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A Decairon Cluster Devoid of Polydentate Ligands

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Introduction

The regioselective allylic amination of olefins by aryl hydroxylamines is catalyzed by iron salts[1] and complexes.[2] We have recently found that the active aminating agent in the iron salt-catalyzed reactions is a novel azodioxide complex.[1b,c] To expand the scope of these reactions and possibly to identify other reactive nitrogen-containing compounds, we have begun to examine the interaction of transition metal salts and complexes with hydroxylamine itself. Although hydroxylamine is widely used as a reductant of transition metal compounds,[3] its function as an oxidant is less precedented[4] and its coordination chemistry is almost unknown.[5] We report herein the formation of a remarkable iron oxide cluster from the interaction of iron(II) chloride with anhydrous hydroxylamine.

Results and Discussion

Low-temperature treatment of a methanolic suspension of $FeCl_2$ with 1.5 molar equiv of NH_2OH in methanol (from $NH_2OH{\cdot}HCl + NaOCH_3$) and subsequent warming produced red crystals of $\{Fe_{10}Cl_8O_4(OCH_3)_{14}(CH_3OH)_6\}{\cdot}2CH_3OH$ (**1**) over the course of a few days. The identity of **1** was established by X-ray diffraction (Table 1), and the compound was found to be a novel decairon cluster, $\{Fe_{10}Cl_8O_4(OCH_3)_{14}(CH_3OH)_6\}{\cdot}2CH_3OH$ (Figure 1). The structure of **1** can be described as consisting of two pentairon subunits, including Fe(1−5) and Fe(1′−5′), related by a crystallographic center of symmetry. Each iron center is formally Fe(III) with a distorted octahedral geometry, as defined by the collection of chloride, methoxide (terminal, μ_2^-, and μ_3^-), oxide (μ_4^-), and methanol ligands. The quality of the crystal data was excellent, allowing the location and isotropic refinement of all hydrogen atoms (except H37), including those of the methanol ligands. The coordination spheres of Fe(1) and Fe(3) are essentially the same, with *trans* chloride and oxide ligands, three *mer*-μ_2-methoxides, and a terminal methanol. The Fe(2) sphere consists of the same ligand set but with *cis* chloride and oxide ligands. The Fe(4) domain features chloride, two *cis* oxides, and three *mer*-μ_2-methoxides. Finally, Fe(5) is surrounded only by oxygen donors, including three *fac*-oxides and three *fac*-μ-methoxides. The methanols of crystallization (not shown) enter into H-bonding interactions with Cl(1), O(6)−H(14), O(9)−H(24), and O(3). The diversity of oxide and methoxide ligands in **1** allows the correlation, in one structure, of the Fe−O lengths and Fe−O−Fe angles with the O-bridging mode (Table 2). The metrical data generally show increasing Fe−O bond lengths and decreasing Fe−O−Fe angles with an increasing extent of bridging of the methoxides (terminal, μ_2, and μ_3). The array of Fe atoms and the coordinated oxygen and chlorine atoms also may be seen to consist of cubic close-packed layers of oxygen atoms and chloride ions with iron atoms occupying the octahedral holes between the layers (Figure 2). The cluster framework embodied in **1** is remarkably robust, remaining intact during ESI−MS analysis.

Table 1. Crystallographic Data for **1**

empirical formula	$C_{22}H_{74}Cl_8Fe_{10}O_{26}$
fw	1596.91
T, K	173(2)
μ(Mo Kα), Å	0.71073
crystal system	monoclinic
space group	$P2(1)/n$
a, Å	15.343(2)
b, Å	10.8467(9)
c, Å	17.620(2)
α, deg	90
β, deg	104.295(8)
γ, deg	90
V, Å^3	2841.4(5)
D_c, mg/m^3	1.866
R1 [$I > 2\sigma(I)$][a]	0.0296
wR2 (all data)[b]	0.0866

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

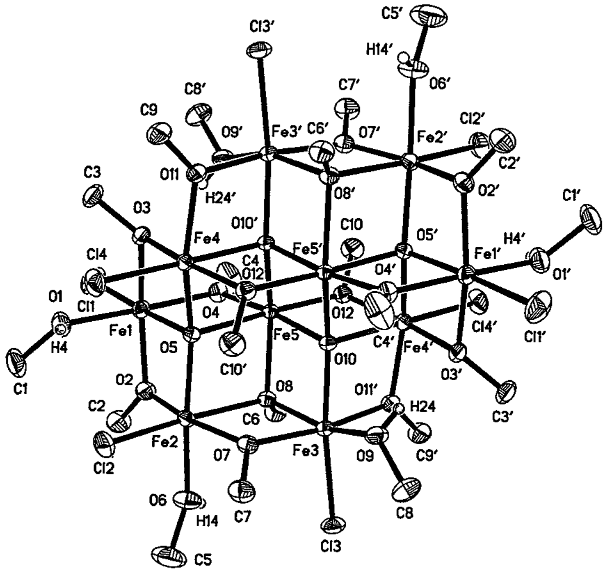

Figure 1. Structure of **1** (ORTEP). Hydrogen atoms (except for those on the methanol ligands) have been omitted for clarity.

Cluster **1** is one of only a few structurally characterized decairon clusters[6] which, along with other multi-iron clusters,[7] are considered to be models for the infinite lattices of iron oxides and hydroxides and for the inorganic core of the iron-storage protein ferritin. These structures are also of interest because of their novel magnetic properties. The structure of **1** is similar to that of $Fe_{10}O_4(OCH_3)_{16}(dbm)_6$[6a] (**2**) but with chloride and methanol ligands in place of the dibenzoylmethanato (dbm)

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(1) (a) Srivastava, R. S.; Nicholas, K. M. *Tetrahedron Lett.* **1994**, 8739. (b) Srivastava, R. S.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1996**, *118*, 3311. (c) Srivastava, R. S.; Nicholas, K. M. *J. Am. Chem. Soc.* **1997**, *119*, 3302.

(2) Johannsen, M.; Jorgensen, K. A. *J. Org. Chem.* **1994**, *59*, 214; **1995**, *60*, 5979.

(3) Keller, A.; Szterenberg, L.; Glowiak, T. *Inorg. Chim. Acta* **1992**, *202*, 19. Bhattacharya, R. *Polyhedron* **1989**, *8*, 2897. Muller, A.; Peters, F.; Pope, M. T.; Gatteschi, D. *Chem. Rev.* **1998**, *98*, 241. Choi, I.; Liu, Y.; Ryan, M. D. *Inorg. Chem.* **1997**, *36*, 3113. Chadhuri, B.; Banerjee, R. *Can. J. Chem.* **1998**, *76*, 350.

(4) Keck, G. E.; McHardy, S. F.; Wager, T. T. *Tetrahedron Lett.* **1995**, *36*, 7419. Srivastava, R. S.; Nicholas, K. M. *J. Am. Chem. Soc.* **1997**, *119*, 3302. Srivastava, R. S.; Nicholas, K. M. *J. Org. Chem.* **1994**, *59*, 5365.

(5) Southern, J. S.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 12406. Engelhardt, L. M.; Newman, P. W. G.; Raston, C. L.; White, A. H. *Aust. J. Chem.* **1974**, *27*, 503.

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Table 2. Selected Bond Parameters for **1**

Bond Lengths, Å			
Fe(1)−O(2)	1.975(2)	Fe(1)−O(3)	1.994(2)
Fe(1)−O(4)	2.004(2)	Fe(1)−O(5)	2.054(2)
Fe(1)−O(1)	2.131(2)	Fe(1)−Cl(1)	2.2852(7)
Fe(2)−O(5)	1.970(2)	Fe(2)−O(7)	1.973(2)
Fe(2)−O(2)	2.000(2)	Fe(2)−O(6)	2.102(2)
Fe(2)−O(8)	2.173(2)	Fe(2)−Cl(2)	2.2813(7)
Fe(3)−O(7)	1.980(2)	Fe(3)−O(11)	1.987(2)
Fe(3)−O(10)	1.996(2)	Fe(3)−O(8)	2.072(2)
Fe(3)−O(9)	2.086(2)	Fe(3)−Cl(3)	2.2964(6)
Fe(4)−O(11)	1.985(2)	Fe(4)−O(12)	2.009(2)
Fe(4)−O(5)	2.010(2)	Fe(4)−O(10)	2.082(2)
Fe(4)−O(3)	2.106(2)	Fe(4)−Cl(4)	2.2876(7)
Fe(5)−O(10)	1.956(2)	Fe(5)−O(12)	1.965(2)
Fe(5)−O(4)	1.965(2)	Fe(5)−O(10)	2.059(2)
Fe(5)−O(5)	2.095(2)	Fe(5)−O(8)	2.104(2)
Bond Angles, deg			
O(2)−Fe(1)−O(3)	156.22(7)	O(2)−Fe(1)−O(4)	94.92(7)
O(3)−Fe(1)−O(4)	91.35(7)	O(2)−Fe(1)−O(5)	78.90(6)
O(3)−Fe(1)−O(5)	79.64(6)	O(4)−Fe(1)−O(5)	80.03(6)
O(2)−Fe(1)−O(1)	88.08(8)	O(3)−Fe(1)−O(1)	83.04(7)
O(4)−Fe(1)−O(1)	172.02(7)	O(5)−Fe(1)−O(1)	93.32(7)
O(2)−Fe(1)−Cl(1)	102.29(5)	O(3)−Fe(1)−Cl(1)	99.62(5)
O(4)−Fe(1)−Cl(1)	97.30(5)	O(5)−Fe(1)−Cl(1)	177.20(5)
O(1)−Fe(1)−Cl(1)	89.26(6)	Fe(1)−O(2)−Fe(2)	100.87(7)
Fe(2)−O(5)−Fe(4)	148.59(9)	Fe(2)−O(5)−Fe(1)	99.20(7)
Fe(4)−O(5)−Fe(1)	101.38(7)	Fe(2)−O(5)−Fe(5)	103.92(7)
Fe(4)−O(5)−Fe(5)	96.86(6)	Fe(1)−O(5)−Fe(5)	96.97(7)

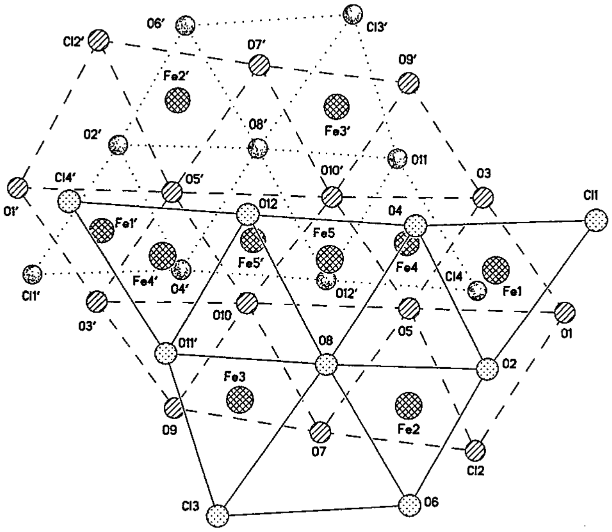

Figure 2. Layered structure of **1**. Top layer of O and Cl atoms connected by solid lines, middle layer by dashed lines, and bottom layer by dotted lines; interstitial Fe atoms Fe(1), (2), (3), (4′), and (5) between top and middle layers; interstitial Fe atoms Fe(4), (3′), (5′), (2′), and (1′) between middle and bottom layers.

ligands. The extended lattice of iron atoms and oxygen/chlorine atoms in **1** (Figure 2) is comparable to that of cluster **2** and that suggested for ferritin based on EXAFS data.[8] Indeed, **1** is unusual among the many polynuclear iron(III) clusters reported to date in that it is devoid of bidentate bridging or chelating ligands and has one of the most "inorganic" sets of ligands of the synthetic multi-iron clusters.[9]

It is also noteworthy that the synthesis of **1** from $FeCl_2$ involves a net 10-electron oxidation. Because anhydrous and anaerobic conditions were maintained in the preparation of **1**, it is likely that hydroxylamine serves as the oxidant[4] and is the source of the incorporated oxide ligands (rather than dioxygen or water). Consistent with this suggestion, cluster **1** was not produced when a solution of $FeCl_2$ in wet methanol (with no added hydroxylamine) stood for several weeks. The ability of hydroxylamine to serve as an oxide source in the formation of iron-oxide clusters could thus provide access to new classes of these interesting species.

Experimental Section

Preparation of $\{Fe_{10}Cl_8O_4(OCH_3)_{14}(CH_3OH)_6\}\cdot 2CH_3OH$ (1). A Schlenk tube was charged with 0.51 g (4.0 mmol) of anhydrous $FeCl_2$ in the drybox, and then 25 mL of dry methanol (from Mg) was added by syringe under nitrogen. The stirred mixture was cooled to −78 °C and then treated with a solution of hydroxylamine prepared from 0.42 g (6.0 mmol) of $NH_2OH\cdot HCl$ and 12 mL of 0.5 M $NaOCH_3$ in methanol. After gradual warming to room temperature, a red-orange solution containing some orange precipitate was produced. After the reaction mixture stood in a sealed flask for two weeks, **1** crystallized as dark red crystals (0.26 g, 42% based on iron), which were separated from the unidentified orange powder manually. IR (KBr, cm^{-1}): 3200 (b), 2964, 1406, 1262, 1097, 1020, 799. MS (ESI, MeOH, *m*/*z*, partial): 1438, 1422, 1408, 1394, 1380, 1360, 1342; each peak maximum exhibits the pattern calculated for an $Fe_{10}Cl_8(OCH_3)_x(O)_4$ cluster. A satisfactory elemental analysis for **1** was not obtained, possibly because of the facile loss of the solvent of crystallization.

Crystal Structure Determination. A red crystal of **1**·2MeOH with dimensions of 0.62 × 0.32 × 0.32 mm^3 was mounted in inert oil and transferred to the cold nitrogen gas stream of the diffractometer for data collection. The data were collected at −100 °C on a Siemens P4 diffractometer.[10] The structure of **1** was determined by the direct method using the SHELXTL system[11] and refined by full-matrix least squares on F^2 using all reflections. All of the hydrogen atoms could be located and refined isotropically with the exception of H37, which is probably disordered and was probably not stable during refinement; its position was fixed at its location in the difference map, and the temperature factor was also fixed at 0.09 Å^2 [$2\Theta_{max} = 55.0°$, $\omega - 2\Theta$ scans, $T = 173(2)$ K]. Of the 6512 reflections measured, 6283 were independent and were used in the structure refinement (Lorentz, polarization, and absorption corrections based on ψ scans were applied), $\mu = 2.919$ mm^{-1}, maximum and minimum transmission = 0.3565 and 0.2649, respectively. The maximum and minimum residual electron densities were 0.436 and −0.440 e Å^{-3}, respectively.

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Supporting Information Available: Atomic coordinates and isotropic displacement parameters; bond lengths and angles; anisotropic displacement factors for **1**; hydrogen coordinates and isotropic displacement parameters; selected torsion angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) (a) Caneschi, A.; Cornia, A.; Fabretti, A. C.; Gatteschi, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2716. (b) Benelli, C.; Parsons, S.; Solan, G. A.; Winpenny, R. E. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1825. (c) Taft, K. L.; Delfs, C. D.; Papefthymiou, G. C.; Foner, S.; Gatteschi, D.; Lippard, S. *J. Am. Chem. Soc.* **1994**, *116*, 823.

(7) Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 344. Powell, A. K.; Heath, S. L.; Gatteschi, D.; Pardi, L.; Sessoli, R.; Spina, G.; Del Gaillo, F.; Pieralli, F. *J. Am. Chem. Soc.* **1995**, *117*, 2491. Walton, S. P.; Fuhrmann, P.; Pence, L. E.; Caneschi, A.; Cornia, A.; Luca Abbati, G.; Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2774. Caneschi, A.; Cornia, A.; Lippard, S. J.; Papaefthymiou, G. C.; Sessoli, R. *Inorg. Chim. Acta* **1996**, *243*, 296. Caneschi, A.; Cornia, A.; Fabretti, A. C.; Gatteschi, D. *Angew. Chem., Int. Ed. Engl.* **1999**, *28*, 1295.

(8) Heald, S. M.; Stern, E. A.; Bunker, B.; Holt, E. M.; Holt, S. L. *J. Am. Chem. Soc.* **1979**, *101*, 67. Theil, E. C.; Sayers, D. E.; Brown, M. A. *J. Biol. Chem.* **1979**, *254*, 8132. Rohrer, J. S.; Islam, Q. T.; Watt, G. D. *Biochemistry* **1990**, *29*, 259. Taft, K. L.; Papaefthymiou, G. C.; Lippard, S. L. *Inorg. Chem.* **1994**, *33*, 1510. Feig, A. L.; Lippard, S. J. *Chem. Rev.* **1994**, *94*, 759.

(9) Hegetschweiler, K.; Schmalle, H. W.; Streit, H. M.; Gramlich, V.; Hund, H.-U.; Erni, I. *Inorg. Chem.* **1992**, *31*, 1299.

(10) Siemens. *XSCANS: X-ray Single-Crystal Analysis System*, version 2.1; 1994.

(11) Siemens. *SHELXTL*, release 5.03; 1994.