of $\delta = 0.51(1)$ mm s^{-1} with quadrupole splitting parameters ΔE_Q of 0.31(6), 0.51(5), 0.70(8), and 0.86(6) mm s^{-1} and corresponding relative areas of 27(2), 28(2), 23(2), and 22(2)%. The four site occupancies of about 25% are in agreement with expectations from crystallography. The smaller area observed for the more distorted sites could reflect the fact that no correction has been made for possible small differences in the Lamb–Mössbauer factor for the four sites. The quadrupole splittings are comparable to those of other high-spin Fe^{III} complexes with Fe_4O_2 butterfly cores;[9, 10] these values are known to vary with the nature of the terminal ligands (ΔE_Q values as low as 0.3 mm s^{-1} have been noted in oxo-bridged systems of various nuclearities).

The magnetic moment behavior of **2** as a function of temperature, in a field of 1 T, is indicative of antiferromagnetic coupling. The effective magnetic moment μ_{eff} (per Fe_8 unit) of 7.9 μ_B at 300 K decreases gradually at first, reaching approximately 2.5 μ_B at 50 K, then more rapidly to approach a plateau just above zero (ca. 0.8 μ_B) at 4 K. This behavior indicates an $S = 0$ coupled ground state. A good fit of the μ_{eff} data was obtained using Hendrickson's tetranuclear model[9] when the assumption was made that **2** consists of two independent tetranuclear butterfly clusters. A plot of the magnetic moment data per Fe_4 group is shown in Figure 2, together with the best-fit curve obtained using $g = 2.00$ and $2J_{12}$ ($= 2J_{wb}$) $= -55$ cm^{-1}; $2J_{23}$ ($= 2J_{bb}$) was indeterminate because of spin frustration. The $2J_{12}$ value is less than that in $[Fe_4(\mu_3\text{-}O)_2(O_2CCH_3)_7(bpy)_2](ClO_4)$[9] ($2J_{12} = -90$ cm^{-1}; bpy = 2,2′-bipyridyl), which also has an $S = 0$ ground state. This value is also lower than that estimated[3] for the central Fe_4O_2 butterfly core (-120 cm^{-1}) in the octanuclear complex $[Fe_8(tacn)_6(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_{12}]^{8+}$ (tacn = 1,4,7-triazacyclononane), which possesses an $S = 10$ ground state because of the parallel alignment of the spins of the four outer Fe^{III} ions.[12, 13] This nanomagnetic compound displays quantum-tunneling phenomena.[14] These differences in $2J_{12}$ values for **2** probably relate to the nonplanarity of the two Fe_4O_2 groups, particularly around O2, compared to the other examples cited.

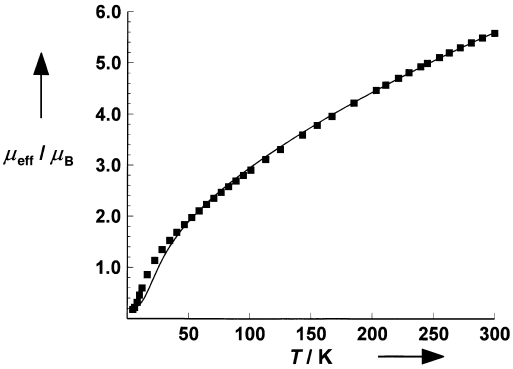

Figure 2. The magnetic moment μ_{eff} of **2** (◆), expressed per Fe_4 unit, as a function of temperature T. The solid line represents the relationship calculated assuming two independent butterfly Fe_4 species[9] with $g = 2.0$ and $2J_{12}$ ($= 2J_{wb}$) $= -55$ cm^{-1}; $2J_{23}$ ($= 2J_{bb}$) was indeterminate, and $2J_{44'}$ assumed to be zero. Inclusion of a temperature independent paramagnetic susceptibility (TIP) $= 900 \times 10^{-6}$ cm^3 mol^{-1} per Fe_4, as in ref. [9], improves the fit at low temperatures using $2J_{12} = -59$ cm^{-1}.

The chainlike, double-butterfly arrangement of the Fe_8O_4 core of **2** is unique amongst the family of known iron–oxo clusters. Of the four structurally characterized Fe_8 complexes, each of which also contains chelating ligands, three—$[Fe_8(tacn)_6(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_{12}]^{8+}$,[12] $[Fe_8(\mu_4\text{-}O)(\mu_3\text{-}O)_4(OAc)_8(tren)_4]^{6+}$ (tren = tris(2-aminoethyl)amine),[15] and $[Fe_8(\mu_4\text{-}O)_4(\mu\text{-}pz)_{12}Cl_4]$ (pz = pyrazine)[16]—have condensed three-dimensional structures while one—$[Fe_8(\mu\text{-}O)_4(\mu\text{-}BMDP)_4(OH)_4(\mu\text{-}OAc)_4]^{4+}$ (BMDP = N,N,N''-Tris((N-methyl)-2-benzimadazolylmethyl)-N'-methyl-1,3-diamino-2-propanol)[17]—contains a square array of Fe atoms. Winpenny and co-workers[18] have recently reported a Cr^{III} complex, $[Cr_8(\mu_4\text{-}O)_4(O_2CPh)_{16}]$, which also exhibits a double-butterfly M_8O_4 core. However, the perpendicular orientation of the two M_4O_2 units, rather than parallel as in **2**, gives rise to a distorted Cr_4O_4 cubane. Iron clusters with a nuclearity of eight reported thus far either have more condensed three-dimensional arrangements of the Fe atoms linked by oxo (and often hydroxo) bridges or are cyclic arrays of Fe atoms linked by carboxylates and alkoxides. Indeed, chainlike structures of equal or greater nuclearity than **2** have not yet been identified.

Experimental Section

2: Compound **1** (0.20 g 0.18 mmol) was suspended in dry toluene (4 mL) containing neopentanol (2.0 g 22.7 mmol). The minimum volume of toluene necessary to dissolve all the alcohol at room temperature was used. Stirring the solution for 24 h at room temperature allowed complete dissolution of the basic Fe carboxylate **1**, giving a red solution. Dark red single crystals of **2** suitable for X-ray study were deposited during the next 7 d (yield ca. 50 %). No other product was deposited from the solution. Crystals of **2** lose solvent on drying under a stream of nitrogen and analyze as the ditoluene solvate: found: C 57.9, H 5.0 %; calcd for $C_{132}H_{132}O_{36}Fe_8$: C 57.8, H 4.8 %.

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[8] X-ray structural analysis of **2** ($C_{146}H_{148}O_{36}Fe_8$): $M_r = 2925.53$, dark red crystals, dimensions $0.20 \times 0.20 \times 0.15$ mm, monoclinic, space group $P2_1/n$ (no. 14); $a = 18.379(1)$, $b = 16.264(1)$, $c = 24.122(1)$ Å, $\beta = 103.756(1)^{\circ}$, $V = 7000.3(6)$ Å^3; $Z = 2$, $\rho_{calcd} = 1.39$ g cm^{-3}; $2\theta_{max} = 58.2^{\circ}$; $F_{000} = 3040$, $T = 123$ K; Nonius Kappa CCD, graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), data corrected for Lorentzian polarization ($\mu(Mo_{K\alpha}) = 8.80$ cm^{-1}); of 17312 independent reflections, 10570 were observed ($I \geq 3\sigma(I)$) and used in the full-matrix least-squares refinement of 856 variables; $R = 0.053$, $R_w = 0.052$ (refined against $|F|$); max./min. residual electron peaks were 1.18/-1.04 e$^-$ Å^{-3}. Non-hydrogen atoms were refined with anisotropic thermal parameters, hydrogen atoms were included but not refined. Neutral atom scattering factors were employed. Crystal structural solution and refinement was performed using the teXsan analysis package (Molecular Structure Corporation, **1992**). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134640. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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$FBeNg^+$ (Ng = He, Ne, Ar): Suitable Cations for Salts of the Lightest Noble Gases?[**]

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Since the isolation by Bartlett of the first stable compound containing xenon,[1] numerous ionic and covalent species of this element and certain analogues of krypton have been synthesized and characterized.[2, 3] It is also well known that helium, neon, and argon form quite stable species in the gas phase,[4] but no "true" chemical compounds of these elements have ever been prepared. Therefore, overcoming the chemical inertness of the lightest noble gases still remains a fascinating challenge of great experimental and theoretical interest.

The ArF^+ cation has been suggested[5] as being suitable for the preparation of salts like $ArF^+AuF_6^-$ and $ArF^+SbF_6^-$. We report here computational results on the structure, stability, and thermochemistry of the $FBeNg^+$ cations (Ng = He, Ne, Ar), which open the challenging but not unrealistic perspective that not only $FBeAr^+$ but also $FBeNe^+$ and even $FBeHe^+$ could form stable salts. Our calculations have been inspired by results reported on the neutral complexes between the BeO molecule and the noble gases.[6, 7] All the OBeNg complexes, including OBeHe, were predicted[6] to be stable with respect to dissociation into ground-state BeO ($^1\Sigma^+$) and Ng (^1S). The heaviest members in this series—OBeAr, OBeKr, and OBeXe—have actually been observed in low-temperature matrix-isolation experiments.[7] The OBe–Ng bond energies were calculated to range from about 3 kcal mol^{-1} for Ng = He to about 13 kcal mol^{-1} for Ng = Xe.[6] It is plausible that, in its singlet ground state $^1\Sigma^+$,[8, 9] the positively charged BeF^+ could fix noble gases even more efficiently than the neutral, isoelectronic BeO.

The results of our calculations (Table 1) fully meet, and perhaps exceed, this qualitative expectation. In fact, all the $FBeNg^+$ species proved to be stable with respect to dissociation into BeF^+ ($^1\Sigma^+$) and Ng (^1S). The enthalpy changes (at 298.15 K) of reaction (1) were computed, at the Gaussian 3 (G3)[10] level of theory, to be 10.6 (Ng = He), 16.0 (Ng = Ne), and 34.5 kcal mol^{-1} (Ng = Ar). These values are indeed

$$FBeNg^+ (^1\Sigma^+) \rightarrow BeF^+ (^1\Sigma^+) + Ng (^1S) \qquad (1)$$

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