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Synthesis of an All-Ferric Cuboidal Cluster $[\text{Fe}^{\text{III}}_4\text{S}_4(\text{SAr})_4]$

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Abstract: An unprecedented, super oxidized all-ferric iron-sulfur cubanoid cluster with all terminal thiolates, $\text{Fe}_4\text{S}_4(\text{STbt})_4$ (**3**) [$\text{Tbt} = 2,4,6\text{-tris}\{\text{bis}\{\text{trimethylsilyl}\}\text{methyl}\}\text{phenyl}$], has been isolated from the reaction of the bis-thiolate complex $\text{Fe}(\text{STbt})_2$ (**2**) with elemental sulfur. This cluster **3** has been characterized by X-ray crystallography, zero-field ^{57}Fe Mössbauer spectroscopy, cyclic voltammetry, and other relevant physico-chemical methods. Based on all data, the electronic ground state of the cluster has been assigned to be $S_{\text{tot}} = 0$.

Cuboidal Fe_4S_4 clusters are ubiquitous in nature, and play crucial roles in biological functions, particularly in electron transfer processes owing to the possibility of their variegated oxidation states.^[1] The Fe_4S_4 core is usually ligated by four cysteine thiolates (S_{cys}) from the protein backbone.



Three different oxidation states are known for biological Fe_4S_4 clusters as in, for example, the ferredoxin (Fd) family ($[\text{Fe}_4\text{S}_4]^{2+}/[\text{Fe}_4\text{S}_4]^{1+}$) and the high-potential iron-sulfur protein (HiPIP) family ($[\text{Fe}_4\text{S}_4]^{3+}/[\text{Fe}_4\text{S}_4]^{2+}$). Additionally, the all-ferrous state $[\text{Fe}_4\text{S}_4]^0$ was noticed in the *A. vinelandii* Fe protein of nitrogenase and in *A. fermentas dehydratase*.^[2] Most notably, the all-ferric $[\text{Fe}_4\text{S}_4]^{4+}$ cluster has not yet been discovered in nature, and not even chemically synthesized with terminal thiolates.

Many Fe_4S_4 clusters have chemically been synthesized, and most of the Fe_4S_4 clusters with terminal thiolates assume the $[\text{Fe}_4\text{S}_4]^{2+}$ core, while there are a few examples of $[\text{Fe}_4\text{S}_4]^{3+}$ that include our previous works.^[1,3,4] Recently, three clusters in the $[\text{Fe}_4\text{S}_4]^0$ state have been reported, although the terminal ligands are not thiolates.^[3b,c,d] Although the all-ferric $[\text{Fe}_4\text{S}_4]^{4+}$ cluster with terminal thiolates has yet to be found in proteins, one ought to consider the possibility of this super-oxidized state under specific conditions; e.g., as a fleeting intermediate. Up to date, the all-ferric $[\text{Fe}_4\text{S}_4]^{4+}$ clusters have been achieved with non-thiolate terminal ligands such as $\text{Fe}_4\text{S}_4\{\text{N}(\text{SiMe}_3)_2\}_4$ and $\text{Cp}_4\text{Fe}_4\text{S}_4$.^[5] We rationalize the stabilization of an all-ferric state in $\text{Fe}_4\text{S}_4\{\text{N}(\text{SiMe}_3)_2\}_4$ to be due to the remarkably strong σ and π -

donor ability of amide.

On the other hand, the existence of an $[\text{Fe}_4\text{S}_4]^{4+}$ core with terminal thiolates was suggested by electrochemical studies (cyclic voltammetry).^[4,6] Since the HiPIP^{ox} state has the $[\text{Fe}_4\text{S}_4]^{3+}$ core buried in a hydrophobic pocket of proteins,^[7] we assume that bulky thiolate ligands provide steric protection and a hydrophobic cavity,^[4a,b] and that they could stabilize an all-oxidized iron-sulfur core against attack by nucleophiles. Accordingly, we have synthesized an unprecedented all-ferric thiolate iron-sulfur cubane cluster, namely $\text{Fe}_4\text{S}_4(\text{STbt})_4$ (**3**) (Figure 1), employing the sterically encumbering thiol TbtSH (Tbt = 2,4,6-tris{bis(trimethylsilyl)methyl}phenyl). In addition to its steric bulk, TbtSH might be favorable to stabilize the high oxidation states due to the σ -donating property of the silyl substituents.

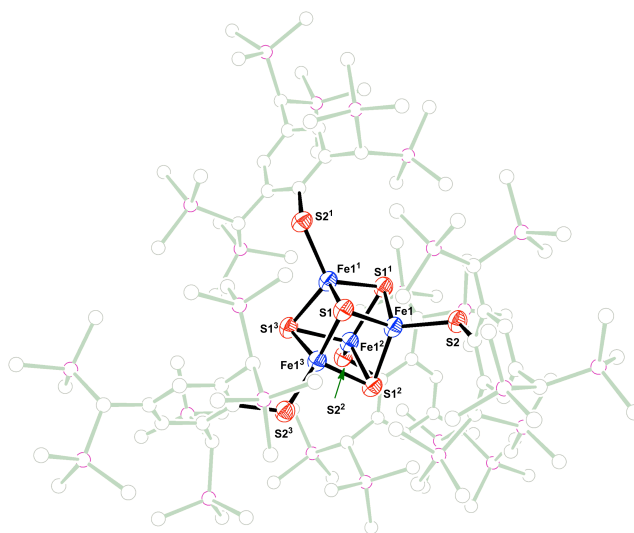


Figure 1. Structure (ORTEP view) of the $\text{Fe}_4\text{S}_4(\text{STbt})_4$ (**3**) showing 50% probability thermal ellipsoids for Fe_4S_4 core and thiolate S atoms. The Tbt groups are represented as sphere for clarity. Selected bond distances (Å): Fe1-Fe1' 2.740(1), Fe1-Fe1'' 2.788(1), Fe1-Fe1''' 2.788(1), Fe1-S1 2.239(1), Fe1-S1' 2.263(1), Fe1-S1'' 2.283(1), Fe1-S2 2.206(1).

Treatment of $\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2$ (**1**) with two equivalents of TbtSH in pentane led to the formation of red brown $\text{Fe}(\text{STbt})_2$ (**2**), in high yield (Scheme S1, Figure S1). Reaction of **2** with one equivalent of elemental sulfur, S_8 , in a mixture of solvents (toluene:hexane = 1:6) gave rise to the unprecedented $\text{Fe}_4\text{S}_4(\text{STbt})_4$ (**3**) in 39% yield as blue square-shaped micro-crystals (Scheme 1). A balanced equation may be written as: $4\text{Fe}^{\text{II}}(\text{STbt})_2 + \frac{1}{2} \text{S}_8 \rightarrow \text{Fe}^{\text{III}}_4\text{S}_4(\text{STbt})_4 + 2\text{TbtS-STbt}$. Here, the four sulfur atoms are reduced to four S^{2-} by eight electrons, among which the four are provided by the formation of the two TbtS-STbt and the other four come from oxidation of four Fe^{2+} to four Fe^{3+} . Formation of the disulfide was confirmed by X-ray analysis (see Figure S2). Alternatively, treatment of the all-ferric $\text{Fe}_4\text{S}_4\{\text{N}(\text{SiMe}_3)_2\}_4$ cluster^[5a,b] with four equivalents of TbtSH also

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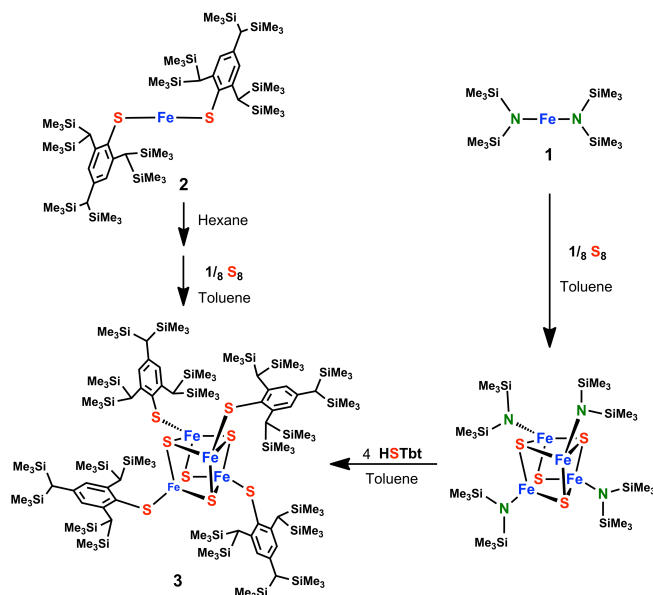
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yielded cluster **3**, albeit in significantly lower yield (~10%). Cluster **3** is soluble in hexane, pentane, diethyl ether, and dichloromethane, giving rise to blue solutions, but does not dissolve in either benzene or toluene. In tetrahydrofuran, **3** converts as the UV-Vis absorption peak shows a blue-shift. The identity of this species, however, remains elusive.



Scheme 1. Schematic representation for the synthesis of $\text{Fe}_4\text{S}_4(\text{STbt})_4$ (**3**).

Complex **2** is a two-coordinate, linear iron-thiolate complex (Figure S1), while the two-coordinated iron-thiolate complexes reported so far are non-linear.^[8] The iron atom is sterically protected by the bulky Tbt groups. The iron might have interaction with the methyl groups of the trimethylsilyl substituents of the Tbt ligands, although the protons were not assignable since the data quality was not high enough.

Cluster **3** is isomorphous with its mono-negative analogue $\text{Na}(\text{THF})[\text{Fe}_4\text{S}_4(\text{STbt})_4]$.^[4b] The iron atoms of **3** are in a distorted tetrahedral geometry, coordinated by three sulfur atoms of the $[\text{Fe}_4\text{S}_4]$ core and one thiolate sulfur (Figure 1). $[\text{Fe}_4\text{S}_4(\text{SR})_4]^n$ clusters with high oxidation states usually have smaller core volume⁹ and shorter Fe–Fe, Fe–S(core) and Fe–S(thiolate) distances compared to clusters with low oxidation states, which is consistent with the reduction of the Fe ionic radius upon oxidation.^[4b] The differences in the Fe–Fe and Fe–S(core) distances are smaller, while the Fe–S(thiolate) differences are larger (Table S2). Thus, as expected, neutral **3** has shorter Fe–Fe, Fe–S(core), Fe–S(thiolate) distances and also smaller core volumes compared to the anionic $[\text{Fe}_4\text{S}_4(\text{STbt})_4]^{1-}$ cluster (Table 1).

The redox properties of **3** have been examined by cyclic voltammetry (CV) in dichloromethane at room temperature. The cluster exhibits two quasi-reversible redox couples at half-wave potentials $E_{1/2}$ of -0.048 V and -0.997 V vs Ag/AgNO_3 , which are ascribed to the $[\text{Fe}_4\text{S}_4]^{4+}/[\text{Fe}_4\text{S}_4]^{3+}$ and $[\text{Fe}_4\text{S}_4]^{3+}/[\text{Fe}_4\text{S}_4]^{2+}$ redox couples, respectively (Figure 2). Previously, we have reported similar redox couples for other FeS clusters with bulky thiolate ligands.^[4b,10]

Table 1. Average Bond Distances (Å) and Core Volumes (Å^3)⁹ for $[\text{Na}(\text{THF})\{\text{Fe}_4\text{S}_4(\text{STbt})_4\}]^{[4b]}$ and all-ferric $\text{Fe}_4\text{S}_4(\text{STbt})_4$ (**3**).

	$[\text{Na}(\text{THF})\{\text{Fe}_4\text{S}_4(\text{STbt})_4\}]^{[4b]}$	$\text{Fe}_4\text{S}_4(\text{STbt})_4$ (3)
oxidation states	$3\text{Fe}^{\text{III}}1\text{Fe}^{\text{II}}$	4Fe^{III}
avg. Fe–Fe	2.785(1)	2.772(1)
avg. Fe–S(core)	2.282(1)	2.262(1)
avg. Fe–S(thiolate)	2.242(1)	2.206(1)
avg. S(thiolate)–C	1.786(3)	1.779(5)
core volume (Fe_4)	2.430	2.363
core volume (S_4)	5.277	5.201
core volume (Fe_4S_4)	9.441	9.221

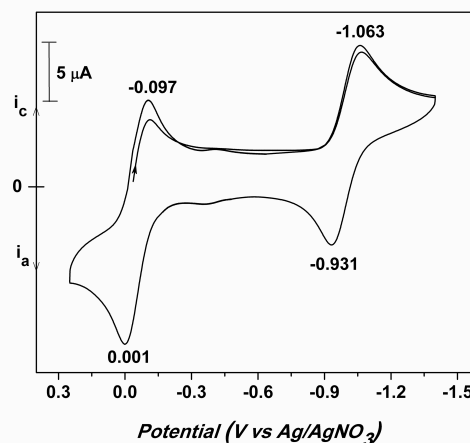
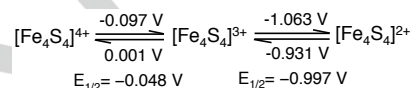


Figure 2. Cyclic voltammetric traces (reductive scan) for $\text{Fe}_4\text{S}_4(\text{STbt})_4$ (**3**) (2 mM) in dichloromethane with a glassy carbon electrode as working electrode, 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ as supporting electrolyte, Ag/AgNO_3 electrode as reference electrode, and a platinum auxiliary electrode. Scan rate = 100 mV/s. The measurement was started from its natural potential observed at -0.037 V, and swept toward reduction.

In the UV-Vis spectra, Fe_4S_4 clusters exhibit a red-shift of their absorption maxima upon oxidation as in the case of $[\text{Fe}_4\text{S}_4\{\text{N}(\text{SiMe}_3)_2\}_4]^{0/1-2-}$, $[\text{Fe}_4\text{S}_4(\text{SAd})_4]^{1-2-}$, and the Fe_4S_4 cluster of *Rhodothermus marinus* HiPIP.^[5,11] Similarly, cluster **3** ($\lambda_{\text{max}}=551$ nm in hexane) exhibits an absorption band at a higher wavelength compared to $[\text{Fe}_4\text{S}_4(\text{STbt})_4]^{1-}$ ($\lambda_{\text{max}}=502$ nm in hexane, Figure S4).

Cluster **3** and its monoanionic analogue were examined by zero-field ^{57}Fe Mössbauer spectroscopy in order to determine the oxidation states of the iron centers (Figure 3, S5 and Table 2). The isomer shift (δ) = 0.33 mm/s for **3** is as expected for high-spin Fe(III) in an anionic sulfur environment.^[12a] A similar value is also reported for the Fe(III)-Fe(III) pair of the valence localized Fe(III) ions of the $[\text{Fe}_4\text{S}_4(\text{STip})_4]^{1-}$ cluster,^[12b] and for the localized Fe(III) centers of the incomplete cubane $[\text{Fe}_3\text{S}_4]^{0}$ clusters.^[12c,d] Similar isomer shift values are reported for valence

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localized Fe^{3+} sites in $[\text{2Fe-2S}]^+$ proteins; e.g., wild-type 2Fe-ferredoxin from *Clostridium pasteurianum* (2FeCpFd) [$\delta = 0.34(2)$ mm/s]^[12e], putidaredoxin from *Pseudomonas putida* [$\delta = 0.35$ mm/s]^[12f] and in $[\text{3Fe-4S}]^+$ proteins in *Ralstonia eutropha* [$\delta = 0.33$ mm/s]^[12g]. Compared to mononuclear Fe(II) and Fe(III) complexes, where the difference in isomer shifts between the Fe(II) and Fe(III) states is usually about 0.4–0.5,^[13,12f,3a] the difference observed here (0.06) is much smaller. This is consistent with the delocalized electronic nature of the clusters, which spreads an additional electron over four iron ions rather than concentrating it on a single iron. Similar small differences in isomer shifts were also found in $[\text{N}(\text{SiMe}_3)_2]^-$ ligated $[\text{Fe}_4\text{S}_4]$ clusters.^[5b]

Table 2. ^{57}Fe Mössbauer Parameters for $[\text{Na}(\text{THF})(\text{Fe}_4\text{S}_4(\text{STbt})_4)]^{[4b]}$ and all-ferric $\text{Fe}_4\text{S}_4(\text{STbt})_4$ (**3**) at 77 K (error in fits were estimated at ± 0.01 mm/s).

Complex	Parameters in mm/s	
	Isomer Shift (δ) in mms^{-1}	Quadrupole Splitting (ΔE_Q) in mms^{-1}
$\text{Fe}_4\text{S}_4(\text{STbt})_4$ (3)	0.33	1.00
$[\text{Na}(\text{THF})(\text{Fe}_4\text{S}_4(\text{STbt})_4)]$	0.39	0.80

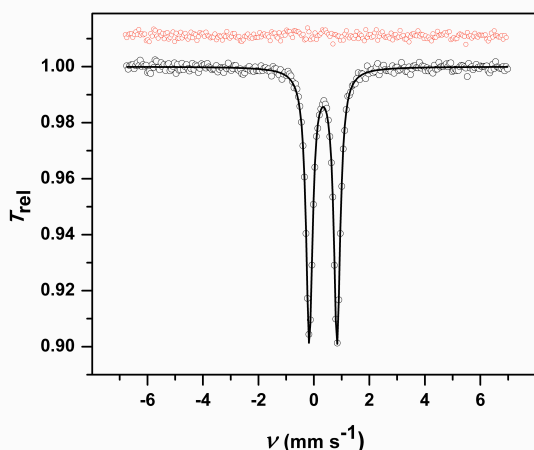


Figure 3. Zero-field ^{57}Fe Mössbauer spectrum of polycrystalline complex $\text{Fe}_4\text{S}_4(\text{STbt})_4$ (**3**) at 77 K. The solid black line is the least-squares fit of calculated spectrum to the experimental data (black circles) for one quadrupole doublet for the parameters quoted in Table 2. The red dots on the top are fitting residuals.

The effective magnetic moment as a function of temperature is shown in Figure 4. The μ_{eff} value per tetramer in **3** is $5.58 \mu_B$ i.e. $\mu_{\text{eff}} = 1.395 \mu_B$ per Fe^{3+} ion, at 300 K, which is much lower than the spin-only value ($5.92 \mu_B$) of an isolated Fe^{3+} ion with uncoupled $5/2$ spin. The magnetic moment decreases monotonically with decreasing temperature to an essentially diamagnetic value of $1.01 \mu_B$ (per tetramer) at 2 K. The behaviour clearly indicates a non-magnetic $S_{\text{tot}} = 0$ total spin ground state, resulting from strong intramolecular anti-ferromagnetic coupling of the high-spin ferric ions.

In principle, and since the spin carriers are all Fe^{3+} ions for **3**, a symmetrical spin Hamiltonian – with all coupling constants

assumed to be equal – could be applied. However, closer inspection of the molecular structure led us to separate the Fe ions into two groups, one with two shorter Fe–Fe distances (2.741 Å) and Fe–S–Fe angles of 74.99° , and four longer Fe–Fe distances (2.788 Å) with Fe–S–Fe angles in the range of about 75.68 – 76.12° . The cube deviates from ideal tetrahedral geometry and is distorted by compression along an S_4 axis, and thus, is of S_4 symmetry rather than T_d . Hence, the isotropic exchange Hamiltonian can be written as in equation (1), pictorially represented in Figure 4.

$$\hat{H} = -2J_1(\hat{S}_1\hat{S}_2 + \hat{S}_3\hat{S}_4) - 2J_2(\hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3 + \hat{S}_2\hat{S}_4) \quad (1)$$

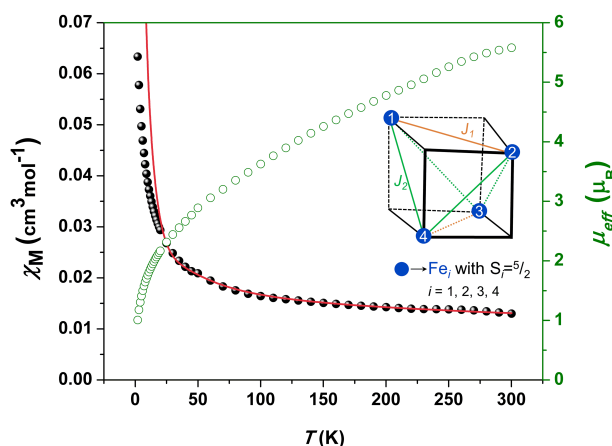


Figure 4. Variable temperature magnetic behaviour of polycrystalline complex $\text{Fe}_4\text{S}_4(\text{STbt})_4$ (**3**). χ_M vs T plot: experimental (filled black circles) and fitted (solid red line); μ_{eff} vs T plot: experimental (green circles). The cube provides a schematic representation of possible magnetic exchange coupling in **3**.

The solid line in Figure 4 thus represents the best fit of the data to eq (1) with $g = 2.00$, $J_1 = -82 \text{ cm}^{-1}$, and $J_2 = -70 \text{ cm}^{-1}$. The poor quality of the fit at lower temperature is possibly accounted for by mixing of the different spin states or by inter-cluster exchange interactions.^[14] Alternatively, the lowest temperature magnetization may also be influenced by zero-field splitting.

The synthesis and characterization of a unique all ferric iron-sulfur cubane cluster with terminal thiolate ligands has been achieved for the first time. The unusually high oxidation state of the cluster is probably supported by the artificial hydrophobic environment at the iron centers, provided by the bulky hydrocarbon substituents of the STbt ligand. The isolation of this all-ferric cubane cluster **3** allows to speculate whether such cluster(s) could play a role in biological systems and transformations; e.g. as fleeting intermediates. Interestingly, this cluster is found to generate a $[\text{Fe}_8\text{S}_7]$ P-cluster core, in a way similar to the native P-cluster maturation process,^[15] the result of which will be reported in due time.^[16]

Experimental Section

Experimental Details. See the Supporting Information. Materials, methods, details of synthesis, and analytical data are provided as

electronic supporting information. The crystallographic information files (CIF) for **2** (CCDC 1559013), **3** (CCDC 1559014), and TbtS-STbt (CCDC 1838285) have been deposited in Cambridge crystallographic data center. The data can be obtained from CCDC via www.ccdc.cam.ac.uk/data_request/cif

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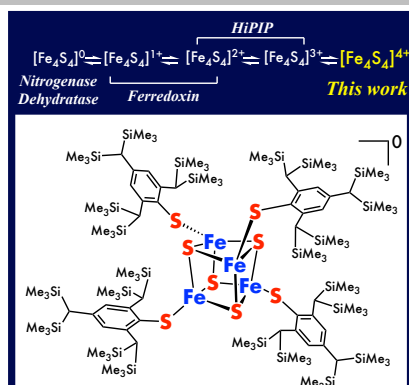
Keywords: Iron-sulfur cubane cluster • high-oxidation state • Mössbauer • Magnetism

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COMMUNICATION

An unprecedented all-ferric thiolate iron-sulfur cubane cluster $\text{Fe}_4\text{S}_4(\text{STbt})_4$ (**3**) with bulky terminal thiolates has been isolated from the reaction of $\text{Fe}(\text{STbt})_2$ with S_8 [Tbt = 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl]. Isolation of **3** raises an interesting possibility that the cuboidal Fe_4S_4 cluster may exist in nature with the unusual all-ferric state.



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Synthesis of an All-Ferric Cuboidal Cluster $[\text{Fe}^{\text{III}}_4\text{S}_4(\text{SAR})_4]$