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Article

A New Class of Binuclear and Trinuclear Iron−Sulfur Clusters Derived from Bis[bis(trimethylsilyl)amido]iron(II)

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The compound $Fe[N(SiMe_3)_2]_2$ is shown to be a useful precursor to dinuclear and trinuclear iron−sulfur−silylamido complexes by reaction with thiols or thiols and sulfur in tetrahydrofuran (THF) or toluene. Reaction with 1 equiv of *p*-tolylthiol affords $[Fe_2(\mu_2\text{-S-}p\text{-tol})_2(N(SiMe_3)_2)_2(THF)_2]$ (**1**); with 0.5 equiv of adamantane-1-thiol, $[Fe_2(\mu_2\text{-S-1-Ad})(\mu_2\text{-}N(SiMe_3)_2)(N(SiMe_3)_2)_2]$ (**2**) is formed. The clusters $[Fe_3(\mu_3\text{-}Q)(\mu_2\text{-SR})_3(N(SiMe_3)_2)_3]$ are available by three methods: (i) self-assembly in the systems $Fe[N(SiMe_3)_2]_2$/RSH/S or Se [Q = S, R = *p*-tol (**3**) and 1-Ad (**5**)]; (ii) reaction of **1** with Q = S or Se to yield **3** or $[Fe_3Se(S\text{-}p\text{-tol})_3(N(SiMe_3)_2)_3]$ (**4**); (iii) reaction of **2** with 1-AdSH and S to give **5**. Structures of **1**−**5** are presented. Complexes **1** and **2** contain planar Fe_2S_2 and Fe_2SN rhombs. Clusters **3**−**5** contain a mixed-valence $Fe_3Q(SR)_3$ core with trigonal (cuboidal) geometry. Of known iron−sulfur clusters, these most closely resemble previously reported $[Fe_3S(S{-}R{-}S)_3]^{2-}$ stabilized by bidentate thiolate ligands. Complexes **1**−**5**, together with a small set of recently described clusters of nuclearities 2, 4, and 8, constitute a new class of iron−sulfur−silylamido clusters. Complexes **3**−**5** constitute a new structure type of mixed-valence iron−sulfur clusters.

Introduction

The compound bis[bis(trimethylsilyl)amido]iron(II)[1,2] has proven to be a versatile precursor in the synthesis of polynuclear iron−sulfur species, often of unusual structural types, by reactions with thiols and/or sulfur in aprotic solvents. As examples, reactions with sterically encumbered thiols afford the two-coordinate monomers $[Fe(SR)_2]$[3,4] and three-coordinate dimers $[Fe_2(\mu_2\text{-SR})_2(SR)_2]$.[4–9] One such dimer, $[Fe_2(SR)_2(SR')_2]$ derived from exceptionally capacious thiols, upon reaction with sulfur affords the high-nuclearity species $[Fe_8S_7(SR)_4(SR')_2]$,[8,10] significant because it is a structural analogue of the P^N cluster of nitrogenase. Other applications utilizing bulky thiols have resulted in the linear cluster $[Fe_3(\mu_2\text{-SR})_4(N(SiMe_3)_2)_2]$,[10] with PhNHNHPh as the coreactant the cubane $[Fe_4(NPh)_4(SR)_4]$,[11,12] and with sulfur the cubane $[Fe_4S_4(N(SiMe_3)_2)_4]$.[13] The compound exists in the monomer–dimer equilibrium $2Fe[N(SiMe_3)_2]_2 \rightleftarrows Fe_2[N(SiMe_3)_2]_4$ in toluene, with the monomer the predominant species at ambient temperature.[2] This finding, together with the isolation of $Fe[N(SiMe_3)_2]_2(THF)$ from synthesis in tetrahydrofuran (THF),[2] makes probable that the monomer is the prevailing reactive form in the examples cited and the reactions described in this work.

In this laboratory, we are investigating the utility of $Fe[N(SiMe_3)_2]_2$ and other reduced and potentially highly reactive Fe^{II} complexes in the formation of high-nuclearity

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Chart 1. Complex Designations and Abbreviations[a]

$[Fe_2(\mu_2\text{-S-}p\text{-tol})_2(N(SiMe_3)_2)_2(THF)_2]$ **(1)**
$[Fe_2(\mu_2\text{-S-1-Ad})(\mu_2\text{-}N(SiMe_3)_2)(N(SiMe_3)_2)_2]$ **(2)**
$[Fe_3(\mu_3\text{-S})(\text{S-}p\text{-tol})_3(N(SiMe_3)_2)_3]$ **(3)**
$[Fe_3(\mu_3\text{-Se})(\mu_2\text{-S-}p\text{-tol})_3(N(SiMe_3)_2)_3]$ **(4)**
$[Fe_3(\mu_3\text{-S})(\mu_2\text{-S-1-Ad})_3(N(SiMe_3)_2)_3]$ **(5)**

[a] Abbreviations: Ad = adamantyl, LS_3 = 1,3,5-tris[(4,6-dimethyl-3-mercaptophenyl)thio]-2,4,6-tris(p-tolylthio)benzene(3−), mes = mesityl, S_2-*o*-xyl = *o*-xylyl-α,α′-dithiolate(2−), tol = tolyl.

iron−sulfur clusters of potential biological relevance. Here we report the first stage of this investigation involving two thiols of differing steric properties.

Experimental Section

Preparation of Compounds. All reactions and manipulations were performed under a pure nitrogen atmosphere using either Schlenk techniques or an inert-atmosphere glovebox. Solvents were passed through an Innovative Technology or an MBraun solvent purification system prior to use. All drying and volume reduction steps were performed in vacuo. Abbreviations are given in Chart 1.

$[Fe_2(\mu_2\text{-S-}p\text{-tol})_2(N(SiMe_3)_2)_2(THF)_2]$. A solution of 0.30 g (0.80 mmol) of $[Fe(N(SiMe_3)_2)_2]$[1,2] was added to a solution of 0.098 g (0.80 mmol) of *p*-tolylthiol in 3 mL of THF. The green-brown reaction mixture was stirred for 2 h and maintained at −28 °C overnight. The solid was collected, washed with copious amounts of hexanes, and dried to afford the product as light-green-yellow crystals. The filtrate was concentrated and a second crop of crystals was obtained, affording a total of 0.59 g (90%). Absorption spectrum toluene: λ_{max} (ϵ_M) 305 (8800) nm. ^{1}H NMR (THF-d_8, −5 °C): δ 16.75 (s, 3), 14.99 (s, 2), 13.89 (s, 18), 3.63 (THF), 1.80 (THF), −17.91 (s, 2).

$[Fe_2(\mu_2\text{-S-1-Ad})(\mu_2\text{-}N(SiMe_3)_2)(N(SiMe_3)_2)_2]$. To a solution of 0.60 g (1.6 mmol) of $[Fe(N(SiMe_3)_2)_2]$ in 3 mL of toluene was added 0.12 g (0.80 mmol) of adamantane-1-thiol. The reaction mixture was stirred vigorously overnight and developed a deep-red color. Slow removal of the solvent led to the separation of a yellow crystalline solid, which was recrystallized from toluene to give the product as 0.37 g (30%) of large yellow prisms. Absorption spectrum (toluene): λ_{max} (ϵ_M) 307 (11 730), 424 (2000) nm. ^{1}H NMR (C_6D_6): δ 1.00 (36), −0.31 (18), −3.62 (s, 3), −6.60 (s, 3), −8.94 (s, 3), −32.48 (s, 6). Anal. Calcd for $C_{28}H_{69}Fe_2N_3SSi_6$: C, 44.24; H, 9.15; Fe, 14.69; N, 5.53; S, 4.22. Found: C, 44.14; H, 9.21; Fe, 14.50; N, 5.40; S, 4.30.

$[Fe_3(\mu_3\text{-S})(\text{S-}p\text{-tol})_3(N(SiMe_3)_2)_3]$. Method A. To a solution of 0.60 g (1.6 mmol) of $[Fe(N(SiMe_3)_2)_2]$ in 3 mL of toluene was added 0.20 g (1.6 mmol) of *p*-tolylthiol in 2 mL of toluene followed by 0.017 g (0.53 mmol) of sulfur. The reaction mixture was stirred vigorously overnight, during which it assumed a deep-red-black color. Slow removal of solvent caused the separation of the product as a black crystalline solid, which was recrystallized from hexanes/toluene to give the product as 0.67 g (40%) of large well-formed black prisms. Absorption spectrum (toluene): λ_{max} (ϵ_M) 323 (26 500), 430 (25 200), 770 (5200) nm. ^{1}H NMR (C_6D_6): δ 29.72 (s, 3), 25.94 (s, 2), 3.49 (s, 18), −13.23 (s, 2). Anal. Calcd for $C_{39}H_{75}Fe_3N_3S_4Si_6$: C, 44.60; H, 7.20, N, 4.00; S, 12.21. Found: C, 44.31; H, 7.08; N, 3.86; S, 12.20.

Method B. To a solution of 0.50 g (0.60 mmol) of $[Fe_2(\text{S-}p\text{-tol})_2(N(SiMe_3)_2)_2(THF)_2]$ in 3 mL of toluene was added 0.013 g (0.40 mmol) of sulfur suspended in 2 mL of toluene. The reaction mixture was stirred overnight. Slow removal of the solvent led to a sticky black solid, which was washed with hexanes and dried to yield the product as 0.25 g (60%) of a black solid. The ^{1}H NMR spectrum of this material was identical with that from method A.

$[Fe_3(\mu_3\text{-S})(\mu_2\text{-S-1-Ad})_3(N(SiMe_3)_2)_3]$. Method A. This compound was synthesized according to method A of the preceding preparation with use of adamantane-1-thiol and was isolated in 30% yield as a black crystalline solid. Absorption spectrum (toluene): λ_{max} (ϵ_M) 306 (12 900), 425 (8000) nm. Anal. Calcd for $C_{48}H_{99}Fe_3N_3S_4Si_6$: C, 48.75; H, 8.44; Fe, 14.17; N, 3.55; S, 10.85. Found: C, 48.53; H, 8.30; Fe, 14.06; N, 3.36; S, 10.42.

Method B. A solution of 0.33 g (0.20 mmol) of adamantane-1-thiol in 2 mL of toluene was added dropwise to a stirred solution of 0.15 g (0.20 mmol) of $[Fe_2(\text{S-1-Ad})(N(SiMe_3)_2)_3]$ in 3 mL of toluene. The reaction mixture was stirred for 1 h; a suspension of 4.0 mg (0.13 mmol) of sulfur was added, forming a black solution. The solution was stirred for 6 h, the solvent was removed in vacuo, the sticky black residue was dissolved in hexanes, and the solution was filtered. Removal of the solvent afforded the product as 0.38 g (25%) of a black solid. The ^{1}H NMR spectrum of this material was identical with that from method A.

$[Fe_3(\mu_3\text{-Se})(\mu_2\text{-S-}p\text{-tol})_3(N(SiMe_3)_2)_3]$. A suspension of 0.032 g (0.45 mmol) of gray selenium was added to a solution of 0.25 g (0.30 mmol) of $[Fe_2(\text{S-}p\text{-tol})_2(N(SiMe_3)_2)_2(THF)_2]$ in 4 mL of toluene, forming a red-black solution. The reaction mixture was stirred for 3 days and filtered, and the filtrate was reduced to dryness. The sticky residue was dissolved in a minimal volume of hexanes maintained at −28 °C overnight. The product was isolated as 0.13 g (28%) of a black crystalline solid. ^{1}H NMR (C_6D_6): δ 29.71 (s, 3), 25.57 (s, 2), 3.66 (s, 18), −13.55 (s, 2).

In the sections that follow, complexes are designated as in Chart 1.

X-ray Structure Determinations. The structures of the five compounds in Table 1 were determined. Diffraction-quality crystals were obtained by maintaining saturated solutions in the indicated solvents at −30 °C for 24 h: **1**, THF; **2** and **3**, toluene; **4** and **5**, hexanes. Data were collected at 193 K on a Siemens (Bruker) SMART CCD-based diffractometer. Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections. Data were collected at 0.3° intervals in Φ and ω for 30 s/frame such that a hemisphere of data was collected. No crystal decay was observed upon re-collection of the first 50 frames at the end of the data collection. Data sets were reduced with SAINT and corrected for Lorentz and polarization effects; absorption corrections were applied with SADABS. Structures were solved by direct methods using *SHELX-97*. Metal and bound ligand atoms were located from *E* maps. Other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a uniform value of U_{iso}. Crystallographic parameters are collected in Table 1.[14]

The structure of compound **1** shows a minor 2-fold disorder of the two carbon atoms (C9 and C10) not bonded to oxygen in the THF ligand. These were modeled over two positions with an occupancy ratio of 3:1. In compound **2**, the Fe1−(S1−Ad)−Fe2 portion is disordered over two nearly identical positions with a 3:1 occupancy. Given the quality and limited resolution of the data for compound **5**, the ether solvate molecule was refined isotropically. One adamantylthiolate ligand is rotationally disordered about the

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[14] See the Supporting Information.

Table 1. Crystallographic Data[a] for Clusters **1**−**5**

	1	**2**	**3**	**4**	**5**
formula	$C_{34}H_{66}Fe_2N_2O_2S_2Si_4$	$C_{28}H_{69}Fe_2N_3SSi_6$	$C_{39}H_{75}Fe_3N_3S_4Si_6$	$C_{39}H_{75}Fe_3N_3S_3SeSi_6$	$C_{52}H_{109}Fe_3N_3OS_4Si_6$
fw	823.07	760.16	1050.36	1097.25	1256.75
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/c$
Z	1	2	4	4	4
a, Å	9.111(1)	9.068(2)	13.768(3)	13.786(1)	12.708(1)
b, Å	11.697(2)	14.670(3)	16.455(4)	16.429(2)	23.124(2)
c, Å	12.785(2)	16.193(3)	24.499(5)	24.572(3)	23.020(2)
α, deg	63.335(2)	87.869(3)	90	90	90
β, deg	82.641(3)	82.904(3)	90.48(3)	90.918(2)	93.909(2)
γ, deg	68.006(2)	88.375(3)	90	90	90
V, Å^3	1127.6(3)	2135.5(7)	5550(2)	5565(1)	6749.3(9)
GOF (F^2)	0.783	1.050	0.998	1.095	1.034
R1,[b] wR2[c]	0.0456, 0.0851	0.0541, 0.1182	0.0495, 0.0956	0.057, 0.1066	0.0498, 0.1125

[a] Obtained at 193 K with Mo Kα_2 radiation ($\lambda = 0.710\,73$ Å). [b] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$.

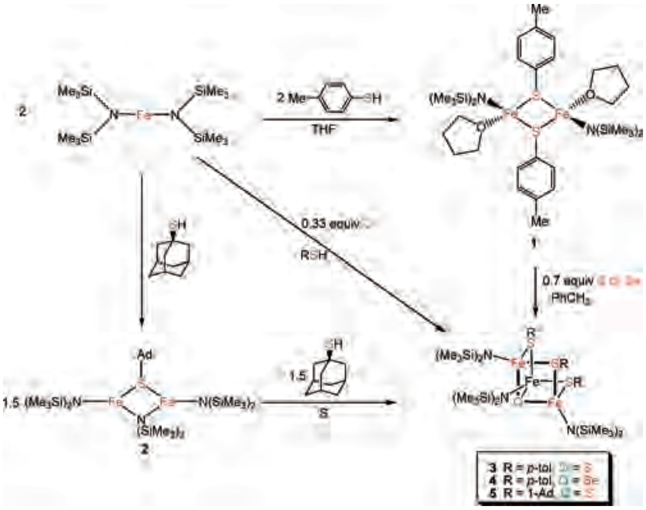

Figure 1. Scheme depicting the synthesis of dinuclear complexes **1** and **2** from Fe[N(SiMe$_3$)$_2$]$_2$ and trinuclear complexes **3**–**5** from **1** and **2**.

S−C bond in two orientations that were refined with equal populations. In the treatment of all disorders, appropriate constraints were applied to bond lengths and anisotropic displacement parameters.

Results and Discussion

The utility of Fe[N(SiMe$_3$)$_2$]$_2$ as a precursor is made evident by the reactions in Figure 1 that afford dinuclear complexes **1** and **2** and trinuclear clusters **3**−**5**. Structures of the reaction products are provided in Figures 2 and 3.

Dinuclear Complexes. The reaction of Fe[N(SiMe$_3$)$_2$]$_2$ with an equimolar amount of *p*-tolylthiol in THF results in thiolate-bridged dinuclear complex **1** (90%) by the stoichiometry of reaction 1. The molecule (Figure 2) is centrosymmetric with distorted tetrahedral coordination at the Fe^{II} sites and a rhombic Fe$_2$S$_2$ core with an Fe···Fe and mean Fe−S distances of 3.145 and 2.403 Å, respectively. Although thiolate-bridged Fe^{II} dimers abound, this complex is closely precedented only by [Fe$_2$(μ_2-Smes)$_2$(N(SiMe$_3$)$_2$)$_2$(THF)$_2$][15] whose core is distinctly different from that of **1**. In this complex, the Fe−S bond lengths differ by only 0.03 Å from **1**, but the rhomb is elongated along the Fe−Fe vector such that the Fe···Fe separation is 3.534 Å and the Fe−S−Fe and S−Fe−S angles are 94.45° and 85.55°, respectively. In **1**, Fe−S−Fe = 81.74(3)° and S−Fe−S = 98.26(3)°. The opposite angular core distortion in the former complex versus **1** arises from steric interactions of the larger mesityl group with neighboring ligands, resulting in an opening of the angle at the μ_2-sulfur atom.

$$2\text{Fe[N(SiMe}_3)_2]_2 + 2p\text{-tolSH} + 2\text{THF} \rightarrow [\text{Fe}_2(\mu_2\text{-S-}p\text{-tol})_2(\text{N(SiMe}_3)_2)_2(\text{THF})_2] + 2(\text{Me}_3\text{Si})_2\text{NH} \quad (1)$$

An equimolar reaction of Fe[N(SiMe$_3$)$_2$]$_2$ and 1-adamantylthiol in THF did not yield a tractable product. The use of 0.5 equiv of thiol led to isolation of **2** in moderate yield (30%). This molecule (Figure 2) contains a planar Fe$_2$NS core with thiolate and silylamide bridges, an Fe···Fe separation of 2.823 Å, and planar three-coordination at the iron sites. The latter feature arises from the reaction stoichiometry and ligand size properties. The μ_2-N(SiMe$_3$)$_2$ bridging functionality is less frequently encountered than terminal binding but is precedented in dinuclear complexes with at least six metals.[2,8,10,16–19] Of the prior examples involving iron, Fe$_2$[N(SiMe$_3$)$_2$]$_4$, containing planar Fe^{II} and a rhombic Fe$_2$N$_2$ core with an Fe···Fe distance of 2.663 Å,[2] is pertinent here. Dimensions of the Fe−N−Fe core portion are similar to that of **2**. In the two complexes, Fe−N bridge bond lengths differ by only 0.02 Å, but the smaller bridge angle of 79.4° vs 85.2° in **2**, occasioned by the presence of a μ_2-sulfur atom, is largely responsible for the longer metal−metal distance in the latter species.

Trinuclear Clusters. Although not obtained in high yields, these clusters are accessible by three methods (Figure 1), which proceed with the apparent stoichiometries of reactions 2–4. Self-assembly reaction 2 (R = *p*-tol and 1-Ad) leads to the formation of clusters **3** (40%) and **5** (30%). Reactions 3 (Q = S and Se) and 4 effectively increase cluster nuclearity and lead to **3** (60%) and **4** (28%) and to **5** (25%), respectively. The formation of a trinuclear cluster from dinuclear species is an unusual reaction. With no other source of iron, cleavage of the dinuclear cluster is required,

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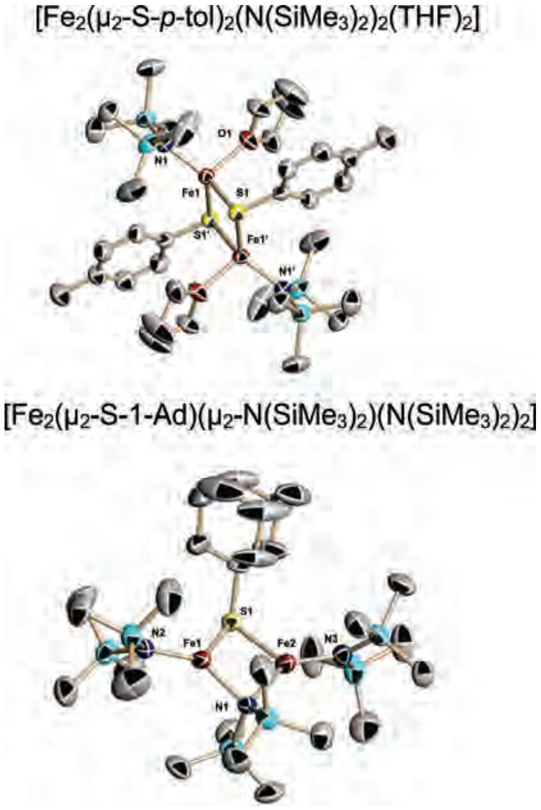

Figure 2. Structures of dinuclear complexes showing 50% probability ellipsoids and atom-labeling schemes; selected interatomic distances (Å) and angles (deg) are indicated. (Top) $[\mathrm{Fe_2}(\mu_2\text{-S-}p\text{-tol})_2(\mathrm{N(SiMe_3)_2})_2(\mathrm{THF})_2]$: Fe1−S1 2.399(1), Fe1−S1′ 2.407(1), Fe1−N1 1.940(3), Fe1−O1 2.092(2), Fe1−Fe1′ 3.145, Fe1−S1−Fe1′ 81.74(3), S1−Fe1−S1′ 98.26(3), N1−Fe1−O1 104.5(1), N1−Fe1−S1 125.48(9), N1−Fe1−S1′ 123.34(8), O1−Fe1−S1 99.55(7), O1−Fe1−S1′ 101.02(7). (Bottom) $[\mathrm{Fe_2}(\mu_2\text{-S-1-Ad})(\mu_2\text{-N(SiMe_3)_2})(\mathrm{N(SiMe_3)_2})_2]$: Fe1−S1 2.337(2), Fe2−S1 2.340(3), Fe1−N1 2.066(3), Fe2−N1 2.094(4), Fe1−N2 1.906(4), Fe2−N3 1.885(4), Fe1−Fe2 2.816, Fe1−S1−Fe2 74.04(9), Fe1−N1−Fe2 85.2(1), S1−Fe1−N1 98.7(1). Disordered ligands are shown in their majority positions.

presumably leading to other products (not isolated) and contributing to the usually modest yields.

$$3\mathrm{Fe[N(SiMe_3)_2]_2} + 3\mathrm{RSH} + \mathrm{S} \rightarrow [\mathrm{Fe_3S(SR)_3(N(SiMe_3)_2)_3}] + 3\mathrm{(Me_3Si)_2NH} \quad (2)$$

$$3[\mathrm{Fe_2}(\text{S-}p\text{-tol})_2(\mathrm{N(SiMe_3)_2})_2(\mathrm{THF})_2] + 2\mathrm{Q} \rightarrow 2[\mathrm{Fe_3Q}(\text{S-}p\text{-tol})_3(\mathrm{N(SiMe_3)_2})_3] + 6\ \mathrm{THF} \quad (3)$$

$$3[\mathrm{Fe_2}(\text{S-1-Ad})(\mathrm{N(SiMe_3)_2})_3] + 3\text{Ad-1-SH} + 2\mathrm{S} \rightarrow 2[\mathrm{Fe_3S}(\text{S-1-Ad})_3(\mathrm{N(SiMe_3)_2})_3] + 3\mathrm{(Me_3Si)_2NH} \quad (4)$$

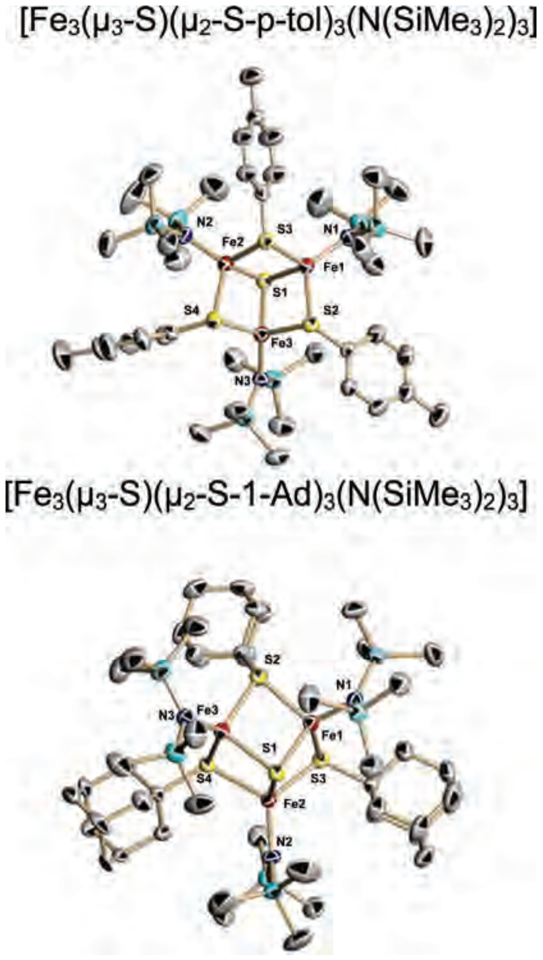

Figure 3. Structures of trinuclear complexes showing 50% probability ellipsoids and atom-labeling schemes. (Top) $[\mathrm{Fe_3}(\mu_3\text{-S})(\mu_3\text{-S-}p\text{-tol})_3(\mathrm{N(SiMe_3)_2})_3]$. (Bottom) $[\mathrm{Fe_3}(\mu_3\text{-S})(\mu_3\text{-S-1-Ad})_3(\mathrm{N(SiMe_3)_2})_3]$. The disordered adamantylthiolate ligand is shown in one of two orientations.

Table 2. Structural Parameters of $[\mathrm{Fe_3S}(\text{S-}p\text{-tol})_3(\mathrm{N(SiMe_3)_2})_3]$

Fe1−S1	2.262(1)	Fe1−S1−Fe2	80.41(3)
Fe2−S1	2.303(1)	Fe1−S1−Fe3	80.51(3)
Fe3−S1	2.317(1)	Fe2−S1−Fe3	82.03(3)
Fe1−S2	2.362(1)	Fe1−S2−Fe3	77.23(3)
Fe1−S3	2.364(1)	Fe1−S3−Fe2	77.15(3)
Fe2−S3	2.363(1)	Fe2−S4−Fe3	79.36(3)
Fe2−S4	2.360(1)	S1−Fe1−S2	101.87(3)
Fe3−S2	2.381(1)	S2−Fe1−S3	96.21(3)
Fe3−S4	2.388(1)	S1−Fe1−S3	101.15(3)
Fe1−N1	1.876(2)	S1−Fe2−S3	99.98(3)
Fe2−N2	1.892(2)	S1−Fe2−S4	99.31(3)
Fe3−N3	1.900(2)	S3−Fe2−S4	97.11(3)
Fe1−Fe2	2.947(1)	S1−Fe3−S2	99.68(3)
Fe1−Fe3	2.960(1)	S1−Fe3−S4	98.09(3)
Fe2−Fe3	3.033(1)	S2−Fe3−S4	94.83(3)
N−Fe−S1	118.2–120.8[a]	N−Fe−S2–4	116.3–120.8[b]

[a] Range of 3. [b] Range of 6.

Clusters **3**−**5** contain the mixed-valence $[\mathrm{Fe_3}(\mu_3\text{-Q})(\mu_2\text{-S})_3]$ core ($2\mathrm{Fe^{III}} + \mathrm{Fe^{II}}$) with a triply bridging sulfide or selenide atom, doubly bridging thiolate ligands, and idealized trigonal symmetry (Figure 3). The structures of **3** and **5** are very similar despite the steric bulk of the ligands and differ in the conformational disorder of one adamantylthiolate ligand over two sites. The metric features of **3** are summarized in Table 2.[14] The structure of **3** consists of the μ_3-S1 atom bonded to three iron atoms with a mean Fe−S−Fe angle of 81.0°, each of which is bridged by two μ_2-S-*p*-tol ligands and terminally coordinated by a bis(trimethylsilylamido) group. The core is thus built of three edge-fused rhombs that include iron atoms with distorted tetrahedral coordination. Because of bridging, the S−Fe−S angles within the rhombs (98.1–101.9°) are substantially smaller than the N−Fe−S angles (116.3–120.8°), which appear also to reflect steric interactions between the terminal silylamido ligands and thiolate substituents. Corresponding dimensions of **5** are nearly identical, and those of **4** differ only because of the larger radius of the μ_3-selenium ligand.[14] The mean Fe−Se bond length is 2.42(3) Å. The pattern of isotropically shifted resonances of the *p*-tolyl group in **3** (*o*-H, +15.5 ppm;

m-H, −23.7 ppm; *p*-Me, −27.4 ppm) is indicative of metal−sulfur antiparallel spin transfer and dominant contact interactions, characteristic features of all iron−sulfur thiolate clusters.

The cores of **3**−**5** present a cuboidal shape resembling that of the $[Fe_3S_4]^0$ core in $[Fe_3S_4(LS_3)]^{3-}$, in which the metals are in the same average oxidation state ($Fe^{2.67+}$).[20] As is the case in nearly all iron−sulfur clusters,[21] no structurally distinct iron sites with different oxidation states are observed. A closer structural relationship is found with the all-ferrous cluster $[Fe_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$[22] and a nearly identical complex derived from durene-1,2-dithiol.[23] In these cases, the chelating dithiolate supplies both bridging and terminal ligands, probably contributing to marked differences in Fe−Fe distances and Fe−S−Fe angles compared to **3** and **5**.

Summary

Complexes **1**−**5** are the most recent additions to a small class of iron−sulfido/thiolato−silylamido clusters with nuclearities of 2,[13,15] 4,[10,13] and 8.[8,10] Complexes **3**−**5**, while topologically precedented, constitute a new class of mixed-valence iron−sulfur clusters. The electronic properties of **3** are currently under investigation. Lastly, the occurrence of the $[Fe_3(\mu_3\text{-S})(\mu_2\text{-SR})_3]$ core in five different molecules suggests that a corresponding $[Fe_3(\mu_3\text{-S})(\mu_2\text{-S}_{Cys})_3]$ might be a viable biological site. While there remain structurally unidentified protein-bound iron−sulfur sites, no information has been forthcoming as to the occurrence of this type of trinuclear entity.

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Supporting Information Available: X-ray crystallographic information for the five compounds in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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