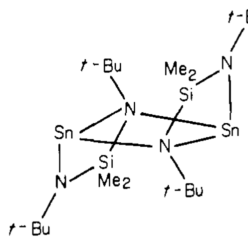
of comment. The terminal Sn–N bond length of 2.067 (4) Å is slightly shorter than known Sn(II)–N bond lengths, which average 2.09 Å.[12] This may be due to reduced crowding with the smaller NMe_2 groups. Another reason might be that the known Sn(II)–N bond lengths[3,7,12] involve d-acceptor silyl groups at nitrogen that may competitively reduce any potential Sn(II)–N d–p π-interaction with the p-orbital on nitrogen. The bridging Sn–N(2) bond distance, 2.266 (5) Å is, as expected, significantly longer than the terminal bond length. However, the equality of all the Sn–N lengths within the Sn_2N_2 core in **1** is unique. The core distances in the cyclic $[(Sn\overline{N(t\text{-Bu})SiMe_2N}(t\text{-Bu}))_2]$ (**5**)[7] have the values 2.244 (7)



5

and 2.389 (7) Å, with the shorter distances belonging to the SnN_2Si ring unit. The longer Sn–N values bridging the two monomeric units may be the result of increased steric crowding upon dimerization and the lack of flexibility within the SnN_2Si ring, which shows only very slight changes in geometry upon dimerization. The weaker nature of the association of $[(Sn\overline{N(t\text{-Bu})SiMe_2N}(t\text{-Bu}))_2]$ is borne out by its monomeric formulation in hydrocarbon solution while **1** remains a dimer. It would be of interest, for comparison, to have structural data on $[(Sn\overline{N(i\text{-Pr})SiMe_2N}(i\text{-Pr}))_2]_2$, which also remains dimeric in solution.

It has been noted in the descriptive section that the Sn–N(1)–C(2) angle on the more crowded (nearest the Sn_2N_2) core) side of the terminal amido groups is much ($\sim$ 20°) larger than the less crowded side, Sn–N(1)–C(1). We feel that this effect is steric in origin, since the interatomic distances between the hydrogens on C(2) and the hydrogens on C(3) and C(4A) are quite short (2.16–2.36 Å). These short contacts may be sufficient to cause considerable widening of the Sn–N(1)–C(2) angle. A further aspect of the structure concerns the angles at each tin, which total 280.4°. This indicates that both tin atoms possess a stereochemically active lone pair. It should be possible to isolate compounds in which both metals behave as donor atoms related to the monodentate stannylenes already known.[13]

Finally it can be seen (Table III) that the nitrogen–carbon distances in the bridging amido groups are all longer than those in the terminal positions. This is more than likely due to the different coordination numbers and hybridization at each nitrogen atom in which the greater s-character in the terminal N(1)–C(1) bond is reflected in the shorter N(1)–C(1) bond length.

It is unfortunate that crystals of the lead analogue proved unsuitable for data collection. Structural data on low-coordinate lead compounds are practically nonexistent.[3,5b] The only structurally characterized (in the solid phase) 2-coordinate lead compound is $Pb[N(SiMe_3)_2]_2$.[3] ^1H NMR shows $Pb(NMe_2)_2$ to have a broad single peak at δ 2.9 in C_6D_5Cl at 0 °C, that splits into two broad lines at −30 °C. It appears from its ^1H NMR behavior that **2** has a similar structure to **1** in solution. However, the apparently different crystallization exhibited by **2** may indicate that its structure in the solid phase differs from that of **1**. Studies on other lead(II) amides involving different alkyl substituents with the objectr of obtaining suitable crystals for X-ray studies are in progress.

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Registry No. 1, 55853-45-7; **2**, 88130-90-9; $Sn(NMe_2)_2$, 55853-40-2; $Pb(NMe_2)_2$, 88130-91-0.

Supplementary Material Available: Tables of hydrogen coordinates, anisotropic thermal parameters, and structure factors (11 pages). Ordering information is given on any current masthead page.

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Gas-Phase Structure of Dimeric Tetrafluorosulfur Chloroimide, $(ClNSF_4)_2$

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The geometric structure of $(ClNSF_4)_2$ was studied by gas electron diffraction. The four-membered SNSN ring is planar with the out-of-plane chlorine atoms in trans positions (C_{2h} symmetry). The S–N bonds (1.734 (4) Å) are lengthened due to angle strain (SNS = 99.3 (0.6)°). The extremely short N–Cl bond lengths (1.638 (10) Å) are rationalized by the large SNCl bond angles (122.1 (0.7)°). Substitution effects on trans and cis S–F bond lengths of the SF_4 groups are discussed.

Introduction

Four-membered ring systems with hexacoordinated chalcogen atoms are known in selenium and tellurium chemistry.[2,3] In contrast to $O{=}SF_4$, the dimeric species of the fluoro oxides of the higher homologues, $(OSeF)_2$ and $(OTeF_4)_2$, are more stable than the monomeric species. This different behavior of sulfur can be rationalized by the different size of the central atoms. Only in the case of sulfur is the formation of an O=X double bond favored, while the p(O)–d(X) interaction is strongly reduced for X = Se or Te. Tetrafluorosulfur imides show similar behavior as $O{=}SF_4$ and $RN{=}SF_4$ (R = F,[4]

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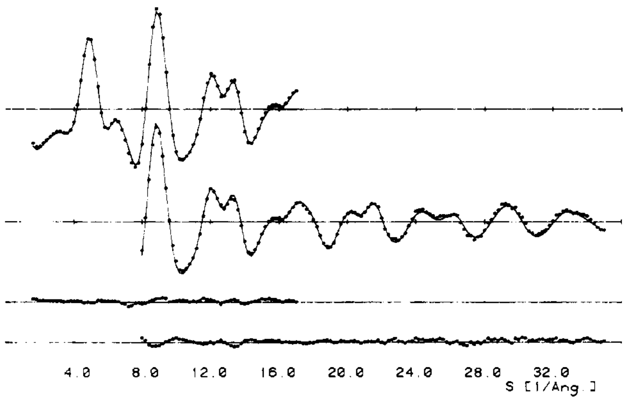

Figure 1. Experimental (···) and calculated (—) molecular intensities and differences.

CF_3,[5] C_2F_5,[6] SF_5,[7] CH_3[8]) have no tendency to dimerization; only $(ClNSF_4)_2$ forms a dimeric four-membered ring. This behavior cannot be rationalized by a simple concept. In phosphorus chemistry the existence of monomeric trifluorophosphazo compounds $RN{=}PF_3$[9] or cyclic dimers $(RNPF_3)_2$ depends on the nature of the substituent R. Electron-withdrawing substituents stabilize the double bond, substituents with +I effect such as CH_3 favor the ring formation.[10] The stability of the monomeric $CH_3N{=}SF_4$, however, demonstrates that this argument does not apply to sulfur chemistry. Neither should steric reasons be important for dimerization, as is evident from the comparison of CH_3NSF_4 or $FN{=}SF_4$ with $(ClNSF_4)_2$. $(ClNSF_4)_2$ was synthesized from NSF_3 and ClF:

$$NSF_3 + ClF \longrightarrow \{ClNSF_4\} \longrightarrow F_5S\text{-}NCl_2$$
$$\{ClNSF_4\} \downarrow \tfrac{1}{2}(ClNSF_4)_2$$

The small yield of only 3.6% indicates that the dimer is only a byproduct of this reaction. Possibly, $(ClNSF_4)_2$ is not formed by direct dimerization of the monomer, but via polar intermediates.

Experimental Section

$(ClNSF_4)_2$ was prepared according to the literature method.[11] It was separated from byproducts and impurities (SF_5NCl_2,[12] SF_5NSF_4,[7] $(SF_5)_2NH$[13]) by fractional condensation (−50, −95, −196 °C) under vacuum. The pure compound, mp +4 °C, remained in the −50 °C trap. The purity was checked by IR and NMR spectroscopy. The compound is very moisture sensitive; even in thoroughly dried glass vessels slow decomposition occurs already below 0 °C to give OSF_2, Cl_2, SiF_4, and N_2. Because chlorine is strong positively polarized ($>N^{\delta-}-Cl^{\delta+}$), KBr IR windows are attacked rapidly, and measurements have to be done with AgCl cells. The electron diffraction intensities were recorded with the Balzers gas diffractograph KD-G2[14] at two camera distances (25 and 50 cm) and an approximately 60-kV accelerating voltage. The sample was kept at 20 °C (vapor pressure of about 7 torr), and the nozzle temperature was 30 °C. The camera pressure never exceeded 10^{-5} torr during the experiment. Two photographic plates for each camera distance were analyzed by the usual procedures.[15] Background scattering recorded without gas was subtracted for the 25-cm data. Averaged molecular intensities are shown in Figure 1, and numerical values for the total scattering intensities in intervals of $\Delta s = 0.2$ Å^{-1} are available as supplementary data.[16]

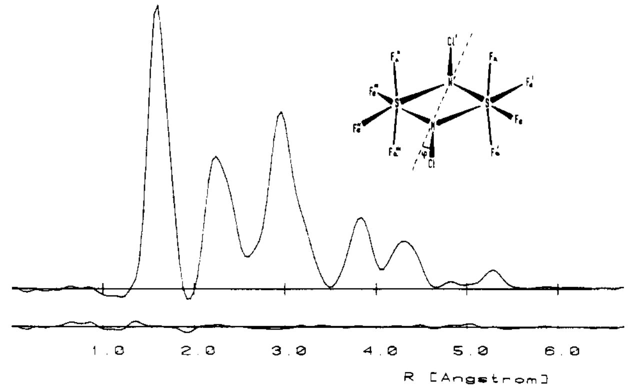

Figure 2. Experimental radial-distribution function and difference curve.

Table I. Results of Least-Squares Analysis (r_a Values in Å and deg)[a]

(a) Geometric Parameters (r_a Values)

$S-F_e$	1.545 (5)	∠SNS	99.3 (0.6)
$S-F_a$	1.590 (6)	∠NSN[b]	80.7 (0.6)
S–N	1.734 (4)	$\angle F_eSF_e$	91.7 (1.3)
N–Cl	1.638 (10)	$\angle F_aSF_a$	176.4 (0.8)
		∠SNCl	122.1 (0.7)
		∠Cl-ring[b]	34.8 (1.4)

(b) Interatomic Distances (Å) and Vibrational Amplitudes

atom pair	dist	mult	amplitude
$S-F_e$	1.55	4	0.044 (8)
$S-F_a$	1.59	4	
N–Cl	1.64	2	0.035 (9)
S–N	1.73	4	
$F_a \cdots F_e$	2.19	8	0.063 (5)
$F_e \cdots F_e'$	2.22	2	0.076 (7)
$N \cdots N'$	2.25	1	
$N \cdots F_a$	2.38	8	
$N \cdots F_e$	2.40	4	
$S \cdots S'$	2.64	1	0.056 (12)
$F_a \cdots F_a''$	2.74	2	0.100[c]
$F_a' \cdots Cl$	2.90	4	0.116 (13)
$F_e \cdots Cl$	2.91	4	
$S \cdots Cl$	2.95	4	0.076 (9)
$S \cdots F_a''$	3.13	4	0.106 (22)
$F_a \cdots F_a'$	3.18	2	0.082 (21)
$N \cdots F_e'$	3.18	4	
$N \cdots Cl'$	3.71	2	0.100[c]
$F_a \cdots Cl$	3.79	4	0.097 (12)
$F_e' \cdots Cl$	4.41	4	
$S \cdots F_e''$	3.88	4	0.071 (13)
$F_a \cdots F_a'''$	4.20	2	0.118 (13)
$F_a \cdots F_e''$	4.24	8	
$F_e \cdots F_e''$	4.80	2	0.099 (51)
$Cl \cdots Cl'$	5.28	1	0.100[c]

(c) Agreement Factors,[d] %

$R_{50} = 4.5$ $R_{25} = 8.9$

[a] Error limits are 3σ values; for atom numbering see Figure 2. [b] Dependent geometric parameter. [c] Not refined. [d] $R = \Sigma_i(w_i\Delta M_i)^2/\Sigma_i(M_i^{\mathrm{exptl}})^2$

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Structure Analysis

A preliminary analysis of the radial-distribution function (Figure 2) confirms the interpretation of the IR and Raman spectra,[11] resulting in a center of symmetry for $(ClNSF_4)_2$ with a planar SNSN ring. The bonds around nitrogen deviate from planarity, and the chlorine atoms are in trans position, i.e. one above and one below the ring plane. The number of independent parameters is reduced to eight due to symmetry constraints, and no further assumptions for the geometric parameters were necessary. Assumptions concerning the vibrational amplitudes are evident from Table I. In the least-squares refinement, a diagonal-weight matrix[15] was applied to the intensities and scattering amplitudes and phases of Haase[17] were used. All geometric parameters and 13 vibrational amplitudes were refined simultaneously. The following six correlation coefficients had values larger than 0.6: $S-F_e/S-F_a = 0.96$, $S-F_e/N-Cl = -0.75$, $S-F_a/N-Cl = 0.73$, $S-F_e/l(S-F) = 0.92$, $S-F_a/l(S-F) = -0.89$, $N-Cl/l(S-F) = 0.68$. Three bond lengths, $S-F_e$, $S-F_a$, and N–Cl, are closely spaced and, consequently, highly correlated. The starting values for these three parameters were varied in a wide range, and their choice had no effect on the final values (Table I). According to a rule of thumb, the number of geomtric parameters, which are well determined in an electron diffraction experiment, correspond to the number of "characteristic features" in the radial-distribution function (Figure 2). Nine such "characteristic features" are apparent in this function, if we include the shoulders of the peaks at 2.3 and 3.0 Å. This may demonstrate that all bond lengths are fairly well determined, despite their high correlations. The N–Cl bond length is determined indirectly by nonbonded distances, mainly by S···Cl (strongest contribution to the peak at 2.95 Å), F_a···Cl (peak at 3.82 Å), and Cl···Cl (peak at 5.28 Å). The results of the least-squares refinement are summarized in Table I. The error limits are based on 3σ values, and the errors for the bond lengths include systematic errors due to assumptions for the vibrational amplitudes.

Discussion

The ring formation in $(ClNSF_4)_2$ leads to SNS bond angles that are almost 40° smaller than in the unstrained compounds $(SF_5)_2NH$[13] and $(SF_5)_2NF$[13] (134.8 and 138.3°, respectively, vs. 99.3° in $(ClNSF_4)_2$). This indicates considerable strain in the cyclic compound. This strain is released partially by lengthening of the S–N bonds by about 0.05 Å (1.734 Å in $(ClNSF_4)_2$ vs. 1.679 (7) and 1.685 (5) Å in $(SF_5)_2NH$ and $(SF_5)_2NF$, respectively). An even larger effect has been observed for the X–O bonds in $(XF_5)_2O$[18] and $(XF_4O)_2$[19] (X = Se, Te). Here, the decrease in the oxygen bond angle upon ring formation is only slightly larger (about 45°), and lengthening of the Se–O and Te–O bonds is about 0.08 Å. The N–Cl bonds point out of the ring plane by an angle of 35°. Despite the small SNS angle (99.3°), the sum of the bond angles around nitrogen (343.5 (1.2)°) is considerably larger than for the tetrahedral configuration (328.5°). This flattening of the nitrogen configuration is due to the large SNCl angles (122.1°). In analogous phosphorus compounds that are bridged via equatorial and axial P–N bonds, $(CH_3NPF_3)_2$[20] and $(CH_3NPCl_3)_2$,[21] the configuration around nitrogen is planar. The N–Cl bonds in $(ClNSF_4)_2$ are extremely short (1.638 (10) Å), when compared with NCl_3 (N–Cl = 1.759 (2) Å and ClNCl = 107.1 (0.5)°)[22] or ClNCO (1.698 (3) Å).[23] The smallest gas-phase value known for an N–Cl bond has been observed for Cl_3VNCl (1.597 (8) Å),[24] where the VNCl group is nearly linear. These three values can be considered as typical for sp^3, sp^2, and sp N–Cl bond orbitals and possible π-bond contributions may be present in Cl_3VNCl. In $(ClNSF_4)_2$ the bonding situation around nitrogen is determined by the unusual bond angles and may be as follows: The two N–S bonds with an angle of 99.3° are formed by orbitals with very high p and low s contributions. This leaves approximately one s and two p electrons to form the nitrogen lone pair and the N–Cl bond orbitals. Depending on the hybridization of the lone-pair orbital, which we do not know, the N–Cl bonds may contain a high s contribution, somewhere between sp^2 and sp. This would rationalize the very short bonds in this compound.

The effect of substituting one fluorine atom in octahedral XF_6 molecules on the axial and equatorial bond lengths and on bond angles has been discussed at some length by Bartell et al.[25] On the basis of the VSEPR model,[26] two effects are discussed. (Since the labeling of axial and equatorial fluorine atoms implies different meaning in mono- and disubstituted XF_6 compounds, the labels trans and cis with respect to the substituent will be used here.)[27] (1) As the bonding pair of the less electronegative substituent moves closer to the cis bonding pairs, the increased repulsion is expected to lengthen the cis bonds as compared to the trans bond and increase the bond angles between substituent and cis bonds. This "primary effect" has the same result for the bond lengths as the "trans effect"[28] on the basis of a molecular orbital picture. (2) If the bond angles between substituent and cis bonds increase substantially, the cis bonding pairs are pushed toward the trans bonding pair, thus lengthening the trans S–F bond. This is called the "secondary relaxation effect". Depending on which effect prevails, the trans bonds will be shorter (primary effect) or longer (secondary effect) than the cis bonds. Experimental studies for monosubstituted SF_6 compounds do not allow a definite conclusion about which effect prevails. Gas-phase studies either assume equal S–F bond lengths or result in a slightly longer trans S–F bond with the difference between trans and cis bond lengths ($\Delta = SF_{trans} - SF_{cis}$) positive but smaller than or very close to the experimental uncertainties: Δ = 0.001 (8) Å for SF_5Cl,[29] 0.014 (22) for SF_5NF_2,[30] 0.015 (22) Å for $(SF_5)_2NH$,[13] and 0.026 (23) Å for $(SF_5)_2NF$.[13] These data indicate near balance of the two effects or a slight dominance of the secondary effect. This is surprising, because bond angles around sulfur deviate very little from 90° (by less than 2°) in these compounds and the secondary effect should become active only with larger angle deformations. In the disubstituted $F_4S(N_2)$ moiety of $(ClNSF_4)_2$, the substitution effect is considerably larger than the experimental uncertainties. The S–F bonds trans to nitrogen (labeled $S-F_e$ in Table I and Figure 2) are shorter by 0.045 (8) Å than the S–F

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bonds in the cis position (labeled S–F_a). Thus, the primary substitution effect dominates, and Δ is negative. The secondary effect cannot be fully active, since angle relaxation as expected from the VSEPR model is prevented by the ring formation. The predicted sequence in bond angles would be NSN > NSF > FSF, while the actual sequence is NSF (NSF_e = 97.3°, NSF_a = 91.4°) > FSF (F_eSF_a = 88.6°, F_eSF_e = 91.7°) > NSN (80.7°). The average S–F bond length (1.568 Å) is slightly longer than the bonds in SF_6 (1.562 (1) Å).[31] A very similar substitution effect is observed for $(SeF_4O)_2$[19] and $(TeF_4O)_2$,[19] where the Se–F and Te–F bonds trans to oxygen are shorter than the cis bonds by 0.030 (16) and 0.046 (16) Å, respectively.

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Registry No. $(ClNSF_4)_2$, 79593-52-5.

Supplementary Material Available: A listing of total scattering intensities (2 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Synthesis and Stereochemistry of Metal(II) Thiolates of the Types $[M(SR)_4]^{2-}$, $[M_2(SR)_6]^{2-}$, and $[M_4(SR)_{10}]^{2-}$ (M = Fe(II), Co(II))†

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Examples of the homoleptic binuclear Fe(II) and Co(II) thiolates of the type $[M_2(SR)_6]^{2-}$ (RS = EtS, S_2-*o*-xyl (*o*-xylene-α,α′-dithiolate)) have been synthesized and structurally characterized by X-ray diffraction methods. The following results were obtained (space group; crystal parameters; *Z*; unique data ($I > 3\sigma(I)$); R/R_w). $(Et_4N)_2[Fe_2(SEt)_6]$ (**1**): $P2_1/n$; a = 9.815 (2) Å, b = 14.588 (2) Å, c = 14.791 (3) Å, β = 100.97 (2)°; 2; 1980; 4.3/4.8. $(Et_4N)_2[Fe_2(S_2\text{-}o\text{-xyl})_3]\cdot 2MeCN$ (**2**): $P2_1/n$; a = 10.62 (1) Å, b = 25.06 (1) Å, c = 18.927 (8) Å, β = 101.94 (6)°; 4; 2042; 6.6/6.9. $(n\text{-}Bu_4N)_2[Co_2(SEt)_6]$ (**3**): *Pbca*; a = 16.672 (7) Å, b = 21.017 (5) Å; c = 33.849 (6) Å; 8; 3067; 6.2/6.1. $(Et_4N)_2[Co_2(SEt)_6]$ (**4**): $P2_1/n$; a = 9.829 (2) Å, b = 14.504 (4) Å, c = 14.772 (4) Å, β = 100.90 (2)°; 2; 1961; 4.7/5.3. All anions are edge-shared imperfect tetrahedral dimers in which the S–M–S and the M–S–M angles of the $M_2(\mu\text{-}S)_2$ bridges are respectively smaller (97–102°) and larger (78–81°) than the values of 109.5 and 70.5° for a perfect tetrahedral dimer. Compounds **1** and **4** are isomorphous and contain centrosymmetric anions with planar bridge units having the anti configuration of ethyl groups. The anion **2** exists in one of several possible isomeric forms and contains one terminal chelate ring and two others furnishing one bridging and one terminal sulfur atom. This connectivity requires an anti bridge unit, which is nonplanar. When crystallized as compound **3**, the anion is stabilized in the syn form with a nonplanar bridge unit. Other structural features of **1**–**4** are described. In acetonitrile solution the equilibrium $3[M_2(SEt)_6]^{2-} \rightleftharpoons 2[M(SEt)_4]^{2-} + [M_4(SEt)_{10}]^{2-}$ (M = Fe(II), Co(II)) was identified by use of ^1H NMR spectra; $K_{eq}(Co) >> K_{eq}(Fe)$. Salts of the new complexes $[Co(SEt)_4]^{2-}$ and $[M_4(SEt)_{10}]^{2-}$ were synthesized in order to identify equilibrium components. The equilibrium was further substantiated by a structure determination of $(Me_4N)_2[Fe_4(SEt)_{10}]$. This compound crystallizes in space group *Pbca* with a = 18.879 (4) Å, b = 24.981 (5) Å, c = 21.599 (4) Å, and Z = 8. On the basis of 2928 unique data ($I > 3\sigma(I)$) the structure was refined to R = 4.6% and R_w = 4.8%. The anion contains a $Fe_4(\mu\text{-}S)_6$ adamantane-like cage and is the ninth M(II)–thiolate complex shown to possess this stereochemistry and the first with alkylthiolate ligands. The chemistry of Fe(II) thiolates is now known to encompass tetrahedral $[Fe(SR)_4]^{2-}$, edge-shared tetrahedral $[Fe_2(SR)_6]^{2-}$, cyclic $[Fe_3(SR)_3X_6]^{2-}$, and cage $[Fe_4(SR)_{10}]^{2-}$, all of which have (distorted) tetrahedral Fe(II) sites. No complexes of higher nuclearity have been detected nor have other structural forms of those with nuclearities of one to four.

Introduction

Assembly of the biologically relevant clusters $[Fe_nS_n(SR)_4]^{2-}$[1] (n = 2,4) in reaction systems containing Fe(II, III) salts, thiolate, and elemental sulfur has been demonstrated to proceed via the intermediacy of the Fe(II)–thiolate complexes $[Fe(SR)_4]^{2-}$ and $[Fe_4(SR)_{10}]^{2-}$.[2] Reaction sequences have been delineated in some detail for the R = Ph case. More recently it has been shown that strongly reducing $[Fe(SEt)_4]^{2-}$ in reactions with sulfur in acetonitrile affords $[Fe_2S_2(SEt)_4]^{2-}$, $[Fe_3S_4(SEt)_4]^{3-}$, and $[Fe_6S_9(SEt)_2]^{4-}$.[3,4] Because the first of these can be converted to $[Fe_4S_4(SEt)_4]^{2-}$ by being heated in acetonitrile, $[Fe(SEt)_4]^{2-}$ serves as a common precursor to all known structural types of Fe–S–SR clusters of synthetic origin except those that appear to require a bidentate thiolate ligand for formation.[5] These observations have led to a systematic investigation of Fe(II)–thiolate chemistry in the form of reactions 1–4[3] in Figure 1. Variation of the RS^-:Fe(II) mole ratio affords the product complexes **1**–**4** whose compositions conform to these ratios. Examples of **1**–**4** have been isolated as quaternary ammonium or phosphonium salts.[2–4,8–14] The

† Whereas it is the policy of *Inorganic Chemistry* to publish (in full papers and notes) all crystal structure coordinates, this procedure has been modified in the case of multiple crystal structure determinations. In such cases, certain crystal structure data will be placed in the supplementary material.

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(5) These are the Fe(II) complexes $[Fe_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$[6] ($S_2$-*o*-xyl = *o*-xylene-α,α′-dithiolate) and a ring-methylated derivative[7] of the same structure.
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