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Synthesis and structure of the tetradeca-iron(III) oxide–alkoxide cluster $[Bu_4N]_2[Fe_{14}O_8(OCH_2CH_3)_{20}Cl_8]$

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Abstract

The iron(III) oxide–alkoxide cluster, di-tetra-*n*-butylammonium octachloro-tetra(μ_3-oxo)-tetra(μ_4-oxo)- icosa(μ_2-ethoxo)-tetradeca-iron(III), has been isolated and its X-ray crystal structure determined.

Keywords: Iron; Oxo compounds; Alkoxides; Cluster compounds; Sulfur; Oxidation; Oxygen

The oxidation of iron compounds to iron oxides is a well known, yet complex process. During our studies of the oxygen sensitivity of iron–thiolate complexes, we reproducibly generate an insoluble orange powder upon exposure of LFeCl (**1**) (L = 4,7-bis(2′-methyl-2′-mercaptopropyl)-1-thia-4,7-diazacyclononane) to dioxygen in solution [1,2]. The oxidation product is insoluble in all common solvents preventing full spectroscopic characterization, but it displays a diagnostic IR spectrum. Similar products were reported by others studying iron–thiolate oxygen sensitivity, but the product was never fully characterized [3–6]. Herein we report the isolation and structure of the iron(III) oxide–alkoxide cluster, $[Bu_4N]_2[Fe_{14}O_8(OCH_2CH_3)_{20}Cl_8]$ (**2**).

Complex **2** is the largest iron(III) oxide–alkoxide cluster known to date. Previously, clusters with 5–10 iron centers have been isolated and structurally characterized [7–15]. Typically, these clusters are derived from iron(III) chloride and the appropriate alkoxide. Chloride from the iron source may be present or absent in the product. These clusters have been studied for a variety of reasons including their magnetic properties [8,14,15] and application to homogenous catalysis [7,9–11]. Very recently, XAS data on whole blood cells from *Perophora annectens* reveal the presence of an iron alkoxide cluster, $[Fe_4\text{-}\mu\text{-}(OR)_5(OR)_{9-10}]$ [16].

Previously, we reported the synthesis of **1** from H_2L, NEt_3, and $[NBu_4][FeCl_4]$ in ethanol [1]. Complex **1** precipitates as a blue solid, which is isolated by filtration leaving a dark brown filtrate. The filtrate was allowed to stand in air over a period of several days yielding **2** as orange block shaped crystals with an infrared spectrum identical to the oxidation product of **1**. The structure of **2** was determined by X-ray crystallography [17–22].

Compound **2** crystallizes in the tetraganol space group $P\bar{4}2_1c$ with $a = 17.0996(10)$ Å and $c = 21.027(3)$ Å.[1] Since crystals of **2** rapidly degrade upon removal from the mother liqueur, all manipulations were preformed in a cold room. Numerous crystals were selected and mounted in an attempt to obtain a more precise crystal structure, however a higher quality data set could not be obtained. The data

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[1] *Crystal data for* **1**: $[Bu_4N]_2[Fe_{14}O_8(OCH_2CH_3)_{20}Cl_8]$, $FW = 2579.62$ g mol^{-1} tetragonal, space group $P\bar{4}2_1c$, $a = 17.0996(10)$ Å, $c = 21.027(3)$ Å, $V = 6148.1(9)$ Å^3, $Z = 2$, $\mu = 1.827$ mm^{-1}, $\rho = 1.393$ g cm^{-3}. Data were collected on a Bruker Smart Apex CCD using Mo Kα radiation. For all 5447 unique reflections (R(int) = 0.2003), the final anisotropic full-matrix least-squares refinement on F^2 for 240 variables data converged at $R_1 = 0.1018$ and $wR_2 = 0.2276$ with a GOF of 1.075.

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set was collected at low temperature, 100 K. A representation of the $[Fe_{14}O_8(OCH_2CH_3)_{20}Cl_8]^{2-}$ dianion is shown in Fig. 1.

Compound **2** contains four unique iron centers, labeled $Fe1^a$, $Fe2^a$, $Fe3^a$, and $Fe4^a$ (Fig. 1). There are 10 additional symmetry generated iron centers. The seven unique oxygen atoms include five μ_2-ethoxides ($O1^a$–$O5^a$), a μ_3-oxo ($O6^a$), and a μ_4-oxo ($O7^a$). For each O-donor, symmetry generates three additional sites. The Fe–OC_2H_5 bond distances (Table 1) fall in the range of 1.946(11)–2.051(10) Å with an average of 2.00(1) Å that is identical within error to a previously reported Fe–OC_2H_5 (μ_2) distance of 2.009(1) Å [14]. The Fe–λ^3O distances fall within error of related structures, 1.911(1) Å, and range from 1.853(10) to 1.954(9) Å with an average of 1.91(1) Å [14]. The Fe–λ^4O distances vary from 1.962(9) to 2.097(10) Å, with an average of 2.00(1) Å near the reported value of 2.011(7) Å [14]. The cluster also contains two unique terminal chlorides, $Cl1^a$ and $Cl2^a$, and six additional symmetry generated chlorides. The Fe1–Cl1 and Fe2–Cl2 distances of 2.341(4) and 2.241(5) Å are within the expected range. Overall, the dianion of **2** contains a cluster of 14 iron centers, 20 μ_2-ethoxides, four μ_3-oxo bridges, four μ_4-oxo bridges, and eight terminal chlorides. Based on charge balance, each iron exists in the ferric state.

The 14 iron centers of **2** are arranged in a pair of point-sharing Fe_7-ditetrahedra (Fig. 2). An Fe_4-tetrahedron can be formed with $Fe1^a$, $Fe2^a$, $Fe3^a$, and $Fe4^d$. $Fe3^a$ sits on the special position $(0.5, 0.5, z)$ and serves as the joining point for the second tetrahedron, which also contains $Fe1^c$, $Fe2^c$, and $Fe4^b$. The tetrahedra are also connected by O6 linkages between $Fe1^c$/$Fe4^d$ and $Fe1^a$/$Fe4^b$. The O6 linkage also extends out to Fe4 positions in the second Fe_7-ditetrahedra, which sits across the cluster and perpendicular to the first. The two Fe_7 cores are also linked together by four μ_2-ethoxides, consisting of $Fe1^a$, $O5^a$, and $Fe4^a$ and their symmetry generated equivalents.

Table 1
Selected bond distances (Å) for **2**

$Fe1^a$–$O1^a$	2.093(9)	$Fe3^a$–$O3^a$	2.010(10)
$Fe1^a$–$O4^a$	1.971(10)	$Fe3^a$–$O4^a$	2.051(10)
$Fe1^a$–$O5^a$	1.952(10)	$Fe3^a$–$O7^d$	1.973(9)
$Fe1^a$–$O6^b$	1.954(9)		
$Fe1^a$–$O7^d$	2.097(10)	$Fe4^d$–$O2^a$	2.047(10)
$Fe1^a$–$Cl1^a$	2.341(4)	$Fe4^d$–$O5^d$	1.976(9)
$Fe2^a$–$O1^a$	1.956(11)	$Fe4^d$–$O6^a$	1.853(10)
$Fe2^a$–$O2^a$	1.946(11)	$Fe4^d$–$O6^d$	1.924(10)
$Fe2^a$–$O3^a$	1.953(11)	$Fe4^d$–$O7^d$	1.962(9)
$Fe2^a$–$O7^d$	1.992(9)		
$Fe2^a$–$Cl2^a$	2.241(5)		

An isolated Fe_4-tetrahedron is shown in Fig. 3. As shown, $Fe2^a$ sits atop of the tetrahedron in a triganol bipyramidal environment with μ_2-ethoxides in all three equatorial positions. The ethoxides $O1^a$, $O2^a$, and $O3^a$ bridge the

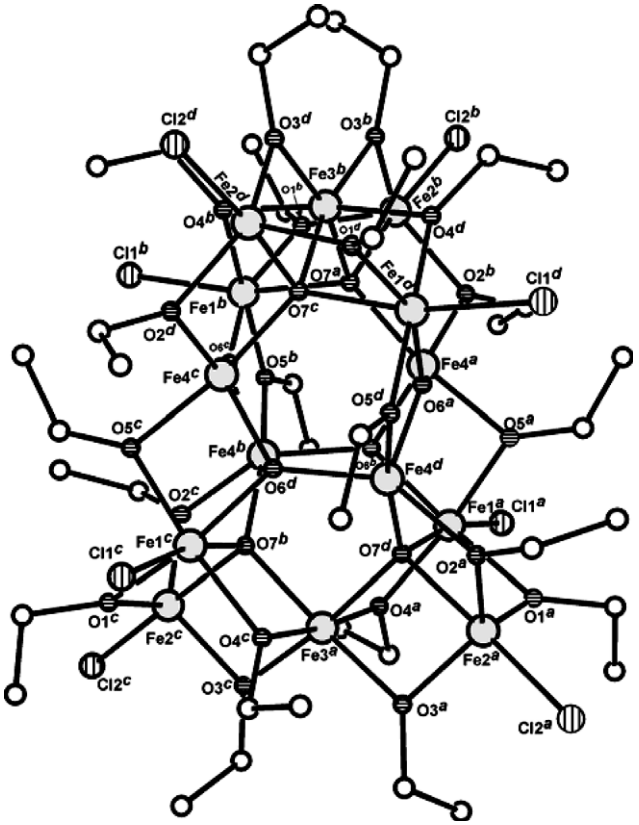

Fig. 1. A PLUTO representation of the dianion of **2**. The atoms from the asymmetric unit are labeled as *a*. Other positions are symmetry generated; *b* $(y, 1-x, -z)$, *c* $(1-x, 1-y, z)$, *d* $(1-y, x, -z)$.

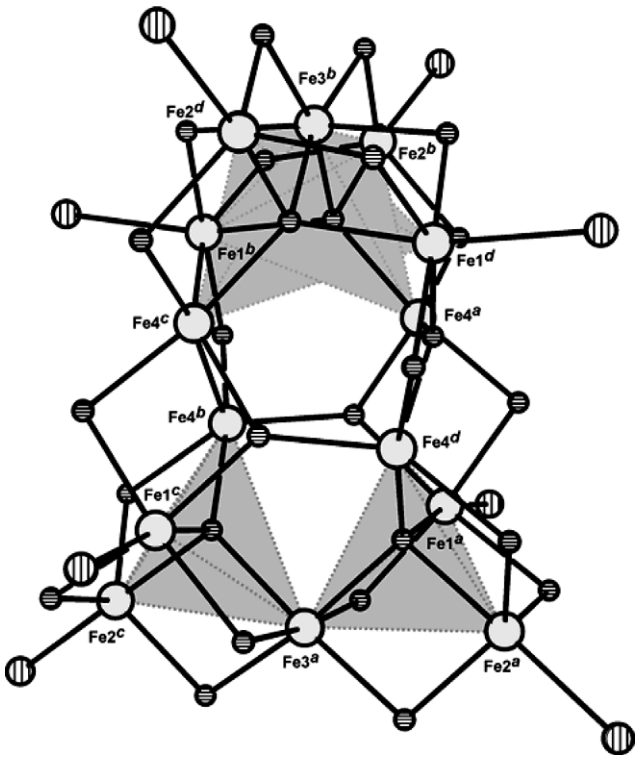

Fig. 2. A PLUTO representation of the dianion of **2**. Carbon atoms have been omitted. The Fe_7-ditetrahedra are outlined in gray. The atoms from the asymmetric unit are labeled as *a*. Other positions are symmetry generated; *b* $(y, 1-x, -z)$, *c* $(1-x, 1-y, z)$, *d* $(1-y, x, -z)$.

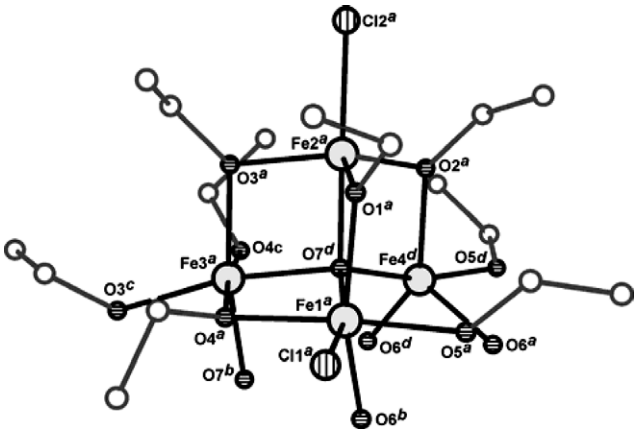

Fig. 3. A PLUTO representation of a Fe_4-tetrahedron from **2**. The atoms from the asymmetric unit are labeled as *a*. Other positions are symmetry generated; *b* $(y, 1-x, -z)$, *c* $(1-x, 1-y, z)$, *d* $(1-y, x, -z)$.

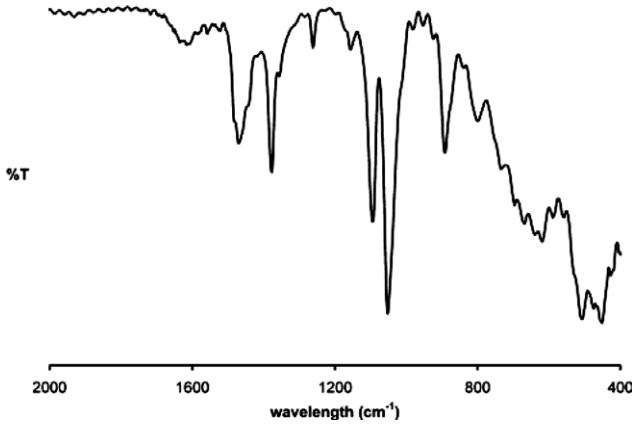

Fig. 4. Infrared spectrum of **2** prepared as a KBr pellet at 4 cm^{-1} resolution.

$Fe2^a$–$Fe1^a$, $Fe2^a$–$Fe3^a$, and $Fe2^a$–$Fe4^d$ edges of the tetrahedron, respectively. A terminal chloride, $Cl2^a$, and a μ_4-oxo, $O7^d$, sit in the axial positions of $Fe2^a$. All four iron centers are coordinated to $O7^d$, which is located on the interior of the Fe_4-tetrahedron. A fourth μ_2-ethoxide, $O4^a$, sits along the $Fe1^a$–$Fe3^a$ edge. The pseudo-octahedral environment about $Fe3^a$ is completed by the symmetry generated equivalents $O3^c$, $O4^c$, and $O7^b$ in the adjoining point-sharing Fe_4-tetrahedron. The environment around $Fe1^a$ is completed by $O6^b$, a μ_3-oxo bridge, which joins a single Fe1 with two Fe4 sites. A μ_2-ethoxy bridge, O5, between Fe1 and Fe4 completes a diamond core and the coordination environment of Fe1 and Fe4.

The infrared spectrum of **2** is shown in Fig. 4. The IR shows weak bands at 457 and 511 cm^{-1}, which are similar to those in α-Fe_2O_3 [23]. The more intense bands at 806 and 893 cm^{-1} are consistent with the presence of alkoxide in the sample. This is further confirmed by the array of bands at 1053, 1095, 1379, and 1471 cm^{-1} [12]. Finally, C–H bending modes are observed at 2875, 2929, and 2960 cm^{-1} (not shown).

In conclusion, the orange, insoluble product from the oxidation of iron–thiolate complexes in alcohol has been identified as an iron(III) oxo-alkoxide cluster. The tetradecairon(III) cluster has an IR spectrum consistent with the thiolate oxidation product upon oxidation of the filtrate from the synthesis of **1**. This cluster, **2**, is the largest member of the growing family of iron(III) oxo-alkoxides.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.07.027.

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