

Systematic Iron(II)-Thiolate Chemistry: Synthetic Entry to Trinuclear Complexes

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The mononuclear tetrahedral Fe(II,III)-thiolate complexes $[\text{Fe}(\text{SR})_4]^{2-}$ ($\text{R} = \text{Ph}$, $2\text{R} = o\text{-xyl}$) have been of principal interest as synthetic analogues of the $\text{Fe}(\text{S-Cys})_4$ sites in reduced and oxidized rubredoxin proteins.¹⁻³ Moreover, these complexes exhibit significant reactivity properties. For example, the reactions of $[\text{Fe}(\text{S}_2\text{-}o\text{-xyl})_2]^-$ with sulfide⁴ and $[\text{Fe}(\text{SPh})_4]^{2-}$ with elemental sulfur⁵ (or an organic trisulfide⁶) yield the protein $(2\text{Fe}-2\text{S})^{2+}$ site analogues $[\text{Fe}_2\text{S}_2(\text{SR})_4]^{2-}$. Another Fe(II)-thiolate species, the adamantane-like complex $[\text{Fe}_4(\text{SPh})_{10}]^{2-}$,^{7,8} reacts quantitatively with 4 equiv of sulfur to yield the $(4\text{Fe}-4\text{S})^{2+}$ site analogue $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$.⁵ The ready preparation of the foregoing Fe(II)-thiolates and their facile reactions with sulfur suggest access to new Fe(II)-SR and Fe-S-SR complexes subject to variation of thiolate and reaction stoichiometry.

In a systematic search for new species the reactions of FeCl_2 (or $(\text{Et}_4\text{N})_2(\text{FeCl}_4)$) with 1-4 equiv of thiolate, summarized in Figure 1, have been examined.⁹ Treatment of 20 mmol of $(\text{Et}_4\text{N})_2(\text{FeCl}_4)$ in 75 mL of acetonitrile with 4 equiv of NaSET (reaction 1), NaCl removal, and volume reduction afforded off-white crystalline $(\text{Et}_4\text{N})_2[\text{Fe}(\text{SET})_4]^{10}$ (38%, $\lambda_{\text{max}}(\epsilon_{\text{M}})$ 316 nm (7150), 340 (sh), 2080 (100) ($^5\text{E} \rightarrow ^5\text{T}_2, \nu_1$)), the first tetrakis(alkylmonothiolato) monomer, **1**. This very strongly reducing species ($E_p(1/-2-) = -1.08$ V) reacted immediately with 1 equiv of sulfur in acetonitrile solution (reaction 2). After THF addition, volume reduction, and diffusive introduction of ether a separable mixture of black plates and black needles was isolated. The former product was identified as $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2(\text{SET})_4]$, whose spectrum (332 nm (15 600), 427 (10 100), 450 (9700)) is quite similar to those of $(2\text{Fe}-2\text{S})^{2+}$ proteins and other dimers, **2**.¹¹ Formation of the latter product was improved in another reaction system (30 mmol of $(\text{Et}_4\text{N})_2[\text{Fe}(\text{SET})_4]$, 1.3 equiv of sulfur, 150 mL of dry acetone, 48 h). Thorough washing (acetone) of the reaction product afforded pure $(\text{Et}_4\text{N})_3[\text{Fe}_3\text{S}_4(\text{SET})_4]$ (**3**, 66%, 282 nm (23 500), 325 (23 900), 422 (18 000), 508 (11 000), 560 (9600)). Reaction with 4 equiv of benzenethiol in acetonitrile under dynamic vacuum gave after unexceptional workup black $(\text{Et}_4\text{N})_3[\text{Fe}_3\text{S}_4(\text{SPh})_4]$ (268 nm (42 700), 323 (sh), 446 (17 500), 511 (14 800), 564 (12 400); $\delta +27$ ($o\text{-H}$), -37.8 ($m\text{-H}$), $+38.8$ ($p\text{-H}$)), whose structure (Figure 2) was determined by X-ray methods.^{12a}

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(9) All operations were performed under a pure Ar atmosphere. Potentials (E_p) were determined vs. SCE by differential pulse polarography. Chemical shifts in ^1H NMR spectra (300 MHz) downfield and upfield of Me_4Si reference are negative and positive, respectively. EPR spectra were obtained at X-band frequencies and at ~ 7 K. Data refer to acetonitrile solutions.

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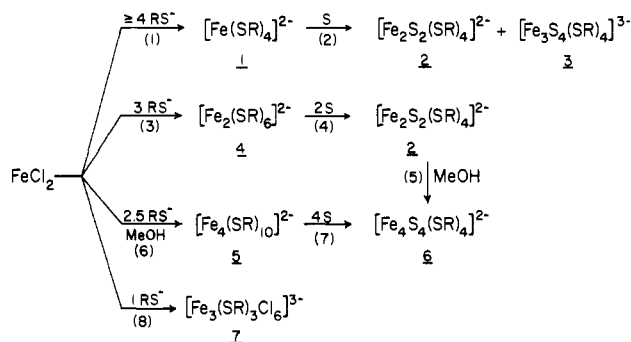


Figure 1. Scheme summarizing synthesis and reactions of compounds formed with Fe(II) and 1-4 equiv of thiolate.

The Fe_3S_4 portion of the anion approaches D_{2d} symmetry and contains the $(\text{Fe}_3\text{S}_4)^+$ core, preceded only in polymeric antiferromagnetic KFeS_2 .¹³ Dimensions of Fe_2S_2 core fragments are very similar to those of their isoelectronic counterparts in KFeS_2 and **2**.^{3,11}

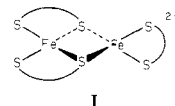
Reaction of 30 mmol each of FeCl_2 and Et_4NCl with 3 equiv of NaSET in 100 mL of propionitrile for 24 h (reaction 3) gave, after NaCl removal, addition of ether (50 mL), and cooling to -25°C , large orange-brown crystals identified as $(\text{Et}_4\text{N})_2[\text{Fe}_2(\text{SEt})_4]$ (**4**, 78%, 340 nm (8400), 2100 (170) (ν_1)). The dimeric nature of the anion was proven by a structure determination^{12b} (Figure 2). The entire anion has imposed centrosymmetry, with a planar Fe_2S_2 central fragment and an anti disposition of $\mu\text{-SET}$ groups. The same structure has also been established for $[\text{Fe}_2(\text{S}_2\text{-}o\text{-xyl})_3]^{2-}$,¹⁴ the first compound isolated with 3:1 $\text{RS}^-:\text{Fe}(\text{II})$ stoichiometry.¹⁵ $[\text{Fe}_2(\text{SET})_6]^{2-}$ ($E_p(1/-2-) = -1.07$ V, irreversible) with >2 equiv of sulfur in acetonitrile rapidly forms $[\text{Fe}_2\text{S}_2(\text{SET})_4]^{2-}$ in $>90\%$ in situ yield (reaction 4, spectrophotometric determination). The occurrence of reaction 5 affording $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ (**6**) in essentially quantitative conversion from **2** has been demonstrated.^{4,5}

At lower $\text{RS}^-:\text{Fe}(\text{II})$ ratios the occurrence of reaction 6, with 2.5 equiv of thiolate/Fe(II), to give $\sim 70\%$ isolated yields of $[\text{Fe}_4(\text{SR})_{10}]^{2-}$ (**5**) salts has been demonstrated,⁵ as have quantitative in situ and $\sim 90\%$ isolated yields of **6** by reaction 7.⁵ Although not performed with this exact stoichiometry, the recent reaction affording the cage complex $[\text{Fe}_4(\mu\text{-SPh})_4\text{Cl}_6]^{2-}$ ¹⁶ is in effect one involving a $\text{PhS}^-:\text{Fe}(\text{II})$ ratio of 1.5:1. Reaction 8, in which this ratio is unity, has also been investigated. A system containing 20 mmol each of FeCl_2 and $(\text{Et}_4\text{N})(\text{SPh})$ in 110 mL of acetonitrile deposited a microcrystalline solid. After the system

(12) Data were collected at ambient temperature on a Nicolet R3m diffractometer using graphite-monochromatized $\text{Mo K}\alpha$ radiation. Structures were solved by a combination of direct methods and subsequent difference Fourier maps; absorption corrections were applied. All Fe and S atoms and all nondisordered C atoms were refined by using SHELXTL programs. (a) $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2(\text{SPh})_4]$: $a = 36.748$ (4) Å, $b = 9.114$ (2) Å, $c = 17.427$ (4) Å, $Pna2_1$, $Z = 4$, 7657 unique data ($I > 3\sigma(I)$), $R(R_w) = 3.9(4.1)\%$. (b) $(\text{Et}_4\text{N})_2[\text{Fe}_2(\text{SET})_6]$: $a = 9.807$ (2) Å, $b = 14.573$ (2) Å, $c = 14.783$ (3) Å, $\beta = 100.93$ (1)°, $P2_1/n$, $Z = 2$, 1980 unique data ($I > 3\sigma(I)$), $R(R_w) = 4.3$ (4.8)%. (c) $(\text{Et}_4\text{N})_3[\text{Fe}_3(\text{SPh})_3\text{Cl}_6]$: $a = 24.488$ (6) Å, $b = 13.489$ (3) Å, $c = 18.197$ (5) Å, $\beta = 110.68$ (2)° $C2/c$, $Z = 4$, 2679 unique data ($I > 3\sigma(I)$), $R(R_w) = 4.9(5.3)\%$.

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similar to that of its Fe(II) analogue, but with syn $\mu\text{-SEt}$ groups (Hagen, K. S.; Holm, R. H., results to be submitted for publication).

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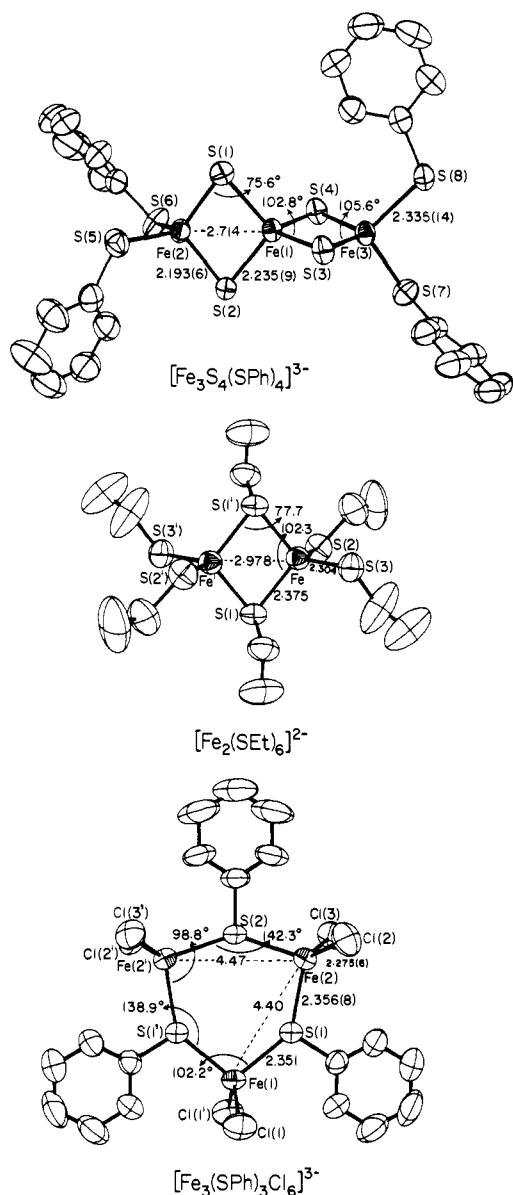


Figure 2. Structures of complexes formed in the reactions of Figure 1, showing 50% probability ellipsoids and selected interatomic distances (Å) and angles (deg); primed and unprimed atoms are related by crystallographic symmetry: (top) $[\text{Fe}_3\text{S}_4(\text{SPh})_4]^{3-}$, mean distances under idealized D_{2d} symmetry are given, $\text{Fe}(1)\cdots\text{Fe}(2)$ 2.703 (2) Å, $\text{Fe}(1)\cdots\text{Fe}(3)$ 2.725 (2) Å; (middle) $[\text{Fe}_2(\text{SET})_6]^{2-}$, centrosymmetric; (bottom) $[\text{Fe}_3(\text{SPh})_3\text{Cl}_6]^{3-}$, C_2 axis along $\text{Fe}(1)\cdots\text{S}(2)$, $\text{Fe}(2)\cdots\text{S}(2)$ 2.365(2) Å, the Fe-Cl distance is the mean of three independent values. Estimated standard deviation values for individual Fe-S, Fe-Cl, and Fe \cdots Fe distances (excluding the latter distances in $[\text{Fe}_3(\text{SPh})_3\text{Cl}_6]^{3-}$) are typically ≤ 0.003 Å.

was cooled to 25 °C, the solid was collected, washed with 4:1 ether-acetonitrile, and recrystallized from acetonitrile to give green crystals of a material shown to be $(\text{Et}_4\text{N})_3[\text{Fe}_3(\text{SPh})_3\text{Cl}_6]$ (7, 39%, 260 nm (29 000), 330 (6900), 1850 (210) (ν_1); δ +41.1 (*o*-H), -12.3 (*m*-H), +32.8 (*p*-H); -30 °C). The structure of $[\text{Fe}_3(\text{SPh})_3\text{Cl}_6]^{3-}$ ^{12c} (Figure 2) contains a $\text{Fe}_3(\mu\text{-SPh})_3$ ring that, remarkably (and unlike the few structurally defined $\text{M}_3(\mu\text{-SR})_3$ cycles¹⁷), is planar. Further, the three phenyl groups are coplanar with this ring. The planar conformation occurs at the expense of very large Fe-S-Fe internal angles (140–142°) and produces Fe \cdots Fe separations of 4.4–4.5 Å. The latter values are substantially larger than those of 2–6,^{3,7,8} and some exchange coupling remains

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($\mu_{\text{Fe}} = 4.18 \mu_{\text{B}}$, CH_3CN , -30 °C). As in all species 1–6 the Fe atoms occupy tetrahedral sites in 7.

These and related^{5,8,16} results disclose an extensive chemistry of Fe(II)-thiolates, with respect to both the existence of a diverse set of discrete complexes with varying nuclearity and, owing to their reducing nature, reactions with sulfur to afford Fe-S-SR clusters. Neither the $[\text{Fe}_3\text{S}_4]^+$ core structure of 3 nor the $\text{Fe}_3(\text{SPh})_3$ ring of 7 has been previously encountered in individual molecules. Indeed, the only prior trinuclear Fe-(S)-SR species of known structure are $[\text{Fe}_3\text{S}(\text{S}_2\text{-}o\text{-xy})_3]^{2-18}$ and a ring-methylated variant¹⁹ and the cyclic nonplanar $(3\text{Fe-3S})^{3+}$ site in *A. vinelandii* ferredoxin I.²⁰ In the latter, deviations from the Fe_3S_3 least-squares plane are ≤ 0.31 Å and mean values of Fe \cdots Fe distances and Fe-S-Fe internal angles are 4.08 Å and 123°, respectively.²¹ $[\text{Fe}_3(\text{SPh})_3\text{Cl}_6]^{3-}$ reveals the feasibility by synthesis of a ring of comparable dimensions, but it is not a site analogue. The $(\text{Fe}_3\text{S}_4)^+$ core of 3, having an EPR signal at $g = 4.3$ and none near $g = 2.0$ in freshly prepared solutions, cannot represent structurally uncharacterized protein 3-Fe sites with the latter signal.²² However, complexes 3 and 7 may serve as precursors, in isomerization, redox, and other reactions, to new Fe-S-SR clusters including protein 3-Fe site representations. This possibility is under investigation.

Acknowledgment. This research was supported by NIH Grant GM 28856. NMR and X-ray diffraction equipment used in this research was obtained by NSF Grants CHE 80-00670 and CHE 80-08891.

Registry No. 1, 82661-04-9; 2, 82661-06-1; 3, 82661-08-3; 4, 82665-06-3; 7, 82661-10-7; $(\text{Et}_4\text{N})_3[\text{Fe}_3\text{S}_4(\text{SPh})_4]$, 82661-12-9; FeCl_2 , 7758-94-3; $(\text{Et}_4\text{N})_2[\text{FeCl}_4]$, 15050-84-7.

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Synthesis and Structure of Tri-*s*-triazine

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From the time of Liebig¹ and Gmelin,² a group of related nitrogen compounds (melem, hydromelic acid, cyameluric chloride, cyameluric acid, etc.) was known that possessed high heat stability, low solubility, and little chemical reactivity. However, these compounds remained structural puzzles for more than a century until Pauling and Sturdivant³ devised the correct formulation for their common nucleus, a coplanar arrangement of three fused *s*-triazine rings (1). We have now synthesized the unsubstituted nucleus, tri-*s*-triazine (1),⁴ for the first time and have determined its physical and spectroscopic properties and its structure by X-ray crystallography. This compound has been the subject of numerous theoretical calculations and predictions^{3,5} as

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