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Inorganic Derivatives of Iron Sulfide Thiolate Dimers and Tetramers: Synthesis and Properties of the Halide Series [Fe₂S₂X₄]²⁻ and [Fe₄S₄X₄]²⁻ (X = Cl, Br, I)

GEOFFREY B. WONG, M. A. BOBRIK, and R. H. HOLM*

Entry to new series of binuclear and tetranuclear iron–sulfide–halide dianions is afforded by a combination of reactions of coordinated thiolate and halide displacement. The previously reported complexes [Fe₂S₂(S₂-*o*-xyl)₂]²⁻ and [Fe₄S₄(SR)₄]²⁻ (R = *t*-Bu, CH₂Ph, Ph) react smoothly with benzoyl halides in acetonitrile to afford [Fe₂S₂X₄]²⁻ and [Fe₄S₄X₄]²⁻ (X = Cl, Br), isolable in good yield as R′₄N⁺ salts, and the corresponding thioesters, which have been isolated from representative reactions. Treatment of the chloride complexes with sodium iodide in acetonitrile yields salts of [Fe₂S₂I₄]²⁻ and [Fe₄S₄I₄]²⁻. Recent x-ray structural results for the binuclear and tetranuclear chloride complexes reveal retention of the Fe₂S₂ and Fe₄S₄ core structures present in the thiolate precursors. These are the first complexes containing these core units in which the terminal ligand atoms are not chalcogens. Significant reactions of the halide complexes include conversion to thiolate species with thiol and base and the binuclear–tetranuclear conversions

$$[Fe_2S_2X_4]^{2-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Fe_4S_4X_4]^{2-}$$
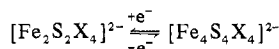
effected chemically or electrochemically. Examination of magnetism, redox potentials, and absorption spectra shows that only the first of these properties is essentially independent of halide vs. thiolate terminal ligation at parity of core structure.
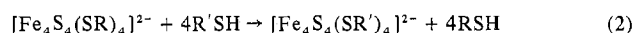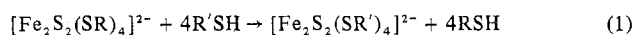
Introduction

The binuclear and tetranuclear iron sulfide thiolate complexes of the general types [Fe₂S₂(SR)₄]²⁻ and [Fe₄S₄(SR)₄]²⁻, respectively, have enjoyed substantial utility as minimal representations, or synthetic analogues, of the active sites of iron–sulfur proteins.[1] Apart from their biological context these complexes and the sites which they represent are new members of the classes $M_nA_nL_m{}^2$ ($m \geq n$ = 2, 4) containing substructural or *core* units M_nA_n. However, they differ significantly in structural and electronic features from other members of the same class. While such differences are implicit in our past[1] and continuing[3,4] pursuit of site analogues, several brief comparisons of these species with certain other complexes of the same class serve to emphasize this point.

The binuclear class M₂A₂L₄ contains numerous members[5] with the edge-shared bitetrahedral structure of [Fe₂S₂(SR)₄]²⁻[6] (e.g., [Fe₂S₂(S₂-*o*-xyl)₂]²⁻, **1**, Figure 1), but only the latter complexes contain the Fe₂S₂ core. This core is found otherwise only in Fe₂S₂(CO)₆, a molecule obviously electronically[7] unrelated to and containing a disulfide bond[8] not found in [Fe₂S₂(SR)₄]²⁻. The cubane-type M₄A₄ core geometry is now an unexceptional inorganic stereochemical unit,[9,10] and specific examples of structurally defined Fe₄S₄ cores include those in [(η⁵-C₅H₅)₄Fe₄S₄],[11] [(η⁵-C₅H₅)₄Fe₄S₄]⁺,[12] [(η⁵-C₅H₅)₄Fe₄S₄]²⁺,[13] Fe₄S₄(NO)₄,[14] and [Fe₄S₄(tfd)₄]²⁻.[15] Details of their core structures depart from those of [Fe₄S₄(SR)₄]²⁻,³⁻ [16,17] (**6**), and no core isoelectronic relationships exist between analogue anions and these species.[13,14,16a] Apart from

redox behavior[13,14,18] and cleavage of dithiolene tetramers with triphenylphosphine,[18] the reaction chemistry of [(η⁵-C₅H₅)₄Fe₄S₄]ᶻ, [Fe₄S₄(NO)₄]ᶻ, and [Fe₄S₄(tfd)₄]ᶻ species has been little investigated. In particular, there is no information as to whether these complexes can be converted to tetranuclear analogues or other new species by ligand replacement reactions.

Recent experimentation with [Fe₂S₂(SR)₄]²⁻ and [Fe₄S₄(SR)₄]²⁻ complexes has been directed toward an elucidation of their reactivity properties beyond the one-electron redox reactions discovered earlier.[1] While this work is still in a developmental stage examples of two general types of reactions, which proceed with retention or nonretention of core structure, have emerged. Cases of nonretention include dimer–tetramer conversions [Fe₂S₂(SR)₄]²⁻,³⁻ → [Fe₄S₄(SR)₄]²⁻.[4b] Reactions proceeding with core retention necessarily involve alteration of terminal ligands, which have proven to be labile and readily replaceable under ambient conditions in substitution reactions (1)[6] and (2).[16b] Inasmuch as the rate-limiting step in reaction

$$[Fe_2S_2(SR)_4]^{2-} + 4R'SH \rightarrow [Fe_2S_2(SR')_4]^{2-} + 4RSH \qquad (1)$$

$$[Fe_4S_4(SR)_4]^{2-} + 4R'SH \rightarrow [Fe_4S_4(SR')_4]^{2-} + 4RSH \qquad (2)$$

2 is proposed to be protonation of coordinated thiolate by R′SH,[19] the observation that reaction of [Fe₄S₄(SEt)₄]²⁻ with benzoyl chloride afforded ethylthiobenzoate[20] engaged our attention as another manifestation of nucleophilic reactivity of a thiolate ligand. The present investigation was undertaken to ascertain the fate of the Fe₄S₄ core which, if not disrupted, was expected to appear in the form of [Fe₄S₄Cl₄]²⁻ by analogy
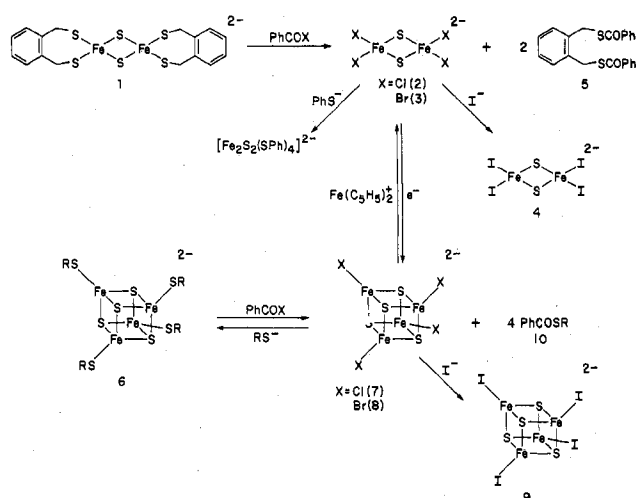
Figure 1. Synthesis and reactions of iron sulfide halide dimers (2–4) and tetramers (7–9).

with reaction 2. This expectation has been realized. The present work provides synthetic entry, by means of reactions of **1** and **6** with benzoyl halides and several metathesis steps, to two new series of fundamental inorganic anions $[Fe_2S_2X_4]^{2-}$ (**2–4**) and $[Fe_4S_4X_4]^{2-}$ (**7–9**) with X = Cl, Br, or I. The structures of **2** and **7** in Figure 1 have been established by x-ray diffraction.[21] Also reported are certain physical properties of halide dimers and tetramers, which are compared with those of $[Fe_2S_2(SR)_4]^{2-}$ and $[Fe_4S_4(SR)_4]^{2-}$ in an attempt to determine their dependence on terminal ligation at parity of core structure.

Experimental Section

Preparation of Compounds. All operations were carried out in a pure dinitrogen atmosphere. Quaternary ammonium or tetraphenylarsonium salts of $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$[4b,6] and $[Fe_4S_4(SR)_4]^{2-}$[16] were obtained by published procedures. All solvents were thoroughly degassed before use.

Halide Dimer Salts. (a) $(R'_4N)_2[Fe_2S_2Cl_4]$. To a stirred slurry of 3.0 g (3.9 mmol) of $(Et_4N)_2[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]$ in 50 mL of acetonitrile was added a solution of 2.3 mL (20 mmol) of benzoyl chloride in 20 mL of acetonitrile. As the solid dissolved the solution changed to a purple-red color. After stirring for 2 h the reaction mixture was filtered and the filtrate volume was reduced in vacuo to ~35 mL, at which point crystals of the dithiobenzoate side product (vide infra) were visible. Slow addition of 400 mL of diethyl ether at ambient temperature redissolved these crystals and caused separation of the desired product as purple-black microcrystals, leaving a purple-brown supernatant solution. The crude product was collected by filtration and dissolved in a minimum volume of acetonitrile. This solution was filtered and warmed to 50 °C, and an approximately equal volume of THF was slowly added until a crystalline product began to separate. Slow cooling to −20 °C caused separation of black crystals, which were collected by filtration, washed with THF, and dried in vacuo for several hours at ambient temperature; yields of the Et_4N^+ salt were 45–65%. A second crop of crystals can be obtained by complete evaporation of the filtrate followed by recrystallization of the residue as described in a preceding step. Anal. Calcd for $C_{16}H_{40}Cl_4Fe_2N_2S_2$: C, 33.24; H, 6.97; N, 4.85. Found: C, 33.23; H, 6.95; N, 4.83.

The Ph_4As^+ salt was obtained as black crystals by an analogous procedure and in comparable yield starting from $(Ph_4As)_2[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]$. Anal. Calcd for $C_{48}H_{40}As_2Cl_4Fe_2S_2$: C, 53.17; H, 3.72; As, 13.82; Cl, 13.08; Fe, 10.30; S, 5.91. Found: C, 52.84; H, 3.53; As, 14.06; Cl, 12.96; Fe, 10.08; S, 6.04.

(b) $(Et_4N)_2[Fe_2S_2Br_4]$. The procedure used is the same as that for $(Et_4N)_2[Fe_2S_2Cl_4]$ except for substitution of benzoyl bromide in place of benzoyl chloride. Owing to the limited stability of $[Fe_2S_2Br_4]^{2-}$ in acetonitrile, the initial reaction producing a purple solution was allowed to proceed for 20 min only before isolating the crude product. Recrystallization of this material from warm (40 °C) acetonitrile/THF was completed within 4 h, affording pure black crystals (40–45%). Anal. Calcd for $C_{16}H_{40}Br_4Fe_2N_2S_2$: C, 25.42; H, 5.33; Br, 42.28;

N, 3.71. Found: C, 25.30; H, 5.33; Br, 41.78; N, 3.70.

(c) $(Et_4N)_2[Fe_2S_2I_4]$. A solution of 4.3 g (29 mmol) of sodium iodide in 30 mL of acetonitrile was added to a stirred solution of 2.0 g (3.5 mmol) of $(Et_4N)_2[Fe_2S_2Cl_4]$ in 50 mL of acetonitrile. The color of the solution changed immediately from purple-red to brown and a finely divided precipitate of sodium chloride appeared. After 20 min the solution was filtered and the filtrate evaporated to dryness in vacuo. The crystalline residue was washed with absolute ethanol (4 × 25 mL), and the remaining solid was collected by filtration and dried in vacuo for several hours. The black crystalline product (74%) was recrystallized by dissolution in a minimum volume of dry acetone at ~45 °C followed by filtration through a very fine frit and cooling of the filtrate to −78 °C. The black crystals (35%) were collected, washed with cold acetone, and dried in vacuo. An analytical sample was obtained by one additional recrystallization. Anal. Calcd for $C_{16}H_{40}Fe_2I_4N_2S_2$: C, 20.26; H, 4.27; I, 53.78; N, 2.97. Found: C, 20.48; H, 3.74, 4.07; I, 53.66; N, 2.77.

Halide Tetramer Salts. (a) $(R'_4N)_2[Fe_4S_4Cl_4]$. In a typical preparation 5.8 g (6.0 mmol) of $(Et_4N)_2[Fe_4S_4(S\text{-}t\text{-}Bu)_4]$ was slurried in 50 mL of acetonitrile. Benzoyl chloride (5.6 mL, 48 mmol) was added to the stirred slurry. The solid gradually dissolved and the solution developed a deep brown color with a purplish black cast. After 1 h reaction time ~100 mL of anhydrous diethyl ether was added, causing the product to separate as a black oil which soon crystallized. This material was collected by filtration, washed with anhydrous ether (2 × 50 mL), and dried in vacuo. Purification was effected by one recrystallization from acetonitrile/isopropyl alcohol initially at ambient temperature; the product was isolated from a solution cooled to −20 °C. This procedure initially yielded an oil which quickly formed black crystals. These were collected by filtration, washed with isopropyl alcohol (2 × 50 mL), and dried in vacuo at room temperature for several hours. The tendency of the product to separate initially as an oil in the recrystallization step can be minimized by the use of a saturated acetonitrile solution followed by slow addition of isopropyl alcohol and cooling. Three analytically pure salts of $[Fe_4S_4Cl_4]^{2-}$, isolated in 80–92% yield as black crystals, were obtained by this procedure. In multiple preparations Me_4N^+ and Et_4N^+ salts were consistently isolated in yields exceeding 80%. In addition to alkylthiolate tetramer dianions, salts of $[Fe_4S_4(SPh)_4]^{2-}$ also served as starting materials, in which case a larger PhCOCl:tetramer mol ratio (ca. 12:1) was employed.

$(n\text{-}Bu_4N)_2[Fe_4S_4Cl_4]$. Anal. Calcd for $C_{32}H_{72}Cl_4Fe_4N_2S_4$: C, 39.28; H, 7.42; Cl, 14.49; Fe, 22.83; N, 2.86; S, 13.11. Found: C, 39.18; H, 7.32; Cl, 14.47; Fe, 22.69; N, 2.94; S, 13.03.

$(Me_4N)_2[Fe_4S_4Cl_4]$. Anal. Calcd for $C_8H_{24}Cl_4Fe_4N_2S_4$: C, 14.97; H, 3.77; N, 4.37. Found: C, 15.07; H, 3.83; N, 4.34.

$(Et_4N)_2[Fe_4S_4Cl_4]$. Anal. Calcd for $C_{16}H_{40}Cl_4Fe_4N_2S_4$: C, 25.49; H, 5.35; N, 3.72. Found: C, 25.44; H, 5.38; N, 3.84.

(b) $(Et_4N)_2[Fe_4S_4Br_4]$. The preparation of this compound is the same as that for $[Fe_4S_4Cl_4]^{2-}$ salts except for the substitution of benzoyl bromide in place of benzoyl chloride. The initial reaction solution developed a reddish brown color as the reaction proceeded. Recrystallization was carried out quickly owing to the limited stability of $[Fe_4S_4Br_4]^{2-}$ in solution. After one recrystallization the product was obtained in pure form in yields ranging from 50 to 65%. Anal. Calcd for $C_{16}H_{40}Br_4Fe_4N_2S_4$: C, 20.62; H, 4.33; Br, 34.30; Fe 23.97; N, 3.01; S, 13.76. Found: C, 20.80; H, 4.25; Br, 34.37; Fe, 23.87; N, 3.13; S, 13.73.

(c) $(Et_4N)_2[Fe_4S_4I_4]$. To a solution of 2.3 g (3.0 mmol) of $(Et_4N)_2[Fe_4S_4Cl_4]$ in 100 mL of acetonitrile was added with stirring 3.6 g (24 mmol) of sodium iodide dissolved in 40 mL of acetonitrile. The color of the solution changed from purplish brown to yellow-brown. After 30 min the reaction mixture was filtered and an equal volume of isopropyl alcohol was added to the filtrate. Partial evaporation of the solvent under reduced pressure afforded fine black crystals, which were filtered off, washed with isopropyl alcohol, and dried in vacuo. This material was recrystallized from 75 mL of dry acetone (solution filtered through very fine frit) to which 150 mL of anhydrous ethyl ether was added. The product was collected, washed with ether, and dried in vacuo for several hours, affording black crystals in 75% yield. Anal. Calcd for $C_{16}H_{40}Fe_4I_4N_2S_4$: C, 17.15; H, 2.50; Fe, 19.95; I, 45.34; N, 3.60; S, 11.46. Found: C, 17.28; H, 2.41; Fe, 20.08; I, 45.19; N, 3.69; S, 11.31.

Thioesters. o-Xylyl-α,α'-dithiobenzoate. To a solution of 7.3 g (43 mmol) of o-xylene-α,α'-dithiol[6] in 50 mL of acetonitrile was added 10.2 mL (88 mmol) of benzoyl chloride, followed by slow addition
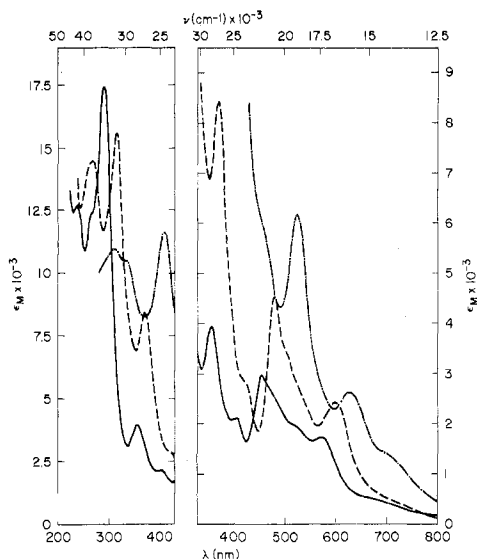
Figure 2. Electronic absorption spectra of the $[Fe_2S_2X_4]^{2-}$ series: X = Cl (—), Br (- - -), and I (–·–) in acetonitrile containing 0.1 M n-Bu$_4$NX.

of 7.5 mL of pyridine. Cooling of the reaction mixture afforded large transparent crystals (14.6 g, 90%). An analytical sample was obtained by recrystallization from acetonitrile: mp 83–85 °C; ^{1}H NMR (CDCl$_3$) δ 4.46 (s, 4, CH$_2$), 7.4 (m, 10, ring-H), 8.0 (m, 4, ring-H). Anal. Calcd for $C_{22}H_{18}O_2S_2$: C, 69.81; H, 4.79; S, 16.94. Found: C, 69.86; H, 4.83; S, 16.69. In the reaction between $(Et_4N)_2[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]$ and benzoyl chloride this compound was isolated in 76% yield from the reaction solution filtrate which remained after collection of the crude product.

Formation of a thioester by-product was verified in a reaction between $(Et_4N)_2[Fe_4S_4(SCH_2Ph)_4]$ and benzoyl chloride which performed in a manner similar to that utilizing the *tert*-butylthiolate tetramer salt. After initial separation of $(Et_4N)_2[Fe_4S_4Cl_4]$ (57% yield after recrystallization), PhCH$_2$SCOPh was isolated from the filtrate in 69% yield: mp 35.5–36.5 °C (four recrystallizations from acetonitrile), lit.[22] 39.5 °C; ^{1}H NMR (CDCl$_3$) δ 4.30 (s, 2, CH$_2$), 7.4 (m, 8, ring-H), 8.0 (m, 2, ring-H).

Reactions of $[Fe_4S_4Cl_4]^{2-}$ with Thiols. Reactions of $[Fe_4S_4Cl_4]^{2-}$ with thiols and base were monitored spectrophotometrically and the reaction products identified by their characteristic visible spectra. To ca. 2 mM solutions of $(Et_4N)_2[Fe_4S_4Cl_4]$ in acetonitrile was added 4.0 equiv of *tert*-butylthiol or benzenethiol and 5.2 equiv of Me$_4$NOH·5H$_2$O. The spectrum[23] of $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$ (λ_{max} 413 nm) or $[Fe_4S_4(SPh)_4]^{2-}$ (λ_{max} 445 nm) developed immediately. From known extinction coefficients the formation of these two tetramers was calculated to be greater than 95%. In an experiment on a preparative scale (Me$_4$N)$_2[Fe_4S_4Cl_4]$ (1.02 g, 1.60 mmol) was dissolved in 100 mL of acetonitrile. Addition of 0.79 mL (7.0 mmol) of *tert*-butylthiol to the purplish brown solution produced no visible reaction. Addition of 1.28 g (7.10 mmol) of Me$_4$NOH·5H$_2$O in 25 mL of methanol resulted in an immediate color change to red-brown. Partial reduction of the solution volume followed by addition of isopropyl alcohol resulted in the separation of a red-brown crystalline solid, which was recrystallized from warm acetonitrile affording 1.17 g (85%) of red-black crystals. The absorption spectrum[23] and elemental analysis demonstrated that this material is identical with (Me$_4$N)$_2[Fe_4S_4(S\text{-}t\text{-}Bu)_4]$, previously prepared by direct tetramer synthesis.[24]

Reaction of $[Fe_2S_2Cl_4]^{2-}$ with Benzenethiol. Addition of 4.4 equiv of benzenethiol to a solution of 23 mg of $(Et_4N)_2[Fe_2S_2Cl_4]$ in 15 mL of acetonitrile produced no visible reaction. Addition of 4.7 equiv of Me$_4$NOH·5H$_2$O in a minimum volume of methanol resulted in an immediate color change to a more intense purple. The spectrum of this solution showed the presence of $[Fe_2S_2(SPh)_4]^{2-\,16}$ with less than 5% contamination by $[Fe_4S_4(SPh)_4]^{2-}$. Concentration of the solution provided a black crystalline solid, the absorbance spectrum of which was the same as previously reported for $[Fe_2S_2(SPh)_4]^{2-}$.[6]

Oxidation of $[Fe_4S_4Cl_4]^{2-}$ to $[Fe_2S_2Cl_4]^{2-}$. (Et$_4$N)$_2[Fe_4S_4Cl_4]$ (60.8 mg, 80.6 μmol) and 0.110 g (670 μmol) of anhydrous tetraethylammonium chloride were dissolved in 15 mL of acetonitrile. Fer-

ricinium tetrafluoroborate[25] (46.3 mg, 170 μmol) in 3 mL of acetonitrile was added dropwise to the stirred solution, producing a gradual color change from purplish brown to brownish red. Spectral examination of this solution, together with the spectra of $[Fe_2S_2Cl_4]^{2-}$ (Figure 2) and $[Fe_4S_4Cl_4]^{2-}$ (Figure 3) measured separately, indicated substantial conversion to the dimer dianion. From the intensity of the 1080-nm band of $[Fe_4S_4Cl_4]^{2-}$ the oxidation reaction was found to be ca. 80% complete.

Stability of $[Fe_2S_2X_4]^{2-}$ and $[Fe_4S_4X_4]^{2-}$ in Solution. Halide dimers and tetramers are immediately decomposed to insoluble black solids upon contact with water. In aprotic media the lability of these complexes necessitated a search for solvent systems suitable for measurement of solution properties of undissociated species. Stabilities were examined by recording visible spectra of solutions at frequent intervals in the presence or absence of added halide salts. Because stability characteristics are important in the present work and in any subsequent utilization of these complexes, certain observations are recorded here in terms of the following categories: stable (+), ≤1% spectral change after 2 h; somewhat stable (+–), noticeable but <5% absorbance decrease during 2 h; unstable (–), large spectral changes or visual decomposition during 2 h or less. Observations refer to ca. 1 mM solutions; halide salt concentrations larger than those given did not produce appreciable spectral changes. $[Fe_2S_2Cl_4]^{2-}$: (+) 0.1 M n-Bu$_4$NCl/MeCN; (+–) MeCN, acetone. $[Fe_2S_2Br_4]^{2-}$: (+) 0.1 M n-Bu$_4$NBr/(MeCN or acetone); (+–) acetone; (–) MeCN. $[Fe_2S_2I_4]^{2-}$: (+) 0.1 M n-Bu$_4$NI/(MeCN or acetone); (–) acetone, MeCN. $[Fe_4S_4Cl_4]^{2-}$: (+) DMF; (+–) 0.1 M n-Bu$_4$NCl/(MeCN, DMF, or acetone), acetone; (–), MeCN, Me$_2$SO. $[Fe_4S_4Br_4]^{2-}$: (+) 0.1 M n-Bu$_4$NBr/(MeCN or acetone), acetone; (+–) MeCN; (–) DMF, Me$_2$SO. $[Fe_4S_4I_4]^{2-}$: (+) 0.1 M n-Bu$_4$NI/acetone, acetone; (+–) 0.1 M n-Bu$_4$NI/MeCN; (–) MeCN, DMF, Me$_2$SO. It should be noted that the unfavorable stability behavior of complexes in acetonitrile did not prevent use of this solvent as a reaction or recrystallization medium owing to shorter times and/or lower temperatures employed compared to those under which stability observations were made. Also, degradation products appeared to remain in solution as evidenced by the somewhat different color of the mother liquor immediately after crystallization of the desired compound was completed.

Physical Measurements. Magnetic measurements (Table I) were performed with a Superconducting Technology, Inc., SQUID-type susceptometer at 4.2–338 K; the instrument was calibrated with a constant-current coil, and measurements were made at 2.0 and 5.9 kG. Electronic absorption spectra were recorded on a Cary Model 14 or 17 spectrophotometer; solvents (Table II) were selected to maximize stabilities of complexes while minimizing solvent absorbance in the ultraviolet region. Cyclic voltammetric measurements were performed with the equipment described elsewhere[4b] using a platinum disk (Beckman 39273) working electrode, SCE reference electrode, and 0.1 M n-Bu$_4$NX supporting electrode with X$^-$ common to the halide species measured. The effect of 0.1 M X$^-$ in shifting the apparent potentials of $[Fe_2S_2X_4]^{2-}$ and $[Fe_4S_4X_4]^{2-}$, and of the standard

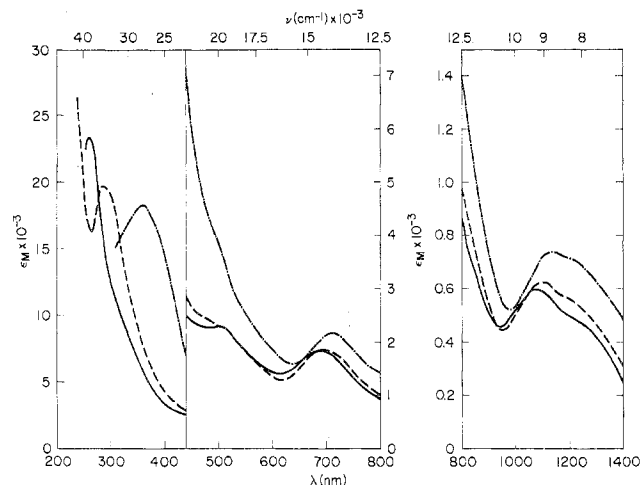**Figure 3.** Electronic absorption spectra of the $[Fe_4S_4X_4]^{2-}$ series: X = Cl in DMF (—); X = Br in acetonitrile containing 0.1 M n-Bu$_4$NBr (- - -); X = I in acetone (–·–).

Table I. Selected Magnetic Susceptibility Data for Chloride Dimer and Tetramer Dianions

T, K	(Et$_4$N)$_2$[Fe$_4$S$_4$Cl$_4$] $10^5\chi_{cor}^{t\,a}$	μ_t,^{c} μ_B	(Et$_4$N)$_2$[Fe$_2$S$_2$Cl$_4$] $10^5\chi_{cor}^{d\,b}$	μ_d,^{c} μ_B
50.2	49.9^d	0.45	26.1^e	0.32
75.2	55.8	0.58	28.3	0.41
100.2	79.4	0.80	43.0	0.59
120.3	103	0.99	59.0	0.75
140.3	127	1.19	77.6	0.93
160.4	148	1.38	94.6	1.10
180.4	165	1.54	110	1.26
200.4	178	1.69	124	1.41
220.4	190	1.83	134	1.54
240.3	198	1.95	143	1.66
259.9	206	2.07	149	1.76
279.5	213	2.18	157	1.87
299.1	219	2.29	161	1.96
318.7	224	2.39	166	2.06
338.1	228	2.48	171	2.15

^{a} Susceptibility per 4 Fe atoms of tetrameric (t) unit. ^{b} Susceptibility per 2 Fe atoms of dimeric (d) unit. ^{c} $\mu = 2.828(\chi_{cor}T)^{1/2}$. ^{d} Diamagnetic correction -477×10^{-6}. ^{e} Diamagnetic correction -398×10^{-6}.

couple [Fe$_4$S$_4$(SPh)$_4$]$^{2-,3-}$[4b,23] was eliminated by use of 0.1 M (n-Pr$_4$N)(PF$_6$) in the reference compartment.

Results and Discussion

Synthesis of [Fe$_2$S$_2$X$_4$]$^{2-}$ and [Fe$_4$S$_4$X$_4$]$^{2-}$. The synthetic scheme is set out in Figure 1. The precursor of halide dimers is [Fe$_2$S$_2$(S$_2$-o-xyl)$_2$]$^{2-}$[6] (1) which in acetonitrile solution at ambient temperature reacts smoothly with benzoyl chloride and benzoyl bromide, affording [Fe$_2$S$_2$Cl$_4$]$^{2-}$ (2) and [Fe$_2$S$_2$Br$_4$]$^{2-}$ (3), respectively, as their Et$_4$N$^+$ salts in 35–65% yield after purification by recrystallization. Similarly, [Fe$_4$S$_4$(SR)$_4$]$^{2-}$ (6, R = t-Bu, CH$_2$Ph, Ph) gave salts of [Fe$_4$S$_4$Cl$_4$]$^{2-}$ (7) and [Fe$_4$S$_4$Br$_4$]$^{2-}$ (8) in 50–90% yield after purification. Metathesis of 2 and 7 with sodium iodide in acetonitrile produced [Fe$_2$S$_2$I$_4$]$^{2-}$ (4) and [Fe$_4$S$_4$I$_4$]$^{2-}$ (9), respectively, as their Et$_4$N$^+$ salts. Thus the combination of benzoyl halide and metathetical reactions affords the new series of strictly inorganic anions [Fe$_2$S$_2$X$_4$]$^{2-}$ and [Fe$_4$S$_4$X$_4$]$^{2-}$, X = Cl, Br, or I. Fluoride complexes were not obtained. The systems 1/PhCOF, 6 (R = CH$_2$Ph)/PhCOF, and 7/Et$_4$NF in aprotic solvents afforded either a black intractable solid or no encouraging reaction.

Formation and isolation of [Fe$_2$S$_2$I$_4$]$^{2-}$ were not entirely expected owing to the usual redox instability of Fe(III)–iodide complexes. Previous examples of coordination compounds with iodide directly bonded to formal Fe(III) include Fe(S$_2$CNEt$_2$)$_2$I[26] and five-coordinate macrocyclic[27] and

porphyrin[28] complexes. Ferricinium[29a] and Et$_4$N$^+$[29b] salts of [FeI$_4$]$^-$ have been isolated but in solution the anion has a half-life of only several minutes.[29c] [Fe$_2$S$_2$I$_4$]$^{2-}$ appears to be the sole example of a complex containing more than one iodide bound to Fe(III) which is sufficiently stable for both isolation and solution studies (in the presence of excess iodide).

The prior observation of thioester (10) formation[20] in reactions of 6 with benzoyl chloride was confirmed. Benzyl thiobenzoate[22] was isolated in 69% yield from reaction of [Fe$_4$S$_4$(SCH$_2$Ph)$_4$]$^{2-}$ and benzoyl chloride. Similarly, the previously unreported diester o-xylyl-α,α'-dithiobenzoate (5) was obtained in 76% yield from reaction of 1 and benzoyl chloride.

Nucleophilic reactivity of coordinated thiolate enjoys substantial precedent, but nearly always in the form of S-alkylation. Of the numerous prior examples[30] of this type of reactivity, several based on bis(2-dimethylaminoethane-thiolato)nickel(II) (11) are pertinent. Reaction 3 affords the
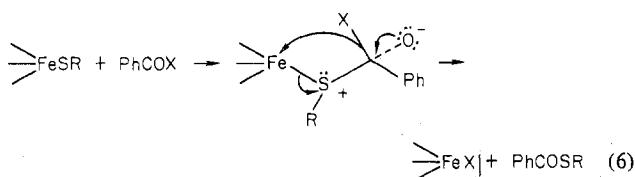

$$(3)$$

$$(4)$$

$$(5)$$
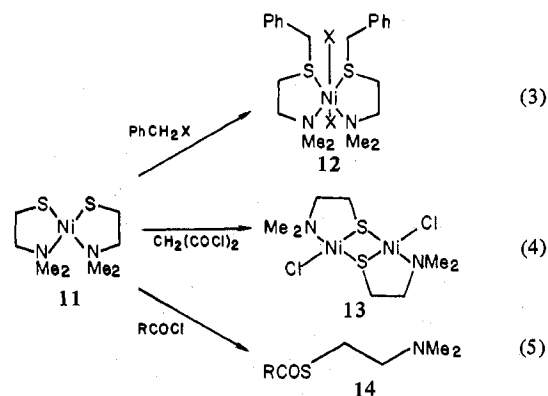
bis(aminothioether) complex 12 in which displaced halide has been coordinatively captured by the metal.[31] Other than those reported here reactions 4 and 5 are the only cases[32] of bound thiolate–acid halide interactions known to us. In the former reaction thioester formation and displacement from the coordination sphere are indicated by the product complex 13; the Ni(II) complex intermediate in the formation of aminothioesters 14 in the latter reaction were not identified. Reactions 3–5, among others, foreshadow those in Figure 1 which, however, provide clean removal of the initial thiolate ligands with concomitant capture of halide. An elementary description of the formation of halide complexes and thioesters is provided by reaction 6, which is analogous to the mechanistic scheme for reaction 2.[19] The only other example of related reactivity of the clusters 6 is formation of thioformimidates from isocyanides and thiols in the presence of [Fe$_4$S$_4$(SR)$_4$]$^{2-,4-}$,

Table II. Electronic Spectra of the Series [Fe$_2$S$_2$X$_4$]$^{2-}$ and [Fe$_4$S$_4$X$_4$]$^{2-}$

Series	λ_{max}, nm (ϵ_M^a) X = Cl	X = Br	X = I
[Fe$_2$S$_2$X$_4$]$^{2-\,b}$	238 (12200)	~260 (sh, 14400)	290 (sh, 10300)
	~265 (sh, 12000)	268 (14600)	311 (10900)
	292 (17200)	315 (15700)	334 (10500)
	357 (3880)	372 (8310)	409 (11600)
	405 (2100)	~420 (sh, 2890)	~460 (sh, 5850)
	455 (3000)	480 (4550)	524 (6130)
	~525 (sh, 1930)	~505 (sh, 3420)	
	571 (1720)	598 (2450)	626 (2690)
	~680 (sh, 490)	~750 (sh, 450)	~700 (sh, 1470)
[Fe$_4$S$_4$X$_4$]$^{2-}$	262 (23100)^c	288 (19000)^b	360 (17900)^d
	~275 (sh, 21000)	~300 (sh, 18600)	~390 (16000)
	~505 (sh, 2330)	~470 (sh, 2490)	~490 (sh, 4070)
	690 (1800)	698 (1850)	710 (2190)
	1080 (580)	1110 (630)	1130 (750)
	~1200 (sh, 490)	~1190 (sh, 570)	~1220 (sh, 710)

^{a} M^{-1} cm^{-1}. ^{b} Solvent medium MeCN, 0.1 M n-Bu$_4$NX. ^{c} Solvent medium DMF. ^{d} Solvent medium acetone.

$$\text{\raisebox{0pt}{$\diagdown$}}\text{FeSR + PhCOX} \longrightarrow \text{\raisebox{0pt}{$\diagdown$}}\text{Fe} \cdots \longrightarrow$$

$$\text{\raisebox{0pt}{$\diagdown$}}\text{FeX} \downarrow + \text{ PhCOSR} \quad (6)$$

the course of which is proposed to involve nucleophilic attack on coordinated isocyanide by a thiolate ligand.[20b] An alternate synthetic route to $[Fe_2S_2X_4]^{2-}$ and $[Fe_4S_4X_4]^{2-}$ by direct displacement of thiolate ligands is suggested by reactions of $[Fe_4S_4(SCH_2CH_2CO_2)_4]^{6-}$ in aqueous solution, from which the preliminary kinetic order $Cl^- \sim Br^- < OH^- < CN^-$ for thiolate displacement by other nucleophiles has been reported.[33] Product species were not isolated in that study.

Structures. The physical properties described in the following reactions do not suffice to prove the structures of the reaction products in Figure 1. Selecting chloride complexes as representative, x-ray crystallographic studies[21] have been performed on the Et_4N^+ salts of $[Fe_2S_2Cl_4]^{2-}$ and $[Fe_4S_4Cl_4]^{2-}$ and show that reactions of **1** and **6** with benzoyl chloride proceed with retention of core structure. Anion structures are summarized in Figure 4. Upon comparison with precursor **1**[6] and **6**[16] structures these results show that core dimensions are nearly unchanged upon RS^-/Cl^- ligand substitution. In particular the idealized D_{2d} Fe_4S_4 core symmetry is retained, indicating that $[Fe_4S_4Cl_4]^{2-}$, as **6**, is an electronically delocalized rather than a trapped valence (2Fe(II) + 2Fe(III)) species.

Reactions of $[Fe_2S_2Cl_4]^{2-}$ and $[Fe_4S_4Cl_4]^{2-}$. As already noted these complexes can be converted to the corresponding iodide species **4** and **9** with excess sodium iodide in acetonitrile. Other experiments conducted on a spectrophotometric scale in acetonitrile solution have demonstrated the conversions $[Fe_4S_4Cl_4]^{2-}/[Fe_4S_4(SR)_4]^{2-}$ (R = Ph, t-Bu) and $[Fe_2S_2Cl_4]^{2-}/[Fe_2S_2(SPh)_4]^{2-}$ effected with thiol and Me_4NOH, and $[Fe_4S_4Cl_4]^{2-}/[Fe_2S_2Cl_4]^{2-}$ using ferricinium ion as the oxidant. Complete Cl^-/RS^- substitution reactions are not of synthetic use owing to the ease of preparation of $[Fe_2S_2(SR)_4]^{2-}$[6] and $[Fe_4S_4(SR)_4]^{2-}$[16] by other means but may be of value in obtaining partially substituted species. Solutions containing $[Fe_4S_4Cl_4]^{2-}$ and cyanide or thiocyanate ions afforded no isolable substituted tetrameric complexes.

Magnetic Properties. Susceptibilities of $(Et_4N)_2[Fe_2S_2Cl_4]$ and $(Et_4N)_2[Fe_4S_4Cl_4]$ were measured from 4.2 to 338 K using a sensitive SQUID-type susceptometer. As for the corresponding thiolate compounds,[17,34,35] these salts showed substantial paramagnetic impurities at low temperatures evidenced by minima in susceptibility curves over the 4.2–100 K range. Impurity corrections were made by fitting the data to an equation of the form $\chi_{impurity} = C/T$ at $T \leq T_{min}$ and taking the intercepts of such plots as apparent temperature-independent paramagnetism. Impurity and the usual diamagnetic corrections were applied at higher temperatures, affording the susceptibilities per dimeric (χ_{cor}^d) and tetrameric (χ_{cor}^t) unit given in Table I. Temperature dependencies of susceptibility are plotted in Figure 5, where the positive temperature coefficients are indicative of intracluster antiferromagnetic behavior as previously observed for $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$,[34] $[Fe_4S_4(SR)_4]^{2-}$,[35] and proteins in equivalent oxidation levels.[1]

Similarities in magnetic properties of chloride and thiolate dimer and tetramer dianions are evident from comparison of the data in Table I with the following μ_t and μ_d values: $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$,[34] 0.16 (55 K), 1.51 (204 K), 2.01 (287 K); $[Fe_4S_4(SPh)_4]^{2-}$,[17] 0.42 (50 K), 1.56 (200 K), 2.17 (299 K), 2.38 (338 K). Using the $\chi^d(T)$ equation[34] developed under the usual Hamiltonian $\mathcal{H} = -2J\tilde{S}_1 \cdot \tilde{S}_2$[36] for spin coupling of two high-spin d^5 ions, the data for $[Fe_2S_2Cl_4]^{2-}$ are best fit with $-J = 158$ cm^{-1} (Figure 5). The lack of agreement between
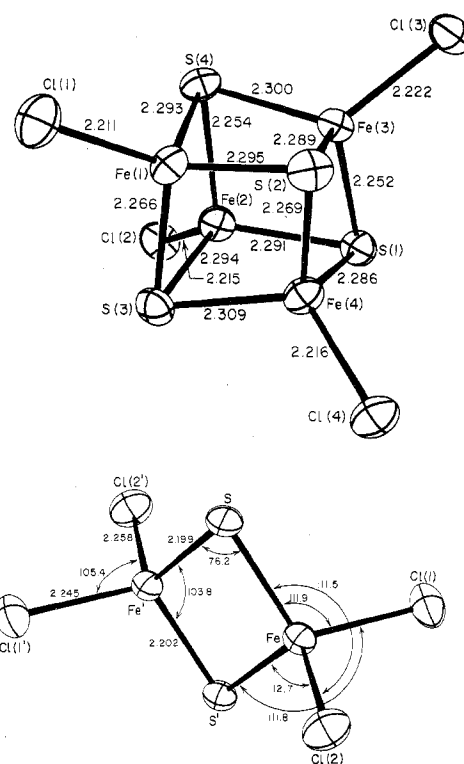

Figure 4. Essential structural features of $[Fe_4S_4Cl_4]^{2-}$ and $[Fe_2S_2Cl_4]^{2-}$ as their Et_4N^+ salts.[21]
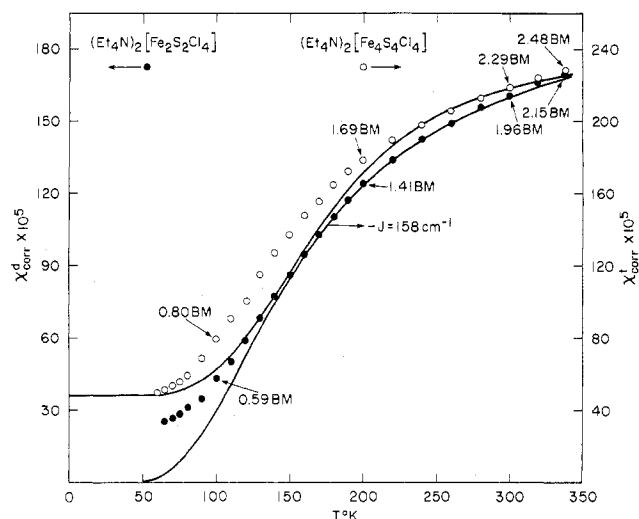
Figure 5. Temperature dependence of the susceptibility of $(Et_4N)_2[Fe_2S_2Cl_4]$ (●) and $(Et_4N)_2[Fe_4S_4Cl_4]$ (○). Arrows refer to susceptibility axes. The lower solid line is a theoretical fit to the dimer data with $-J = 158$ cm^{-1}. The upper line is an attempted fit to the tetramer data with $-J = 220$ cm^{-1}.

theory and experiment at $T < 140$ K presumably arises from inadequate impurity correction. A similar treatment for $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$ but with a more satisfactory impurity correction derived from measurements at higher fields yields $-J = 148 \pm 8$ cm^{-1}.[34] Thus comparison of magnetic properties of the pairs $[Fe_2S_2Cl_4]^{2-}/[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$ and $[Fe_4S_4Cl_4]^{2-}/[Fe_4S_4(SR)_4]^{2-}$[37] indicate that antiferromagnetic interactions are nearly independent of the terminal ligands. Such behavior is entirely consistent with the close structural similarity of Fe_2S_2 and Fe_4S_4 cores in chloride and thiolate dianions.

Voltammetry. Previous electrochemical studies[4b,6,23] have established the electron-transfer series $[Fe_2S_2(SR)_4]^{2-,3-,4-}$ and
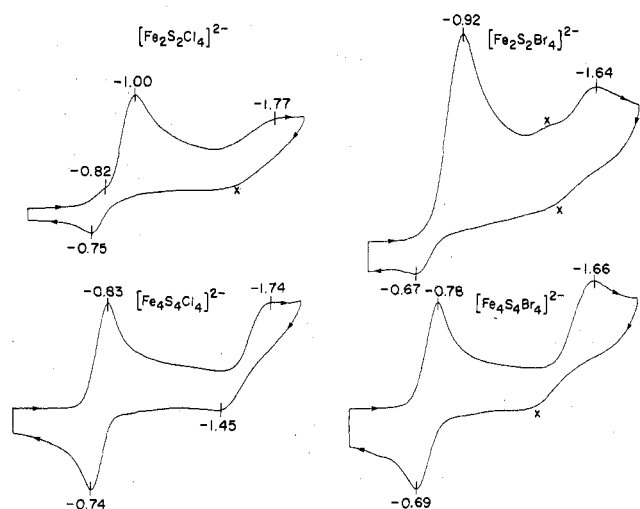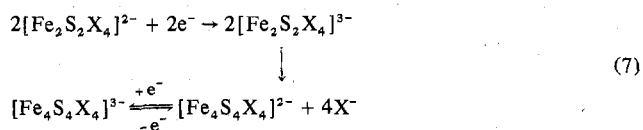
Figure 6. Cyclic voltammograms of $[Fe_2S_2X_4]^{2-}$ and $[Fe_4S_4X_4]^{2-}$ (X = Cl, Br) recorded at 100 mV/s in acetonitrile solution containing 0.1 M n-Bu$_4$NX. Potentials are vs. SCE; ×, unidentified features.

$[Fe_4S_4(SR)_4]^{2-,3-,4-}$. Cyclic voltammograms for 2.0 mM acetonitrile solutions of $[Fe_2S_2X_4]^{2-}$ and $[Fe_4S_4X_4]^{2-}$ (X = Cl, Br) over the −0.5 to −2.0 V interval vs. SCE are set out in Figure 6. The latter two species exhibit nearly reversible 2−/3− couples for which $E_{1/2} \simeq -0.79$ V (Cl) and −0.74 V (Br). The 3−/4− reductions, identified as the second cathodic features, are grossly irreversible as is the first reduction of $[Fe_4S_4I_4]^{2-}$ ($E_p^c = -0.73$ V). Further reduction of this species is ill-defined. In the dimer series the first reductions of all three complexes are irreversible with $E_p^c = -1.00$ (Cl), −0.92 (Br), and ~−0.69 V (I). No well-developed anodic processes at potentials more positive than −0.5 V were observed in either series.

Examination of the behavior of halide and thiolate tetramers and dimers under comparable cyclic voltammetric conditions reveals significant similarities and differences reflected in stabilities of reduced species and potentials of corresponding couples. $[Fe_4S_4X_4]^{2-}$ (X = Cl, Br) and $[Fe_4S_4(SR)_4]^{2-\,4b,23}$ exhibit essentially reversible 2−/3− couples but the latter far more closely approach reversible 3−/4− behavior.[4b] Reduction of $[Fe_2S_2X_4]^{2-}$ (X = Cl, Br) gives an initial cathodic peak associated with the 2−/3− couple but the second cathodic peaks (−1.77, −1.64 V) and the features (−0.75, −0.67 V) observed in the reverse scan are obviously associated with tetramer redox processes. This behavior is consistent with reaction scheme 7, which for $[Fe_2S_2Cl_4]^{2-}$ could not be suppressed at chloride

$$2[Fe_2S_2X_4]^{2-} + 2e^- \rightarrow 2[Fe_2S_2X_4]^{3-}$$
$$\downarrow$$
$$[Fe_4S_4X_4]^{3-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Fe_4S_4X_4]^{2-} + 4X^- \qquad (7)$$

concentrations up to 0.8 M. An analogous scheme holds for the reduction of $[Fe_2S_2(SR)_4]^{2-}$ except that reduced dimers are sufficiently stable that the 3−/4− process is observable together with tetramer 3−/4− and 2−/3− couples.[4b] Collective spectral, electrochemical, and chemical observations clearly demonstrate that in corresponding oxidation levels all halide dimers and tetramers are substantially more labile than are analogous thiolate complexes derived from either aliphatic or aromatic thiols.

Half-wave potentials of the couples $[Fe_4S_4(SR)_4]^{2-,3-\,6,23}$ and $[Fe_2S_2(SR)_4]^{2-,3-\,6}$ measured in aprotic media exhibit the following regular behavior: (i) values are increasingly negative in the order R = alkyl > C_6H_4X and dimer > tetramer (R constant); (ii) potentials are more negative than −1.0 V except

when X is electron attracting (e.g., NO_2, $^+NMe_3$); (iii) potentials tend to vary linearly with R substituent constants σ^* or σ_p such that the more electron-releasing substituents effect the more negative potentials. From half-wave or peak potentials for the two halide series the dimer > tetramer order in (i) is followed. In contrast to (ii) all halide potentials are ≤ -1.0 V.[38] Property (iii) cannot be directly related to halide dimers and tetramers, whose potentials shift to more negative values in the order I < Br < Cl,[39] a not uncommon sequence in the reduction of organic compounds.[42] The present and previous data suffice to show that effective electron affinities of Fe_2S_2 and Fe_4S_4 core units, as measured by solution potentials, are extremely sensitive to the nature of terminal ligands. A range of 0.7–0.8 V exists for 2−/3− couples of dimers and tetramers when halide and thiolate substituents are included.

Electronic Absorption Spectra. Solution spectra of the $[Fe_2S_2X_4]^{2-}$ and $[Fe_4S_4X_4]^{2-}$ series are shown in Figures 2 and 3, respectively. Based on band shapes and band maxima the spectra within each series appear to consist of a series of corresponding features which are progressively displaced to lower energy in the order X = Cl < Br < I. Apparent band correspondences are set out in the rows of Table II. The complexity of the chromophores precludes any definite band assignments, which must await a theoretical model. The spectra are presented primarily as characterization data; however, certain observations are noted. (i) Halide-dependent band energy shifts and intensities at wavelengths below ca. 600–700 nm in the dimer and tetramer series are consistent with X → core charge-transfer excitations in which acceptor core orbitals may be mainly Fe 3d-like in character. (ii) Energies of corresponding bands in (i) follow the order of Jørgensen's optical electronegativities χ_{opt}, Cl (3.0) > Br (2.8) > I (2.5),[43] but no set of such bands adheres to the relation ΔE_{CT} (cm^{-1}) = 30 000 $[\chi_{opt}(X) - \chi_{opt}(X')]$ for the energy difference of the first allowed charge-transfer band for complexes with the same metal ion (or core). (iii) Based on band shapes and intensities the prominent charge-transfer band of $[Fe_4S_4(SR)_4]^{2-}$ (λ_{max} 415–460 nm, ϵ 16 000–18 000)[23] most probably correlates with the 260–360-nm features in the halide tetramer series, but is far more red shifted than would be predicted from $\chi_{opt}(S) \sim 2.5$–2.8.[44,45] (iv) Striking coincidences in band energies are observed between $[Fe_2S_2X_4]^{2-}$ and $[FeX_4]^{-\,29c,46}$ spectra at energies above ca. 2.7, 2.1, and 1.4 μm^{-1} for X = Cl, Br, and I, respectively. Results for $[Fe_2S_2Cl_4]^{2-}$ (2.80, 3.42, 3.77, 4.20 μm^{-1}) and $[FeCl_4]^{-\,46}$ (2.75, 3.18, 3.68, 4.12 μm^{-1}) are illustrative. Features of $[FeX_4]^-$ spectra in the indicated ranges are unquestionably X → Fe charge-transfer bands;[46,47] ligand field bands are spin forbidden and have been located only below 2.0–2.2 μm^{-1}.[48] Charge-transfer band correspondences between $[Fe_2S_2X_4]^{2-}$ and $[FeX_4]^-$ pose a dilemma in spectral assignments. If as in $[FeX_4]^-$ spectra the above energies are lower limits for X → core charge-transfer absorptions in the $[Fe_2S_2X_4]^{2-}$ series, the seemingly convincing relationship of spectral features of the series members (Figure 2) is more apparent than real. We doubt that this is the case and conclude that interelectronic repulsion and ligand field splittings in the mononuclear and binuclear species are sufficiently different that the former are not fully reliable spectral guides to the latter. In the $[Fe_2S_2X_4]^{2-}$ series energy ranges for X → core and internal core transitions partially overlap such that transitions of either type cannot be reliably assigned at present.

Registry No. (Et$_4$N)$_2$[Fe$_2$S$_2$(S$_2$-o-xyl)$_2$], 56083-11-5; (Ph$_4$As)$_2$-[Fe$_2$S$_2$(S$_2$-o-xyl)$_2$], 58501-17-0; (Et$_4$N)$_2$[Fe$_2$S$_2$Br$_4$], 65045-61-6;

$(Et_4N)_2[Fe_2S_2I_4]$, 65045-63-8; $(Et_4N)_2[Fe_4S_4(S\text{-}t\text{-}Bu)_4]$, 62873-87-4; $(n\text{-}Bu_4N)_2[Fe_4S_4Cl_4]$, 65103-98-2; $(Me_4N)_2[Fe_4S_4Cl_4]$, 65103-99-3; $(Et_4N)_2[Fe_4S_4Cl_4]$, 62758-02-5; $(Et_4N)_2[Fe_4S_4Br_4]$, 65208-04-0; $(Et_4N)_2[Fe_4S_4I_4]$, 65208-05-1; **5**, 65045-40-1; *o*-xylene-α,α'-dithiol, 41383-84-0; PhCOCl, 98-88-4; $(Me_4N)_2[Fe_4S_4(S\text{-}t\text{-}Bu)_4]$, 52678-92-9; $[Fe_4S_{s4}(SPh)_4]^{2-}$, 52325-39-0; $[Fe_2S_2(SPh)_4]^{2-}$, 55939-69-0; $(Et_4N)_2[Fe_2S_2Cl_4]$, 62682-81-9; $(Ph_4As)_2[Fe_2S_2Cl_4]$, 65045-64-9.

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(2) Symbols and abbreviations: A, bridging ligand; L, terminal ligand; S₂-*o*-xyl, *o*-xylyl-α,α'-dithiolate; tfd, $(CF_3)_2C_2S_2$.
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(38) The relatively low $[Fe_4S_4X_4]^{2-,3-}$ potentials suggested that the trianions should be accessible by chemical reduction and less oxidatively unstable than $[Fe_4S_4(SR)_4]^{3-}$. However, the reductive method which affords thiolate trianions in good yield[4] when applied to $[Fe_4S_4Cl_4]^{2-}$ gave only a black intractable solid.
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Contribution from the Department of Chemistry,
The University of Mississippi, University, Mississippi 38677

Group 5 Boranes. 3. Transition-Metal Complexes of Arsaboranes[1,2]

J. L. LITTLE* and S. S. PAO

In aqueous sodium hydroxide, cobalt chloride and nickel chloride react with $B_{10}H_{12}As^-$ to give $Co(B_{10}H_{10}As)_2^{3-}$ and $Ni(B_{10}H_{10}As)_2^{2-}$, respectively. Reacting $B_{10}H_{12}AsCH_3$, C_5H_6, $CoCl_2$, and excess KOH in anhydrous ethyl alcohol gives $(C_5H_5)Co(B_{10}H_{10}As)^-$. The piperidinium salt of $B_9H_{10}As_2^-$ treated in aqueous sodium hydroxide with cobalt chloride gives $Co(B_9H_9As_2)_2^-$, while $(C_5H_5)Co(B_9H_9As_2)$ is produced by reacting the piperidinium salt of $B_9H_{10}As_2^-$ with $CoCl_2$, C_5H_6, and triethylamine in THF. Alternatively, $(C_5H_5)Co(B_9H_9As_2)$ may be produced by reacting 1,2-$B_{10}H_{10}As_2$, C_5H_6, and $CoCl_2$ in piperidine.

Transition-metal complexes of 11-particle icosahedral fragments containing one[3-5] or two carbon atoms,[6] one sulfur,[7] selenium,[8] tellurium,[8] or phosphorus atom,[2] and both C and P[9] or C and As[10] are known.

We now report complexes of this cage fragment containing one or two arsenic atoms. Preparation of the ligands themselves has already been reported.[11]

Experimental Section

Preparations of III and V were carried out in a nitrogen atmosphere. Salts of $B_{10}H_{12}As^-$ and $B_9H_{10}As_2^-$ plus 1,2-$B_{10}H_{10}As_2$ and $B_{10}H_{12}$-$AsCH_3$ were prepared according to literature methods.[11] Hydrous