#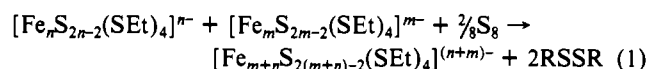 Oxidation by Elemental Sulfur and Coupling of Fe/S Complexes. Synthesis and Structural Characterization of (Et4N)4[Fe4S6(SEt)4], a New Fe/S Cluster with a Linear Fe4 Backbone

The facile oxidation of metal-coordinated thiolate ligands with either S_8 or organic trisulfides, RSSSR, and the concomitant, in situ, generation of sulfido or polysulfido ligands have been found effective for the synthesis of sulfido or polysulfido complexes.[1,2] Investigations of this reaction with the tetrahedral $[M(SPh)_4]^{2-}$ complexes (M = Fe, Mn, Ni, Zn, Cd) have resulted in the high-yield syntheses of such complexes as the $[Fe_2S_2(SPh)_4]^{2-}$ and $[Fe_2S_{12}]^{2-}$ dimers[1] and the $[Mn(S_5)(S_6)]^{2-}$, $[Ni(S_4)_2]^{2-}$, $[Zn(S_4)_2]^{2-}$, $[Zn(S_5)_2]^{2-}$, and $[Cd(S_5)_2]^{2-}$ polysulfido complexes.[2] A similar reaction of $[Fe(SEt)_4]^{2-}$ with sulfur in 1:1 and 4:3 molar ratios affords the linear $[Fe_2S_2(SEt)_4]^{2-}$ and $[Fe_3S_4(SEt)_4]^{3-}$ complexes, respectively.[3] This latter reaction can be described as oxidative coupling of the $[Fe(SEt)_4]^{2-}$ and $[Fe_2S_2(SEt)_4]^{2-}$ anions and suggests that similar coupling reactions between members of the $[Fe_nS_{2n-2}(SEt)_4]^{n-}$ series under controlled stoichiometry may generate other members of the same series of polynuclear linear complexes (eq 1).[4]

$$[Fe_nS_{2n-2}(SEt)_4]^{n-} + [Fe_mS_{2m-2}(SEt)_4]^{m-} + \tfrac{2}{8}S_8 \rightarrow$$
$$[Fe_{m+n}S_{2(m+n)-2}(SEt)_4]^{(n+m)-} + 2RSSR \quad (1)$$

Recently, we reported[5] the synthesis of the {[Mo(CO)_3]-[Fe_3S_4(SEt)_3]}^{3-} cluster by the reaction of (CH_3CN)_3Mo(CO)_3 with $[Fe_3S_4(SEt)_4]^{3-}$ (I). The latter was obtained by the procedure described previously[3] from the reaction of $(Et_4N)_2[Fe(SEt)_4]$ with elemental sulfur in acetone at 25 °C, in an approximate 3:4 molar ratio. Following isolation of the crystalline $(Et_4N)_3(I)$, a new microcrystalline Fe/S complex (II) can be isolated in small yield as a Et_4N^+ salt, when an additional amount of sulfur is added to the acetone filtrate. Analytical data[6] suggest the formulation $(Et_4N)_4[Fe_4S_6(SEt)_4]$ for this compound, which shows an electronic spectrum distinct from that of $(Et_4N)_3(I)$ and is EPR silent at temperatures >14 K. The synthesis of $(Et_4N)_4(II)$ also can be accomplished in 30% yield by the reaction of $[Fe(SEt)_4]^{2-}$ and sulfur in a 4:6 ratio in acetone solution. The formation of II can be envisioned as a result of the oxidative coupling between either $[Fe(SEt)_4]^{2-}$ and $[Fe_3S_4(SEt)_4]^{3-}$ or two $[Fe_2S_2(SEt)_4]^{2-}$ anions by elemental sulfur (eq 1). The reaction of II with o-durenedithiol (L) results in the formation of the $[Fe_4S_6(L)_2]^{4-}$ derivative (III), which has been obtained in crystalline form as the Et_4N^+ salt.[6] The structure of $(Et_4N)_4(II)$ has been determined.[7] The cen-
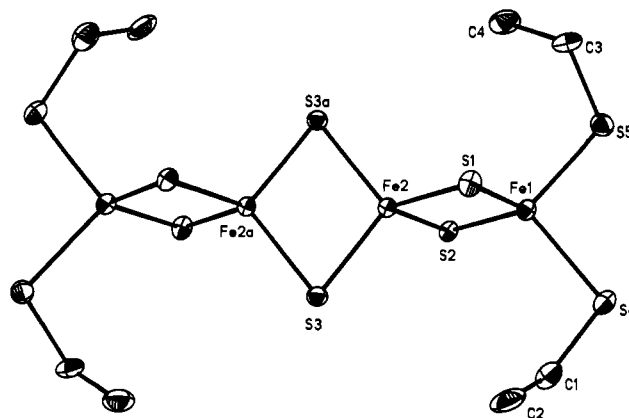

Figure 1. Structure and labeling of the anion in $(Et_4N)_4[Fe_4S_6(SEt)_4]$. Thermal ellipsoids as drawn by ORTEP represent the 50% probability surfaces. Selected distances and angles not reported in the text: Fe–S_t, 2.324 Å, Fe–S–Fe, 75.6 (1)°, S_b–Fe–S_b, 104 (1)°, S_t–Fe–S_t, 98.95 (7)°.
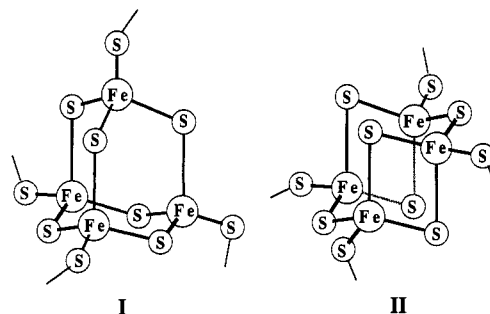

Figure 2. Other possible structural isomers for the $[Fe_4S_6(SEt)_4]$ stoichiometry.

trosymmetric $[Fe_4S_6(SEt)_4]^{4-}$ anion (Figure 1) contains as an outstanding structural feature a linear Fe_4S_6 chain that can be described in terms of a central $[Fe_2S_6]^{6-}$ unit capped at either end by $[Fe(SEt)_2]^+$ subunits. The anion closely approaches D_{2h} symmetry and contains four edge-shared $Fe^{III}S_4$ tetrahedra. The nearly linear array of the Fe atoms in II is apparent in the Fe1–Fe2–Fe2a angle of 179.21 (4)°. The central Fe–Fe distance at 2.747 (1) Å is somewhat longer than the two symmetry-equivalent terminal Fe–Fe distances (2.732 (1) Å). All Fe–Fe distances in II are slightly longer than the Fe–Fe distance in $[Fe_2S_2(S-p-C_6H_4Me)_4]^{2-}$ (2.691 (1) Å)[8] and the Fe–Fe distance in $[Fe_3S_4(SC_6H_5)_4]^{3-}$ (2.714 Å).[3] The three structurally distinct Fe–S_b distances in II also are metrically separated into three sets with Fe–S_b pair distances of 2.213 ± 002 Å (Fe1–S1, Fe1–S2), 2.250 ± 002 Å (Fe2–S1, Fe2–S2), and 2.233 ± 002 Å (Fe2–S3, Fe2–S3a). The three, alternatively orthogonal, Fe_2S_2 rhombic units are very nearly planar. As suggested previously for the $[Fe_2S_4]^+$ core in I, the $[Fe_4S_6]$ core in II represents a second example of a soluble fraction of the $(Fe^{III}S_4)_n$ chains present in the extended structure of $KFeS_2$.[9] Other reasonable structures with the $[Fe_4S_6(SR)_4]$ stoichiometry that contain tetrahedral FeS_4 structural units can be envisioned (Figure 2). These hypothetical structures, which are derived by the judicious removal of ML units from the pentlandite-type cages found in the structurally characterized $[M_8S_6(L)_8]^{n-}$ clusters (M = Co, L = SPh, n = 4;[10] M = Fe, L = I, n = 3[11]), as yet have not been synthesized.

The Moessbauer spectrum of $(Et_4N)_4(II)$ shows two broad lines ($\delta_{av}{}^{12}$ = 0.29 mm/s; $\Delta_{Eq,av}$ = 0.59 mm/s) that can be fitted with

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(2) Coucouvanis, D.; Patil, P. R.; Kanatzidis, M. G.; Detering, B.; Baenziger, N. C. *Inorg. Chem.* **1985**, *24*, 24–31.
(3) Hagen, K. S.; Watson, A. D.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 3905–3913.
(4) The validity of this equation for n = 1 is based on the assumption that the highly reducing $[Fe(SEt)_4]^{2-}$ anion rapidly is oxidized to $[Fe(SEt)_4]^-$ in the presence of elemental sulfur.
(5) Coucouvanis, D.; Al-Ahmad, S.; Salifoglou, A.; Dunham, R. W.; Sands, R. H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1353.
(6) Analytical data: Calcd for $(Et_4N)_4(II)$, $Fe_4S_{10}N_4C_{40}H_{100}$ (MW 1181.44): Fe, 18.9; S, 27.1; N, 4.74; C, 40.7; H, 8.55. Found: Fe, 18.8; S, 26.8; N, 4.67; C, 40.5; H, 8.60. Calcd for $(Et_4N)_4(III)$, $Fe_4S_{10}N_4C_{52}H_{104}$ (MW 1329.6): Fe, 16.8; S, 24.1; N, 4.21; C, 47.0; H, 7.90. Found: Fe, 16.5; S, 24.0; N, 3.80; C, 46.9; H, 7.43.
(7) Single crystals of $(Et_4N)_4(II)$ obtained by the slow diffusion of diethyl ether into an acetonitrile solution of the compound, are monoclinic. The space group is $P2_1/n$, with a = 14.170 (4) Å, b = 13.846 (3) Å, c = 15.594 (3) Å, β = 93.04 (2)°, and Z = 2; D_{calcd} = 1.28, d_{obsd} = 1.28 (1) g/cm³. Of the 8567 single-crystal X-ray diffractometer data collected at −130 °C (Mo Kα, $2\theta_{max}$ = 50°), 2830 were unique. The structure was solved by direct methods and Fourier techniques. The refinement of the structure by full-matrix least-squares methods was based on 2471 unique reflections ($I > \sigma(I)$). Anisotropic temperature factors were used for non-hydrogen atoms, and the H atoms were included in the structure factor calculation at their calculated positions (d_{C-H} = 0.96 Å) but were not refined. At the current stage of refinement on 263 parameters with all atoms present in the asymmetric unit, R = 0.055 and R_w = 0.042. An empirical absorption correction was applied to the data (transmission range 0.939–0.814; μ = 12.94 cm⁻¹).

(8) Mayerle, J. J.; Denmark, S. E.; De Pamphilis, B. V.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1975**, *97*, 1032.
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(12) Isomer shift, δ, and quadrupole splittings, Δ_{Eq}, have been obtained at 125 K vs Fe. For $(Et_4N)_4(III)$, δ_{av} = 0.28 and Δ_{Eq} = 0.69.

two quadrupole doublets in a 1:1 ratio with very similar δ and Δ_{EQ} values. The presence of two Fe sites is consistent with the structure shown in Figure 1. The Moessbauer parameters for II are similar to those reported[3] for the $Fe^{III}S_4$ sites in $(Et_4N)_3(I)$. Similar Moessbauer spectra are obtained[12] for III. The ambient-temperature magnetic moment of $(Et_4N)_4(II)$ (S = integer) at 1.23 μ_B/Fe atom is appreciably smaller than that reported[3] for $(Et_4N)_3(I)$ (3.39 μ_B; $S = {}^5/_2$). As a result of residual paramagnetism, the antiferromagnetically coupled linear oligomers display isotropically shifted ^1H NMR spectra. Resonances attributed to the ethanethiolate ligands in II are observed at 8.22 ppm (CH_3) and 73.3 ppm (CH_2) vs TMS. A signal at 8.3 ppm was observed previously[3] coincident with the synthesis of I and was considered to be associated with an unidentified paramagnetic precursor to the $[Fe_6S_9(SEt)_2]^{4-}$ cluster. The latter and $[Fe_4S_4(SEt)_4]^{2-}$ form by thermolysis of I in solution at 80 °C. The electronic spectra of II and III in CH_3CN solution[13] resemble the spectrum reported[3] for I but do not show the low-energy absorption at 720 nm. The cyclic voltammogram of $(Et_4N)_4(II)$ in CH_3CN solution (Pt electrode vs SCE) shows two irreversible reduction waves at $E_{1/2}$ = –1.27 and –1.58 V and qualitatively is similar to that of $(Et_4N)_4(I)$. The latter shows[3] irreversible waves at –1.66 and –1.79 V.

The reaction of II with $(CH_3CN)_3Mo(CO)_3$ or anhydrous $FeCl_2$ in CH_3CN solution affords in high yield the $\{[Mo(CO)_3]-[Fe_3S_4(SEt)_3]\}^{3-4}$ or $[Fe_4S_4(SEt)_4]^{2-}$[14] cluster, respectively. In solution, II slowly converts to a mixture of $[Fe_6S_9(SEt)_2]^{4-}$,[3]

$[Fe_4S_4(SEt)_4]^{2-}$,[14] and $[Fe_2S_2(SEt)_4]^{2-}$,[8] as evidenced by changes in the isotropically shifted ^1H NMR spectra. This instability of II in solution also is evident in changes in the electronic spectra that commence when solutions of II are allowed to stand for ca. 1 h at ambient temperature. No such changes are observed in CH_3CN solutions of III. The latter apparently is stabilized by the bidentate terminal ligands. The stability of II, limited as it is, may be due to the EtS^- terminal ligands. The reaction of II with thiophenol results in the formation of the known trimeric $[Fe_3S_4(SPh)_4]^{3-}$ complex anion.[3] Prior to recrystallization, samples of II contain <1% of an EPR-active impurity ($S = {}^1/_2$, $g_{av} \sim 2.00$) that may be due to the noninteger-spin $[Fe_5S_8(SEt)_4]^{5-}$ linear pentamer that could form by the oxidative coupling of I and $[Fe_2S_2(SEt)_4]^{2-}$ (eq 1). The reaction of preisolated I with elemental sulfur in a 1:1 ratio was undertaken in an attempt to obtain the $[Fe_6S_{10}(SEt)_4]^{6-}$ linear hexamer. Upon completion, this reaction shows the 560-nm CT absorption in I shifted to 620 nm with a concomitant loss of the $S = {}^5/_2$ EPR signal characteristics of I. Attempts to isolate this highly unstable complex currently are in progress.

(13) Electronic spectra (CH_3CN solution), nm (ϵ): for $(Et_4N)_4(II)$, 588 (13 290), 500 (17 470), 408 (27 060), 318 (34 450), 280 (34 700); for $(Et_4N)_4(III)$, 590 (17 200), 500 (16 690), 408 (25 490), 318 (27 400), 270.

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Articles

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Synthesis and Characterization of Alkaline-Earth-Metal β-Diketonate Complexes Used as Precursors for Chemical Vapor Deposition of Thin-Film Superconductors

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Several of the β-diketonate metal complexes used for metal organic chemical vapor deposition (MOCVD) of thin-film superconductors have been characterized by thermogravimetric analysis, mass spectrometry, and gas chromatography/mass spectrometry. The volatility of the alkaline-earth-metal chelates has been studied, and it has been determined that one reason the alkaline-earth-metal chelates are less volatile than other metal β-diketonates is that they exist as oligomers. For example, one barium β-diketonate chelate consists of a cluster of five metal ions bridged by β-diketonate carbonyl oxygens and water molecules. It has also been found that the addition of uncomplexed (protonated) β-keto enolate ligand to the carrier gas stream greatly improves the gas chromatographic behavior of these alkaline-earth-metal chelates, probably owing to adduct formation accompanying the dissociation of the oligomers. The results of these studies, as well as the implications for using these chelates together with auxiliary ligands for MOCVD, will be discussed.

Introduction

Recently, several research groups have made high-quality thin films of the $YBa_2Cu_3O_7$ superconductor by using metal organic chemical vapor deposition (MOCVD) with volatile metal β-diketonate complexes. For example, Watanabe et al.[1] have prepared thin-film superconductors with a critical current density of 190 000 A/cm² at 10 T and an onset of superconductivity at 89 K by using this technique. A recent report from workers at Mitsubishi in-

dicated that critical current densities in the absence of magnetic field of films prepared by MOCVD from β-diketonates were approximately 6 300 000 A/cm².[2] One difficulty in making these films is that the barium chelates are less volatile and thermally stable than the copper and rare-earth-metal precursors. This has led to renewed interest in studying the stabilities, compositions, and thermal properties of alkaline-earth-metal β-diketonates.[3,4]

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