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A New Structural Type in Iron-Sulfide-Thiolate Chemistry: Preparation, Properties, and Structure of the Hexanuclear Cluster $[Fe_6S_9(S\text{-}t\text{-}C_4H_9)_2]^{4-}$

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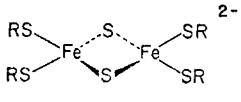
A reaction system containing $FeCl_3/Li_2S/Li(S\text{-}t\text{-}Bu)/LiOMe$ in methanol solution in the initial mole ratios 6:9:(4-8):12 affords the hexanuclear cluster $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$, which has been obtained in 50-70% purified yield as its $(Me_3NCH_2Ph)^+$ salt. The compound $(Me_3NCH_2Ph)_4[Fe_6S_9(S\text{-}t\text{-}Bu)_2]\cdot MeOH$ crystallizes in the triclinic space group $C_i^1\text{-}P\bar{1}$ with $a = 17.617$ (10) Å, $b = 19.958$ (10) Å, $c = 10.162$ (7) Å, $\alpha = 98.73$ (4)°, $\beta = 101.97$ (3)°, $\gamma = 72.54$ (3)°, and $Z = 2$ ($T = 125$ K). On the basis of 4864 unique data ($F_o^2 > 3\sigma(F_o^2)$) the structure has been refined to $R = 5.9\%$. The $[Fe_6S_9]^{2-}$ core of the cluster is formed of eight nonplanar Fe_2S_2 rhombs that are fused by edge sharing to give four $Fe(\mu_2\text{-}S)(\mu_3\text{-}S)Fe$, two $Fe(\mu_2\text{-}S)(\mu_4\text{-}S)Fe$, and two $Fe(\mu_3\text{-}S)(\mu_4\text{-}S)Fe$ subunits. Their arrangement produces a structure of idealized C_{2v} symmetry in which the twofold axis contains the μ_4-S atom and is normal to the Fe_4 plane of a pyramidal $Fe_4(\mu_4\text{-}S)$ fragment, the central portion of the structure. All Fe atoms are present in tetrahedral FeS_4 sites; the thiolates are terminally coordinated to two Fe atoms at the exterior of the structure. The cluster is mixed valence but does not contain localized Fe(II,III) sites. The $[Fe_6S_9]^{2-}$ core represents a new structural type in iron-sulfide-thiolate chemistry, and $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ is the only discrete cluster known to contain three types of bridging sulfur atoms. Other significant properties of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ include chemically reversible redox reactions affording a 3-/4-/5- electron-transfer series and ligand substitution with 2 equiv of benzenethiol to give $[Fe_6S_9(SPh)_2]^{4-}$, which has been characterized in Me_2SO solution. Large excesses of the thiol (≳28 equiv) degrade the initial cluster to $[Fe_4S_4(SPh)_4]^{2-}$ and $[Fe_2S_2(SPh)_4]^{2-}$, which are formed in a ~1.8:1 ratio. Properties common to the three known types of Fe/S/SR clusters, containing Fe_2S_2, Fe_4S_4, and Fe_6S_9 core units, are briefly summarized.

Introduction

In the course of developing the chemistry of iron-sulfide-thiolate complexes,[2-4] we have demonstrated the spontaneous formation of two types of clusters, $[Fe_2S_2(SR)_4]^{2-}$ (**1**) and $[Fe_4S_4(SR)_4]^{2-}$ (**2**), in reaction systems composed of Fe(II,III) salts, sulfur or sulfide, and thiolates. Recently, reaction sequences leading to the formation of these clusters have been elucidated.[5] Structures of two examples of **1**[6] and of two related complexes, $[Fe_2S_2Cl_4]^{2-}$[7] and $[Fe_2S_2(S_5)_2]^{2-}$,[8] which also possess the $[Fe_2S_2]^{2+}$ core oxidation level, have been established by X-ray diffraction methods. Structures of some six cubane-type clusters having the $[Fe_4S_4]^{2+}$ level have been determined, including four examples of **2**,[9] $[Fe_4S_4Cl_4]^{2-}$,[7] and $[Fe_4S_4(OPh)_4]^{2-}$.[10] In addition, structures of two one-electron reduction products of **2**, $[Fe_4S_4(SR)_4]^{3-}$ (**3**), have been reported.[11] All structures have the common features of tetrahedrally coordinated Fe atoms and core units that are planar (**1**) or are built up of nonplanar (**2**, **3**) Fe_2S_2 rhombs.



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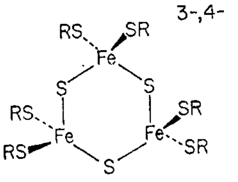
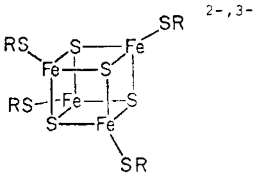


4 (3-), 5 (4-)



2 (2-), 3 (3-)

Recent findings make it clear that natural and synthetic Fe/S/SR clusters are not confined to the preceding two structural types. A cyclic Fe_3S_3 core unit has been crystallographically identified in *Azotobacter vinelandii* ferredoxin (Fd) I.[12] Spectroscopic studies have demonstrated the presence of this structure, or one similar to it, in a number of proteins[13,14] including chemically oxidized clostridial Fd,[14] which in its native form contains two Fe_4S_4 clusters. Reasonable, but as yet unsynthesized, analogues of the protein 3-Fe sites are $[Fe_3S_3(SR)_6]^{3-,4-}$ (**4**, **5**), which should contain the $[Fe_3S_3]^{3+,2+}$ core oxidation levels deduced for the proteins from Mössbauer spectroscopic results.[13a,b] The emergence of this new cluster type has prompted our search for heretofore unknown polynuclear Fe/S/SR species using variations of the

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reaction conditions that afford **1** and **2**. While this work was in progress, the preparation and structure of $[Fe_6(\mu_3\text{-}S)_8(PEt)_6][BPh_4]_2$ was described.[15] Although not a thiolate species the $[Fe_6S_8]^{2+}$ core unit is a significant addition to the family of iron(II,III)-sulfide clusters. Research in this laboratory has led to the synthesis and structural definition of two new members of this family, $[Fe_3(\mu_2\text{-}S)_4(SR)_4]^{3-}$ [16] and $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$.[17] The synthesis, structure, and properties of the latter are described herein, augmenting a brief report communicated earlier.[17a]

Experimental Section

Preparation of $(Me_3NCH_2Ph)_4[Fe_6S_9(S\text{-}t\text{-}Bu)_2]\cdot MeOH$. All operations were carried out under a pure dinitrogen atmosphere; solvents were degassed prior to use. To a solution of 85 mmol of LiOMe (from 0.58 g of lithium) in 70 mL of methanol was added 2.8 mL (25 mmol) of 1,1-dimethylethanethiol and a filtered solution of 4.87 g (30 mmol) of $FeCl_3$ in 70 mL of methanol, producing a brown solution and a light green solid. To this mixture was added 2.70 g (45 mmol) of anhydrous lithium sulfide. When the resultant dull orange-brown reaction mixture was heated at ~55 °C for 1–2 h, an essentially homogeneous red-brown solution was formed. The reaction mixture was stirred overnight at ambient temperature and then filtered into a solution of 7.0 g of $(Me_3NCH_2Ph)Br$ in 20 mL of methanol. The crude product separated as black microcrystalline flakes. After collection by filtration this material was recrystallized from 1:1 v/v Me_2SO/methanol. Small black prisms were obtained in yields of 50–70% in multiple preparations. In the solid and solution states the compound is sensitive to dioxygen. Analytical results are consistent with a methanol solvate; this formulation was confirmed by X-ray crystallography. Anal. Calcd for $C_{49}H_{86}Fe_6N_4OS_{11}$: C, 41.01; H, 6.04; Fe, 23.35; N, 3.90; S, 24.58. Found: C, 40.90; H, 5.82; Fe, 23.61; N, 4.20; S, 23.99. Absorption spectrum (Me_2SO): λ_{max} (ϵ_M) 319 (32000), 412 (24500), ~530 (sh, ~12000) nm. Single crystals suitable for X-ray diffraction experiments were grown from 2:1 v/v Me_2SO/methanol solutions maintained at -20 °C.

X-ray Data Collection and Reduction. Crystals of $[Me_3NCH_2Ph]_4[Fe_6S_9(S\text{-}t\text{-}Bu)_2]\cdot MeOH$ were sealed in glass capillaries under an Ar atmosphere. Preliminary Weissenberg and precession photographs showed that the compound crystallizes in the triclinic space group C_1^1-$P1$ or C_i^1-$P\bar{1}$. The latter space group was proven to be correct on the basis of subsequent structure solution and refinement. Diffraction data were collected on a crystal of approximate dimensions 0.15 × 0.16 × 0.37 mm bathed in a N_2-cold stream of a Picker FACS-1 diffractometer. Lattice parameters at 125 K were obtained by automatic centering of 17 reflections in the range $0.2775 \le \lambda^{-1} \sin\theta \le 0.3637$ Å^{-1} with use of Mo Kα_1 radiation. During the data collection the average value of the intensities of six standard reflections decreased by about 14%. Intensities were corrected for decomposition and absorption. Crystal data and the details of data collection are given in Table I.

Structure Solution and Refinement. The structure was solved by a combination of direct methods (MULTAN 80) and a sharpened, origin-removed Patterson synthesis. An E map revealed positions of all non-hydrogen atoms of the anion as well as several atoms of the cations. The remaining atoms were located from a subsequent Fourier map. The isotropic refinement of non-hydrogen atoms converged to the values $R = 0.109$ and $R_w = 0.123$. In the first cycle of anisotropic refinement all non-hydrogen atoms of the cations were refined with fixed contributions of non-hydrogen atoms of the anion and methanol solvate molecule. In the next cycle the atoms of the anion and the solvate molecule were refined with fixed contributions of the cation atoms. This cycling process was repeated. At this stage of the anisotropic refinement $R = 0.068$ ($R_w = 0.079$). The refinement was followed by a difference Fourier synthesis that showed positions of several hydrogen atoms. The parameters of the remaining hydrogen atoms were calculated, and all hydrogen atoms (except that of the OH group of the solvate molecule) were taken in their idealized positions as a fixed contribution to the structure factors. Each hydrogen atom was assigned a thermal parameter 1.0 Å^2 greater than that of the carbon atom to which it is attached. The difference Fourier map revealed also two peaks of height about 0.25 that of a typical carbon atom. These two peaks are attributed to a second methanol solvate molecule. This molecule was refined with isotropic thermal parameters, affording an occupancy of 0.26 (2). The final anisotropic least-squares refinement on $|F_o|$ for 4864 unique data led to the values $R = 0.059$ and $R_w = 0.068$. The standard error in an observation of unit weight is 1.89 e.

Table I. Crystal Data and Intensity Collection for $(Me_3NCH_2Ph)_4[Fe_6S_9(S\text{-}t\text{-}Bu)_2]\cdot{\sim}1MeOH$

formula	$C_{49}H_{86}Fe_6N_4OS_{11}$[a]
mol wt	1435.06[a]
space group	C_i^1-$P\bar{1}$
a, Å	17.617 (10)
b, Å	19.958 (10)
c, Å	10.162 (7)
α, deg	98.73 (4)
β, deg	101.97 (3)
γ, deg	72.54 (3)
V, Å^3	3318
Z	2
d_{calcd}, g cm^{-3} (125 K)	1.444[a]
d_{obsd}, g cm^{-3} (298 K)	1.44[c]
T of data collection, K	125[b]
cryst vol, mm^3	0.0088
radiation	graphite-monochromatized Mo Kα ($\lambda(K\alpha_1) = 0.7093$ Å)
linear abs coeff, cm^{-1}	16.5
transmission factors	0.794–0.831
detector aperture	6 mm wide, 6 mm high, 32 cm from cryst
takeoff angle, deg	3.3
scan speed, deg min^{-1}	2.0 in 2θ
$\lambda^{-1} \sin\theta$, limits, Å^{-1}	0.0431–0.5052, $3.5° \leqslant 2\theta(\text{Mo } K\alpha_1) \leqslant 42.0°$
bkgd counts	10 s at end of each scan with rescan option[d]
scan range, deg	1.2 below Kα_1 to 1.2 above Kα_2
data collected	$\pm h, \pm k, l$
p factor	0.04
no. of unique data ($F_o^2 > 3\sigma(F_o^2)$)	4864

[a] For methanol monosolvate. [b] The low-temperature system is based on a design by: Huffman, J. C. Ph.D. Thesis, Indiana University, 1974. [c] Determined by flotation in $CHCl_3/CH_2Cl_2$. [d] Lenhert, P. G. *J. Appl. Crystallogr.* 1975, *8*, 568–570.

The following results are tabulated: positional parameters (Table II), bond distances and angles (Table III), least-squares planes (Table IV) of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$, positional and thermal parameters of all non-hydrogen atoms (Table S-I[18]), bond distances and angles for cations and the methanol solvate (Table S-II), hydrogen parameters (Table S-III), and structure amplitudes (Table S-IV).

Other Physical Measurements. All measurements were performed under a pure argon atmosphere; solvents were purified by standard procedures and were degassed before use. Absorption spectra were recorded on a Cary Model 219 spectrophotometer. Electrochemical measurements were made with standard Princeton Applied Research instrumentation using a glassy carbon working electrode. Solutions contained 0.1 M $(n\text{-}Bu_4N)(ClO_4)$ supporting electrolyte; potentials were measured at ~25 °C vs. a saturated calomel electrode (SCE). ^1H NMR spectra were obtained with a Bruker WM-300 spectrometer; shifts downfield of the Me_4Si reference are designated as negative. Solution magnetic susceptibilities were determined by the conventional NMR method[19] using Me_4Si solution and reference shift differences. Diamagnetic corrections were applied, and the susceptibility of Me_2SO solvent was taken from the results of Gerger et al.[20]

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Table II. Positional Parameters for the Atoms of $[(CH_3)_3NCH_2C_6H_5]_4[Fe_6S_9(S\text{-}t\text{-}C_4H_9)_2]\cdot CH_3OH$

Atom	x[a]	y	z	Atom	x[a]	y	z
FE(1)	-0.043999(95)	-0.173744(77)	0.29315(16)	C(16)	-0.3819(10)	0.0814(10)	0.2815(20)
FE(2)	-0.163445(94)	-0.198671(78)	0.40294(17)	C(17)	-0.31844(91)	0.02428(81)	0.2989(15)
FE(3)	-0.113674(97)	-0.338133(80)	0.32014(17)	C(18)	-0.24879(78)	0.02077(67)	0.2622(13)
FE(4)	0.005784(97)	-0.312792(79)	0.20532(17)	C(19)	-0.06439(75)	0.43816(62)	0.3197(13)
FE(5)	0.074428(98)	-0.220199(83)	0.14069(17)	C(20)	-0.19334(77)	0.42619(62)	0.1903(12)
FE(6)	-0.246786(99)	-0.287186(81)	0.43633(18)	C(21)	-0.11047(74)	0.33853(56)	0.3403(13)
S(1)	-0.12719(17)	-0.24525(14)	0.19579(29)	C(22)	-0.17660(69)	0.45816(58)	0.4358(12)
S(2)	0.08261(18)	-0.24911(15)	0.34966(30)	C(23)	-0.25737(80)	0.45116(68)	0.4352(14)
S(3)	-0.10050(19)	-0.11559(15)	0.46834(31)	C(24)	-0.32769(85)	0.49848(71)	0.3748(16)
S(4)	-0.11904(18)	-0.29045(15)	0.53881(31)	C(25)	-0.40346(83)	0.49343(80)	0.3723(18)
S(5)	0.00593(18)	-0.41028(15)	0.28718(33)	C(26)	-0.41177(96)	0.43864(90)	0.4335(22)
S(6)	-0.02703(18)	-0.11893(15)	0.13183(32)	C(27)	-0.34517(91)	0.39061(79)	0.4991(18)
S(7)	-0.29613(18)	-0.17705(15)	0.37205(33)	C(28)	-0.26790(87)	0.39607(76)	0.4959(16)
S(8)	-0.22607(19)	-0.37110(15)	0.26407(34)	C(29)	0.19345(86)	0.08680(71)	0.2128(15)
S(9)	0.03773(18)	-0.30969(15)	0.00770(31)	C(30)	0.24227(77)	0.09373(65)	0.0134(12)
S(10)	0.18991(19)	-0.20904(17)	0.09151(36)	C(31)	0.17654(88)	0.20023(63)	0.1383(13)
S(11)	-0.31919(19)	-0.30929(17)	0.57609(35)	C(32)	0.31055(82)	0.13270(64)	0.2321(13)
O(1)	-0.34099(75)	-0.20561(65)	0.0407(12)	C(33)	0.37424(84)	0.06306(65)	0.2484(15)
N(1)	-0.09609(62)	0.09028(46)	0.25646(94)	C(34)	0.38429(95)	0.02912(74)	0.3621(16)
N(2)	-0.13748(57)	0.41633(47)	0.32201(99)	C(35)	0.4432(11)	-0.03430(83)	0.3771(16)
N(3)	0.23215(59)	0.12684(46)	0.1492(10)	C(36)	0.49059(93)	-0.06371(83)	0.2832(21)
N(4)	0.17485(59)	0.42769(50)	0.1374(10)	C(37)	0.4819(10)	-0.0291(11)	0.1748(22)
C(1)	0.23976(90)	-0.15960(86)	0.2386(15)	C(38)	0.4239(10)	0.0341(10)	0.1577(21)
C(2)	0.30637(90)	-0.14043(86)	0.1880(16)	C(39)	0.12219(79)	0.40318(64)	0.2018(14)
C(3)	0.27997(92)	-0.20835(92)	0.3525(15)	C(40)	0.12369(79)	0.47195(64)	0.0299(13)
C(4)	0.17946(95)	-0.09418(76)	0.2846(16)	C(41)	0.23253(85)	0.36505(62)	0.0782(14)
C(5)	-0.42778(76)	-0.27965(68)	0.5078(15)	C(42)	0.21881(76)	0.47102(64)	0.2407(14)
C(6)	-0.44164(83)	-0.29680(73)	0.3557(17)	C(43)	0.27726(78)	0.49880(68)	0.1946(14)
C(7)	-0.47117(78)	-0.31773(80)	0.5704(17)	C(44)	0.35551(97)	0.45971(85)	0.1908(21)
C(8)	-0.46042(78)	-0.20042(66)	0.5408(16)	C(45)	0.4094(11)	0.4863(11)	0.1467(29)
C(9)	-0.07413(75)	0.05088(60)	0.3786(12)	C(46)	0.3885(11)	0.5517(11)	0.1110(25)
C(10)	-0.12166(89)	0.16759(60)	0.3024(13)	C(47)	0.3111(12)	0.59269(85)	0.1199(19)
C(11)	-0.02323(82)	0.07576(67)	0.1912(14)	C(48)	0.25312(85)	0.56934(69)	0.1599(14)
C(12)	-0.16023(72)	0.06758(54)	0.1541(11)	C(49)	-0.4085(11)	-0.2358(11)	0.0174(20)
C(13)	-0.23681(75)	0.07569(61)	0.2037(13)	C(50)	-0.3825(37)	0.3314(32)	0.1334(60)
C(14)	-0.30266(96)	0.13417(71)	0.1881(16)	O(2)	-0.2938(23)	0.2999(20)	0.1493(38)
C(15)	-0.3739(10)	0.13841(98)	0.2264(21)				

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

Results and Discussion

Synthesis of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$. Reaction 1 represents one

$$4FeCl_3 + 4Li_2S + 6LiSR \xrightarrow[N_2]{MeOH} Li_2[Fe_4S_4(SR)_4] + RSSR + 12LiCl \quad (1)$$

of several methods for the assembly of $[Fe_4S_4(SR)_4]^{2-}$ clusters from simple reactants under anaerobic conditions.[5,9a,21] The reaction affords the clusters **2** in good yield (usually >50% after purification of R'_4N^+ salts by recrystallization) and appears to be generally applicable to *mono*functional thiolates.[22] Since the introduction of the basic method in 1973[9a] a number of experiments with varying mole ratios of reactants have resulted in yield changes in isolated salts of **2**, but no new clusters have been identified.[24] More recently such variations have been reexamined, but these used amounts of LiOMe in excess of that required to form LiSR from RSH in methanol. In one case (R = *t*-Bu) it was observed that an intensely colored filtrate remained after isolation of the known compound $[n\text{-}Bu_4N]_2[Fe_4S_4(S\text{-}t\text{-}Bu)_4]$,[9a] which is nearly insoluble in methanol. Addition of $(Me_3NCH_2Ph)Br$ to the filtrate caused separation of a crystalline solid whose composition was established as $[Me_3NCH_2Ph]_4[Fe_6S_9(S\text{-}t\text{-}Bu)_2]\cdot MeOH$ by X-ray crystallography and subsequent elemental analysis. Further empirical variation of the mole ratios of the reactants and other parameters led to the development of reaction system 2 (y = 4–8), in which formation of $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$ has been eliminated.

$$6FeCl_3 + 9Li_2S + yLi(S\text{-}t\text{-}Bu) \xrightarrow[\Delta,\ N_2]{12LiOMe} Li_4[Fe_6S_9(S\text{-}t\text{-}Bu)_2] + (t\text{-}BuS)_2 + (y-4)Li(S\text{-}t\text{-}Bu) + 18LiCl \quad (2)$$

In arriving at reaction system 2, which affords the new cluster in 50–70% purified yield as its $(Me_3NCH_2Ph)^+$ salt, we made the following observations. (i) The reaction has an absolute requirement for excess LiOMe under the conditions investigated thus far. Substitution of LiOMe by NaOMe gave only an intractable black solid and an essentially colorless supernatant. The use of y equiv of LiOMe (to generate y equiv

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(21) Christou, G.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1093.

(22) When *o*-xylyl-α,α′-dithiolate is employed, the binuclear cluster $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$ (**1**) is obtained.[6,23]

(23) Reynolds, J. G.; Holm, R. H. *Inorg. Chem.* **1980**, *19*, 3257.

(24) The only exception to this statement occurs with a variation of the reaction system, in which certain R'_4N cations are cointroduced with the sulfide source. Under these conditions binuclear species **1**, shown to be an intermediate in the formation of **2**,[5] are trapped as insoluble salts.[23]

Table III. Selected Bond Distances (Å) and Angles (Deg) in $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$

	Fe–μ_2-S		
Fe(1)–S(6)	2.218 (3)	Fe(4)–S(9)	2.209 (4)
Fe(2)–S(7)	2.209 (4)	mean	2.211 (5)[a]
Fe(3)–S(8)	2.209 (4)		
Fe(1)–S(3)	2.218 (4)	Fe(4)–S(5)	2.228 (3)
Fe(2)–S(3)	2.210 (3)	mean	2.220 (8)
Fe(3)–S(5)	2.225 (4)		
Fe(5)–S(6)	2.260 (3)	Fe(6)–S(8)	2.238 (4)
Fe(5)–S(9)	2.243 (4)	mean	2.248 (10)
Fe(6)–S(7)	2.251 (3)		
	Fe–μ_3-S		
Fe(1)–S(2)	2.299 (3)	Fe(4)–S(2)	2.290 (4)
Fe(2)–S(4)	2.310 (3)	mean	2.297 (10)
Fe(3)–S(4)	2.290 (4)		
Fe(5)–S(2)	2.249 (4)	Fe(6)–S(4)	2.262 (4)
		mean	2.256
	Fe–μ_4-S		
Fe(1)–S(1)	2.321 (3)	Fe(4)–S(1)	2.316 (4)
Fe(2)–S(1)	2.304 (4)	mean	2.317 (9)
Fe(3)–S(1)	2.326 (3)		
	Fe–S(*t*-Bu)		
Fe(5)–S(10)	2.273 (4)	Fe(6)–S(11)	2.262 (4)
		mean	2.268
	Fe–Fe		
Fe(1)–Fe(4)	2.716 (3)	Fe(2)–Fe(3)	2.712 (3)
		mean	2.714
Fe(1)–Fe(2)	2.773 (3)	Fe(3)–Fe(4)	2.808 (3)
		mean	2.791
Fe(1)···Fe(3)	3.896 (3)	Fe(2)···Fe(4)	3.889 (3)
		mean	3.893
Fe(1)–Fe(5)	2.712 (3)	Fe(4)–Fe(5)	2.711 (3)
Fe(2)–Fe(6)	2.709 (3)	mean	2.708 (6)
Fe(3)–Fe(6)	2.698 (3)		
	S···S		
S(2)···S(6)	3.513 (4)	S(4)···S(8)	3.495 (5)
S(2)···S(9)	3.510 (5)	mean	3.512 (14)
S(4)···S(7)	3.530 (4)		
S(1)···S(3)	3.550 (5)	S(1)···S(5)	3.550 (4)
		mean	3.550
S(1)···S(2)	3.685 (5)	S(1)···S(4)	3.695 (5)
		mean	3.690
S(1)···S(6)	3.679 (4)	S(1)···S(9)	3.614 (5)
S(1)···S(7)	3.600 (5)	mean	3.641 (40)
S(1)···S(8)	3.672 (4)		
	C–S[b]		
C(1)–S(10)	1.873 (14)	C(5)–S(11)	1.840 (14)
		mean	1.857

	Fe–μ_2-S–Fe		
Fe(1)–S(6)–Fe(5)	74.6 (1)	Fe(4)–S(9)–Fe(5)	75.0 (1)
Fe(2)–S(7)–Fe(6)	74.8 (1)	mean	74.9 (2)
Fe(3)–S(8)–Fe(6)	74.7 (1)		
Fe(1)–S(3)–Fe(2)	77.5 (1)	Fe(3)–S(5)–Fe(4)	78.2 (1)
		mean	77.9
	Fe–μ_3-S–Fe		
Fe(1)–S(2)–Fe(5)	73.2 (1)	Fe(4)–S(2)–Fe(5)	73.3 (1)
Fe(2)–S(4)–Fe(6)	72.7 (1)	mean	73.0
Fe(3)–S(4)–Fe(6)	72.7 (1)		
Fe(1)–S(2)–Fe(4)	72.6 (1)	Fe(2)–S(4)–Fe(3)	72.3 (1)
		mean	72.5
	Fe–μ_4-S–Fe		
Fe(1)–S(1)–Fe(2)	73.7 (1)	Fe(3)–S(1)–Fe(4)	74.4 (1)
		mean	74.1
Fe(1)–S(1)–Fe(4)	71.7 (1)	Fe(2)–S(1)–Fe(3)	71.7 (1)
		mean	71.7
Fe(1)–S(1)–Fe(3)	113.9 (1)	Fe(2)–S(1)–Fe(4)	114.6 (1)
		mean	114.3
	S–Fe–μ_2-S		
S(10)–Fe(5)–S(6)	113.1 (1)	S(11)–Fe(6)–S(8)	112.6 (1)
S(10)–Fe(5)–S(9)	110.2 (1)	mean	112.1
S(11)–Fe(6)–S(7)	112.5 (1)		
	S–Fe–μ_3-S		
S(10)–Fe(5)–S(2)	115.9 (1)	S(11)–Fe(6)–S(4)	112.3 (1)
	μ_2-S–Fe–μ_2-S		
S(6)–Fe(5)–S(9)	111.9 (1)	S(7)–Fe(6)–S(8)	113.7 (1)
S(3)–Fe(1)–S(6)	122.2 (1)	S(5)–Fe(4)–S(9)	124.9 (1)
S(3)–Fe(2)–S(7)	123.2 (1)	mean	123.2
S(5)–Fe(3)–S(8)	122.5 (1)		
	μ_2-S–Fe–μ_3-S		
S(6)–Fe(1)–S(2)	102.1 (1)	S(9)–Fe(4)–S(2)	102.6 (1)
S(7)–Fe(2)–S(4)	102.7 (1)	mean	102.3 (4)
S(8)–Fe(3)–S(4)	101.9 (1)		
S(3)–Fe(1)–S(2)	114.5 (1)	S(5)–Fe(4)–S(2)	113.1 (1)
S(3)–Fe(2)–S(4)	113.8 (1)	mean	114.0
S(5)–Fe(3)–S(4)	114.5 (1)		
S(6)–Fe(5)–S(2)	102.4 (1)	S(8)–Fe(6)–S(4)	101.9 (1)
S(9)–Fe(5)–S(2)	102.8 (1)	mean	102.5 (5)
S(7)–Fe(6)–S(4)	102.9 (1)		
	μ_2-S–Fe–μ_4-S		
S(3)–Fe(1)–S(1)	102.9 (1)	S(5)–Fe(4)–S(1)	102.7 (1)
S(3)–Fe(2)–S(1)	103.7 (1)	mean	103.0 (5)
S(5)–Fe(3)–S(1)	102.5 (1)		
S(6)–Fe(1)–S(1)	108.3 (1)	S(9)–Fe(4)–S(1)	106.0 (1)
S(7)–Fe(2)–S(1)	105.8 (1)	mean	107.1
S(8)–Fe(3)–S(1)	108.1 (1)		
	μ_3-S–Fe–μ_4-S		
S(2)–Fe(1)–S(1)	105.8 (1)	S(2)–Fe(4)–S(1)	106.3 (1)
S(4)–Fe(2)–S(1)	106.4 (1)	mean	106.2 (3)
S(4)–Fe(3)–S(1)	106.4 (1)		

[a] Standard deviation of a single observation is equal to $[(\Sigma x^2 - (\Sigma x)^2/n)/(n-1)]^{1/2}$; when no value is given with the mean value of more than two quantities, the variations exceed those expected for a sample taken from the same population. [b] C–C and C–C–C ranges and mean values: 1.497–1.542, 1.520 (18) Å; 108.4–112.1, 109.8°.

of Li(S-*t*-Bu)) or the use of excess LiOEt in ethanol reaction solvent resulted in formation of only $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$, isolated in 40–50% yield based on available $t\text{-}BuS^-$. (ii) Substitution of $FeCl_3$ by $FeCl_2$ gave an intractable black solid as in (i) (presumably FeS). (iii) Use of the unit mole ratio of $FeCl_3/Li_2S$ in the presence of *y* equiv of thiolate afforded $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$, isolated in 75% crude yield based on available sulfide. The formation of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ thus appears to be circumscribed by a fairly narrow range of reaction conditions. In particular, these conditions suppress the pathway for assembly of $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$, perhaps by means of an iron–methoxide intermediate, which has not been identified. This cluster joins **1** and **2** in a group of three species that spontaneously self-assemble from elementary reagents in methanol solution.

Description of the Structure. The compound $[Me_3NCH_2Ph]_4[Fe_6S_9(S\text{-}t\text{-}Bu)_2]\cdot MeOH$ crystallizes in triclinic space group C_i^1-$P\bar{1}$ and contains well-separated cations, anion, and solvate molecules. Cations, *t*-Bu groups, and methanol solvate molecules have unexceptional structures and are not considered further.[18] The structure of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ is described in terms of the interatomic distances in Table III and the best weighted least-squares planes in Table IV. Perspective and projection representations of the structure are set out in Figure 1, and stereoviews of the unit cell contents and of the cluster itself are provided in Figure 2.

Table IV. Best Weighted Least-Squares Planes for $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$

plane no.	A	B	C	D
	$Ax + By + Cz - D = 0$ (triclinic coordinates)			
1	7.725	−2.059	7.865	2.258
2	7.791	−2.019	7.840	2.296
3	7.023	−1.215	4.918	3.199
4	7.148	8.650	−9.614	−4.697
5	17.059	5.909	0.425	−3.737
6	5.455	8.916	7.657	−1.232
7	10.342	14.973	3.547	−1.934
8	3.904	−7.061	−8.654	−2.802
9	−1.764	−17.423	5.580	7.965
10	12.358	−9.289	−0.050	3.045

atom	dev from plane, Å									
	1	2	3	4	5	6	7	8	9	10
Fe(1)	0.066 (2)	0.010 (2)	0.044 (2)	0.061 (2)			−0.083 (2)			
Fe(2)	0.058 (2)	−0.010 (2)	0.048 (2)		−0.054 (2)			0.080 (2)		
Fe(3)	0.078 (2)	0.011 (2)			−0.065 (2)	0.049 (2)			−0.086 (2)	
Fe(4)	0.046 (2)	−0.010 (2)		0.059 (2)		0.047 (2)				−0.078 (2)
Fe(5)	−0.123 (2)						−0.094 (2)			−0.087 (2)
Fe(6)	−0.141 (2)							0.090 (2)	−0.091 (2)	
S(1)			−0.151 (3)	−0.216 (3)	0.201 (3)	−0.149 (3)				
S(2)				−0.229 (3)			0.299 (3)			0.273 (3)
S(3)			−0.198 (3)							
S(4)					0.219 (3)			−0.275 (3)	0.312 (3)	
S(5)						−0.194 (3)				
S(6)							0.342 (3)			
S(7)								−0.324 (3)		
S(8)									0.373 (3)	
S(9)										0.298 (3)

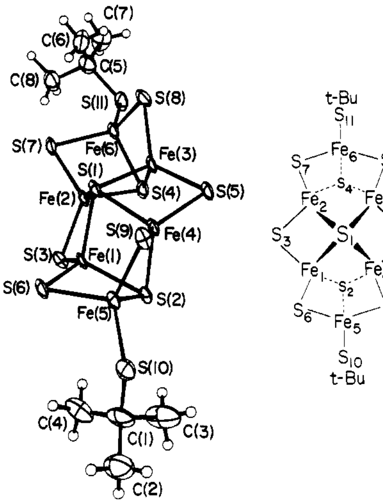

Figure 1. Right: plane projection formula illustrating atom-labeling scheme and idealized C_{2v} symmetry of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$. Left: structure of the anion, with probability ellipsoids drawn at the 50% level except for the hydrogen atoms, which are artifically small.

The $[Fe_6S_9]^{2-}$ core of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ is formed of eight Fe_2S_2 rhombs (**6**) (cf. Figure 3, which includes formulas **6**–**12**). These are decidedly nonplanar (planes 3–10) and are fused such that two ($Fe_2(1,4)S_2(1,2)$ and $Fe_2(2,3)S_2(1,4)$) share all their edges and each of the remaining six has two unshared edges at the exterior of the structure. This arrangement necessarily generates six doubly bridging (μ_2-S(3,5–9)), two triply bridging (μ_3-S(2,4)), and one quadruply bridging (μ_4-S(1)) sulfur atom(s). Each Fe atom is present in an approximately tetrahedral site (**7**). Except for Fe(5) and Fe(6), which have one terminal thiolate ligand each, ligands in the sites **7** are exclusively core sulfur atoms. The core contains three types of subunits **6**: four Fe(μ_2-S)(μ_3-S)Fe, two Fe(μ_2-S)(μ_4-S)Fe, and two Fe(μ_3-S)(μ_4-S)Fe groups. These are arranged in a structure of idealized C_{2v} symmetry in which the C_2 axis contains μ_4-S(1) and is perpendicular to the nearly perfect Fe(1–4) plane (plane 2) of the fragment **8**. All six Fe atoms are coplanar to within ~0.2 Å (plane 1). In Table III metrical parameters are arranged in ostensibly equivalent sets under this symmetry. Shown in Figure 4 are mean dimensions of the three subunits **6** and the fragment **8**. As would be expected bond distances decrease in the order Fe–(μ_4-S) > Fe–(μ_3-S) > Fe–(μ_2-S). Dimensions of the subunits, especially those of Fe(μ_2-S)(μ_3-S)Fe and Fe(μ_3-S)(μ_4-S)Fe, are similar to the corresponding values in **1**–**3** and related complexes. Tabulations of metrical data and a detailed discussion of the structures of those clusters are presented elsewhere.[4]

The $[Fe_6S_9]^{2-}$ core structure has not been found in any previous discrete cluster nor, to our knowledge, is it in its entirety a portion of the structure of any Fe–S mineral.[25] Among the numerous structurally characterized, discrete metal–sulfur clusters $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ is the only species containing three types of bridging sulfur atoms. Of these types μ_4-S is by far the least frequently encountered and, as noted by Vahrenkamp,[26] it has been observed in two bonding modes: at the center of an approximate tetrahedron of metal atoms and on the same side of a set of four metal atoms (e.g., **8**). The former is documented in five Fe–S–CO clusters[27] and a few other cases as well.[26] The other bridging mode had been established only in $[Ni_9S_9(PEt_3)_6]^{2+}$,[28] $Co_4S_2(CO)_{10}$,[29] and $[Co_8S_6(SPh)_8]^{4-,5-}$.[30] In the latter three cases the μ_4-S atom

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(25) For a review of many such structures cf.: Vaughan, D. J.; Craig, J. R. "Mineral Chemistry of Metal Sulfides"; Cambridge University Press: New York, 1978.

(26) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322.

(27) (a) $[MeSFe_2(CO)_6]_2S$: Coleman, J. M.; Wojcicki, A.; Pollick, C. J.; Dahl, L. F. *Inorg. Chem.* **1967**, *6*, 1236. (b) $[t\text{-}BuSFe_2(CO)_6]_2S$: de Beer, J. A.; Haines, R. J. *J. Organomet. Chem.* **1970**, *24*, 757. (c) $Fe_4(CO)_{12}S(C_5H_4N)(C_5H_4NS)$: Le Borgne, G.; Grandjean, D. *Ibid.* **1975**, *92*, 381. (d) $Fe_4(CO)_{12}S(CSNMe_2)(CNMe_2)$: Dean, W. K.; Vanderveer, D. G. *Ibid.* **1978**, *146*, 143. (e) $Fe_4(CO)_{12}S(SCH_2C_5H_4FeC_5H_5)(SMe)$: Patin, H.; Mignani, G.; Mahe, C.; Le Marouille, J.-Y.; Benoit, A.; Grandjean, D. *Ibid.* **1981**, *210*, C1.

(28) Ghilardi, C. A.; Midollini, S.; Sacconi, L. *J. Chem. Soc., Chem. Commun.* **1981**, 47.

(29) Wei, C. H.; Dahl, L. F. *Cryst. Struct. Commun.* **1975**, *4*, 583.

(30) Christou, G.; Hagen, K. S.; Holm, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1744, and unpublished results.

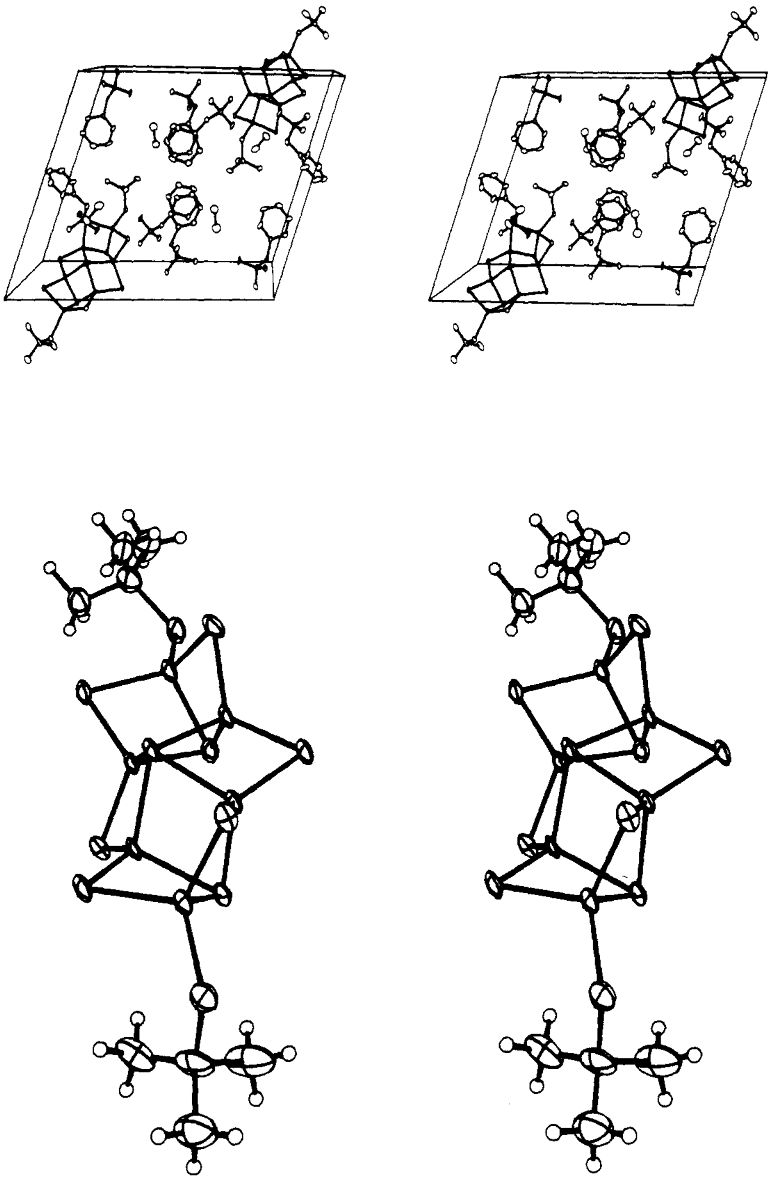

Figure 2. Top: stereoview of the crystal packing diagram for $[Me_3NCH_2Ph]_4[Fe_6S_9(S\text{-}t\text{-}Bu)_2]\cdot MeOH$ viewed down the *c* axis, with 20% probability ellipsoids shown. Bottom: stereoview of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$, with 50% probability ellipsoids of non-hydrogen atoms shown.

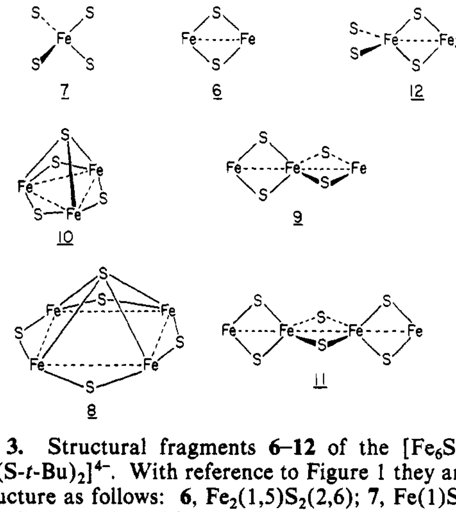

Figure 3. Structural fragments **6–12** of the $[Fe_6S_9]^{2-}$ core of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$. With reference to Figure 1 they are located in the structure as follows: **6**, $Fe_2(1,5)S_2(2,6)$; **7**, $Fe(1)S_4$; **8**, $Fe_4(1\text{–}4)S_5(1\text{–}5)$; **9**, $Fe_3(1,2,5)S_4(1\text{–}3,6)$; **10**, $Fe_3(1,4,5)S_4(1,2,6,9)$; **11**, $Fe_4(1,2,5,6)S_6(1\text{–}4,6,7)$; **12**, $Fe_2(1,2)S_6(1\text{–}4,6,7)$. Several fragments occur more than once.

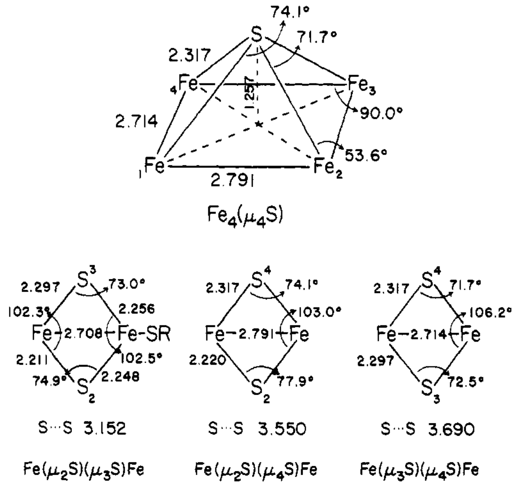

Figure 4. Several structural fragments of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ showing mean values of bond distances and angles averaged under idealized C_{2v} symmetry.

is centered above a plane of four metal atoms. This arrangement closely resembles fragment **8**, in which the bridging atom lies 1.257 Å above the Fe_4 mean plane (Figure 4).

Although the $[Fe_6S_9]^{2-}$ core is formally mixed valence (4 Fe(III) + 2 Fe(II)), there is no convincing structural evidence for localized Fe(II,III) sites. If a localized situation is pursued under the idealized C_{2v} cluster symmetry, a seemingly reasonable assignment is atoms Fe(5,6) as Fe(II) and atoms Fe(1–4) as Fe(III). Certain bond distances involving common atoms (e.g., Fe(5)–S(6), 2.260 (3) Å, vs. Fe(1)–S(6), 2.218 (3) Å) are consistent with this assignment whereas others are not (e.g., Fe(5)–S(2), 2.249 (4) Å, vs. Fe(1)–S(2), 2.299 (3) Å). Terminal Fe–SR distances are a more effective monitor of oxidation states in molecules with closely related Fe atom site structures.[4] Here the appropriate comparison is with clusters **2** and **3**, which are not localized and have Fe mean oxidation states of +2.50 and +2.25, respectively. Mean values of terminal distances are 2.25–2.26 Å for **2**[9] and 2.30 Å for **3**.[11] The corresponding value for $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ is 2.268 Å (Table III), showing that Fe(5,6) are best not regarded as Fe(II) or as Fe(III). Any other division of Fe atoms into sets of two and four with different oxidation states also cannot be supported by the structural data. This conclusion is sustained by ^{57}Fe isomer shifts[17] whose values (δ +0.28, +0.29 mm/s) for the two overlapping quadrupole doublets observed adhere to the linear correlation of δ with (mean) oxidation states in tetrahedral FeS_4 sites.[31] Electron delocalization is a property of all mixed-valence Fe/S/SR clusters except $[Fe_2S_2(SR)_4]^{3-}$, the one-electron reduction product of **1**, whose spectroscopic properties are consistent with the presence of antiferromagnetically coupled, localized Fe(II,III) sites.[32]

Further scrutiny of the $[Fe_6S_9]^{2-}$ core reveals the presence of certain structural fragments besides **6** and **8** that upon terminal thiolate coordination might be capable of independent existence. These are shown in schematic form in Figure 3. Fragment **9** is in fact the core unit of $[Fe_3S_4(SR)_4]^{3-}$.[16] Its isomeric form **10**, which is the core of **2** minus one Fe atom, is unknown in other compounds as is **8** and the linear tetranuclear fragment **11**. The latter is in principle derivable from **12**, which occurs as the discrete ion $[Fe_2S_6]^{6-}$ in Na_3FeS_3.[33] The occurrence of **6** as the core of **1** has already been noted. With a single exception all synthetic and native Fe/S/SR clusters in which thiolates are terminal ligands only[34] contain as the fundamental structural building block subunit **6**; in these cases Fe···Fe distances are 2.7–2.8 Å.[4,33] The exception is the 3-Fe site in *A. vinelandii* Fd I. Here the Fe_3S_3 core is described as having the twist-boat conformation and Fe···Fe distances are 4.2–4.4 Å.[12] An acceptable synthetic analogue of the protein site must possess or closely approach these structural features. Our experience in the synthetic and structural chemistry of Fe/S/SR clusters clearly suggests that species such as **4** and **5**, not composed of Fe_2S_2 units or otherwise not having Fe···Fe separations in the preceding range, may be unstable toward those clusters that have one or both properties.

Spectroscopic and Redox Properties. In order to characterize further $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ and assess its stability in anaerobic solutions, we determined certain fundamental properties. Of various aprotic solvents Me_2SO has been found to provide the best combination of solubility and stability; it has been employed as the solvent in determining the cluster properties that follow. The UV/visible spectrum of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$, shown in Figure 5, contains bands at 319, 412, and ~530 (sh) nm. The spectrum bears some resemblance to that of $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$ (λ_{max} (ϵ_M) 303 (19 600), 419 (15 900) nm in Me_2SO) but is readily distinguished from it by the band profile[9b] and the prominent shoulder at ~530 nm. Further, the spectrum bears no resemblance to those of the reduced clusters **3** ($[Fe_4S_4(SCH_2Ph)_4]^{3-}$, 358 (17 600) nm in

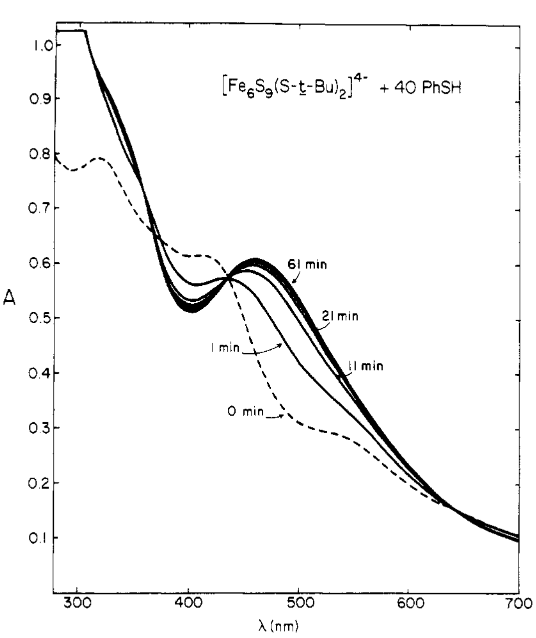

Figure 5. Time dependence of absorption spectra of a reaction system in Me_2SO solution initially containing 2.4 mM $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$, to which 40 equiv of benzenethiol was added. The spectrum at 0 min refers to a solution with no added thiol.

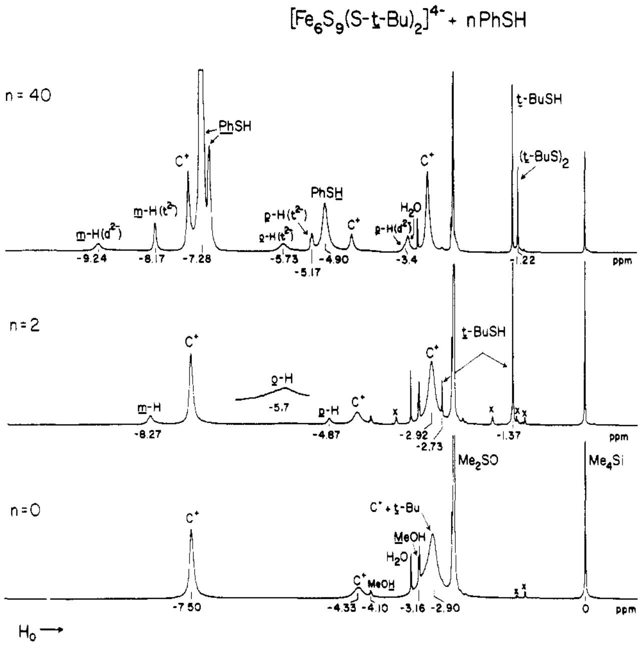

Figure 6. ^1H NMR spectra (300 MHz, ~296 K) of a 6.8 mM solution of $[Me_3NCH_2Ph]_4[Fe_6S_9(S\text{-}t\text{-}Bu)_2]$ in $Me_2SO\text{-}d_6$ to which n = 2 and 40 equiv of benzenethiol was added. Signal assignments are indicated as follows: d^{2-}, $[Fe_2S_2(SPh)_4]^{2-}$; t^{2-}, $[Fe_4S_4(SPh)_4]^{2-}$; C^+, cation (×, impurity). The upper two spectra were recorded 60–90 min after addition of thiol.

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(34) Very recently the trinuclear Fe(II) complex $[Fe_3S(S_2\text{-}o\text{-}xylMe_2)_3]^{2-}$ (S_2-*o*-xylMe$_2$ = 4,5-dimethyl-*o*-xylyl-α,α'-dithiolate) has been described.[35a] It is the only synthetic or native Fe/S/SR species with an atom ratio Fe:S > 1. The complex has idealized C_{3v} symmetry, with each thiolate ligand furnishing a bridging and a terminal sulfur atom, and it contains a pyramidal $[Fe_3(\mu_3\text{-}S)]^{4+}$ core having a mean Fe···Fe distance of 2.799 Å. Prior to the report of this complex we had synthesized and characterized the isostructural Co(II) analogue, $[Co_3S(S_2\text{-}o\text{-}xyl)_3]^{2-}$, and thereafter have prepared $[Fe_3S(S_2\text{-}o\text{-}xyl)_3]^{2-}$ by a rational route.[35b]

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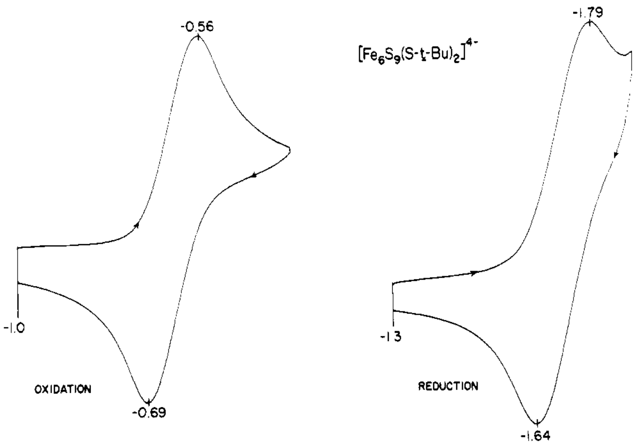

Figure 7. Cyclic voltammograms (100 mV s^{-1}) illustrating the oxidation and reduction reactions of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ in Me_2SO solution. Peak potentials vs. SCE are given.

acetonitrile[36]) or the binuclear species **1** ($[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$, five bands at 290–600 nm in Me_2SO[6]) with alkylthiolate ligands. As with **1**–**3** the bands presumably arise from thiolate → core charge-transfer excitations. The ^1H NMR spectrum of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$, given in Figure 6, contains in addition to resolved cation and methanol solvate resonances a broad feature at −2.90 ppm. This arises from coincident cation methyl and cluster *t*-Bu group resonances and corresponds to an isotropic shift of the latter of −1.5 ppm. This shift arises from the paramagnetism of the cluster whose magnetic moment is 2.74 μ_B in solution at 299 K. The value of 1.12 μ_B/Fe atom is similar to those of **1** and **2** (1.0–1.4 μ_B, ~300 K), which exhibit antiferromagnetic spin coupling;[11a,37] similar interactions are probable in $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$. As shown by the cyclic voltammetric results in Figure 7, the cluster exhibits the three-membered electron-transfer series (3), in which the

$$[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{3-} \underset{}{\overset{-0.63\ V}{\rightleftharpoons}} [Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-} \overset{-1.72\ V}{\rightleftharpoons} [Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{5-} \quad (3)$$

steps are essentially chemically reversible from the criterion $i_{pc}/i_{pa} \cong 1$. No other equivalently reversible reactions were observed outside of the −0.3 to −1.9 V interval of Figure 7. The indicated $E_{1/2}$ values do not correspond to those of $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$, which in DMF solution undergoes two reductions at −1.42 (2−/3−) and −2.16 V (3−/4−) and one oxidation (2−/1−) at −0.12 V.[38] The clusters **1** show two reductions (2−/3−, 3−/4−) at −1.0 to −1.8 V in aprotic solvents[6,23,32] but no reversible oxidation reactions. The foregoing properties collectively demonstrate that $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ does not degrade to the previously characterized clusters **1**–**3** in Me_2SO solution and provide presumptive evidence for maintenance of the crystalline state structure in solution.

A number of attempts to isolate the 3− cluster in series 3 by reactions of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ with one-electron oxidants resulted in cluster degradation, a problem not encountered on the shorter time scale of cyclic voltammetry. Owing to the very negative potential of the 4−/5− reaction, no attempt has been made to isolate the extremely oxidatively sensitive reduced cluster. Consequently, further investigation of the clusters in series 3 has been confined to the 4− species.

Ligand Substitution and Cluster Degradation Reactions. A significant property of clusters **1** and **2** is the ligand substitution reaction (4),[6,9b,39,40] which is the basis for the core extrusion

$$[Fe_nS_n(SR)_4]^{2-} + 4R'SH \rightarrow [Fe_nS_n(SR')_4]^{2-} + 4RSH \quad (4)$$
$$(n = 2,4)$$

$$[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-} + 2PhSH \rightarrow [Fe_6S_9(SPh)_2]^{4-} + 2t\text{-}BuSH \quad (5)$$

method of identification of $[Fe_nS_n]^{2+}$ units in proteins.[4,39,40] A corresponding reaction (5) of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ has been demonstrated. Addition of 2 equiv of benzenethiol to a solution of the cluster in Me_2SO, under reduced pressure to remove liberated *t*-BuSH, yields $[Fe_6S_9(SPh)_2]^{4-}$. This cluster has not been isolated but it has been identified by the following observations. (i) The absorption spectrum (λ_{max} (ϵ_M) 300 (40 000), ~350 (sh, 32 000), ~420 (sh, 25 200), ~530 (sh, 14 100) nm) is similar to that of the starting cluster but is shifted to lower energies. (ii) The NMR spectrum of the 2-equiv reaction system (Figure 6) reveals a sharpening and decreased intensity of the −2.90-ppm resonance, signals of released *t*-BuSH at −2.73 and −1.37 ppm, and one set of three isotropically shifted resonances at −8.27, −5.7 (br), and −4.87 ppm. From relative intensities and line widths these are unambiguously assigned to *m*-, *o*-, and *p*-H, respectively, of coordinated benzenethiolate. The signs and magnitudes of the isotropic shifts (*o*-H, +1.6; *m*-H, −0.97; *p*-H, +2.43 ppm) are consistent with a contact mechanism.[41] (iii) The reaction product shows one oxidation and one reduction reaction with $E_{1/2} = -0.50$ and −1.57 V, respectively, indicating a series analogous to (3). Properties i–iii are not those of $[Fe_2S_2(SPh)_4]^{2-}$[6,23] or $[Fe_4S_4(SPh)_4]^{2-,3-}$[36,38,41] and are entirely consistent with the occurrence of reaction 5, in which the $[Fe_6S_9]^{2-}$ core structure remains intact.

When a large excess of thiol over that required in reaction 5 is introduced, the core structure of $[Fe_6S_9(SPh)_2]^{4-}$ is ruptured. Addition of ≥27.5 equiv of benzenethiol to a solution of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ in Me_2SO results in a reaction that is complete in 70 min or less. Absorption spectral changes of a reaction system with 40 equiv, presented in Figure 5, culminate with formation of a chromophore whose band maximum (458 nm) is coincident with that of pure $[Fe_4S_4(SPh)_4]^{2-}$ in Me_2SO. If this cluster is assumed to be the only reaction product absorbing significantly at 458 nm, it is formed in ≥96% yield based on total Fe. With ≲20 equiv of thiol, limiting spectra, obtained in 2–3 h, indicate incomplete reaction. The limiting spectrum in Figure 5 does not, however, correspond to $[Fe_4S_4(SPh)_4]^{2-}$ as the only visible chromophore. The absorbance ratio $A_{458}/A_{550} = 1.68$ deviates from the value (2.18) for pure $[Fe_4S_4(SPh)_4]^{2-}$, indicating the presence of another (minor) product. Spectra of solutions from the core extrusion reaction of a ~2:1 mixture of proteins with 4-Fe and 2-Fe sites give nearly the same absorbance ratio.[39]

The 40-equiv reaction system has been further examined by NMR spectroscopy in an attempt to detect additional reaction products. The spectrum after completion of the reaction (Figure 6) is devoid of the resonances of $[Fe_6S_9(SPh)_2]^{4-}$. Formation of $[Fe_4S_4(SPh)_4]^{2-}$ (t^{2-}) is confirmed by the appearance of signals at −8.17 (*m*-H), −5.73 (*o*-H), and −5.17 (*p*-H) ppm.[41] Also detected as a reaction product is $[Fe_2S_2(SPh)_4]^{2-}$ (d^{2-}), on the basis of the resonance at −9.24 ppm (*m*-H) and the partially resolved feature at −3.4 ppm (*p*-H).[23]

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The broad *o*-H signal expected near −4.9 ppm[23] is obscured by the free thiol signal. From the relative intensities of *m*-H signals the ratio t^{2-}:d^{2-} is ~1.8:1. This value requires a net decrease in Fe atom mean oxidation state upon product formation, accounting for the appearance of disulfide in the spectrum. Formation of $[Fe_2S_2(SPh)_4]^{2-}$ could not be directly detected in spectrophotometric experiments because its visible spectrum (λ_{max} (ϵ_M) 493 (11 600) nm in Me_2SO[6]) is obscured by the more intense 458-nm absorption.

In contrast to the results with benzenethiol, treatment of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ with ≥30 equiv of 1,1-dimethylethanethiol gave no reaction and with 40 equiv of ethanethiol afforded a product with a broad, isotropically shifted resonance at −15.8 ppm. This signal does not correspond to that of $[Fe_4S_4(SEt)_4]^{2-}$ (−12.5 ppm in Me_2SO[42]) and is assigned to the methylene protons of $[Fe_6S_9(SEt)_2]^{4-}$. These observations suggest that core disruption may require protonation of core sulfur atoms, a process facilitated by the more acidic nature of aryl vs. alkyl thiols.

Summary. The species $[Fe_6S_9(SR)_2]^{4-}$ represents a fourth characterized structural type of Fe/S/SR clusters. With inclusion of $[Fe_6S_8(PEt_3)_6]^{2+}$ these Fe–S core units having the indicated (idealized) symmetries have now been established: $[Fe_2S_2]^{2+}$ (D_{2h}[6-8]), $[Fe_4S_4]^{2+}$ (D_{2d}[9,10]), $[Fe_4S_4]^{+}$ (D_{2d},[11a] C_{2v}[11b]), $[Fe_6S_8]^{2+}$ (O_h[15]), $[Fe_3S]^{4+}$ (C_{3v}[35]), $[Fe_6S_9]^{2-}$ (C_{2v}). All but $[Fe_3S]^{4+}$ may be regarded as constructed of planar or nonplanar Fe_2S_2 units **6**. The clusters $[Fe_6S_9(SR)_2]^{4-}$ exhibit certain properties in common with **1**–**3**: (i) visible RS → core charge-transfer spectra, which shift to lower energies when R = aryl vs. alkyl; (ii) antiferromagnetically coupled Fe sites; (iii) contact-shifted ^1H NMR spectra; (iv) electron-transfer series whose members are interrelated by chemically reversible one-electron reactions with potentials less negative for R = aryl vs. alkyl; (v) electronically delocalized structures in mixed-valence clusters as revealed by Mössbauer spectroscopy and the absence of structurally distinct Fe(II,III) sites from X-ray diffraction results; (vi) facile thiolate substitution reactions with retention of core structure. That disruption of the $[Fe_6S_9]^{2-}$ core with large excesses of benzenethiol produces $[Fe_2S_2(SPh)_4]^{2-}$ and $[Fe_4S_4(SPh)_4]^{2-}$ is not surprising in view of the stability of their core structures containing the unit **6**. Lastly, as observed in our initial report[17] of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{2-}$, the Fe_6S_9 core may be considered a candidate for structurally uncharacterized redox sites in Fe–S proteins. As with clusters containing Fe_2S_2 and Fe_4S_4 (but not as yet Fe_3S_3) cores, it can be readily assembled from simple reactants in a manner similar to the reconstitution of protein 2-Fe and 4-Fe sites with Fe(II,III) and sulfide reagents. However, as yet no analytically well-characterized proteins with the ratio S^{2-}:Fe > 1 are known, and we are not aware of any protein with an absorption spectrum closely similar to that of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$ (Figure 5). The synthesis and properties of a fifth structural type of Fe/S/SR clusters, $[Fe_3S_4(SR)_4]^{3-}$ containing the core unit **9**, will be described elsewhere.[16]

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Registry No. $(Me_3NCH_2Ph)_4[Fe_6S_9(S\text{-}t\text{-}Bu)_2]\cdot MeOH$, 80976-82-5; benzenethiol, 108-98-5.

Supplementary Material Available: Positional and thermal parameters of all non-hydrogen atoms, bond distances and angles for cations and methanol solvate molecules, and calculated and observed structure amplitudes (24 pages). Ordering information is given on any current masthead page.

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Metal Complexes Containing Diastereoisomers and Enantiomers of *o*-Phenylenebis(methylphenylarsine) and Its Phosphorus Analogue. 3. Preparation and Stereochemistry of Octahedral Bis(bidentate)dichlororuthenium(II) Complexes

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A detailed investigation of the stereochemistry of *cis*- and *trans*-$[RuCl_2(\text{bidentate})_2]$ containing the diastereoisomers and enantiomers of *o*-phenylenebis(methylphenylarsine) and its phosphorus analogue has been undertaken. The trans complexes were prepared in high yield from the ligands and a prereduced form of commercial ruthenium(III) chloride in the presence of aqueous formaldehyde. The optically active, racemic, meso, syn, and anti forms of the *trans*-dichloro complexes were isolated for both ligands, and each of these was subsequently isomerized to the corresponding cis compound by reaction with triethylaluminum. The various diastereoisomeric *cis*-dichloro compounds were also separated and characterized. Whereas the *trans*-dichloro isomers were relatively inert, the cis complexes readily underwent stereospecific halogen substitution by iodide ions and carbon monoxide.

Introduction

Bivalent ruthenium forms stable octahedral complexes containing chelating di(tertiary arsines) and phosphines of the type *cis*- and *trans*-$[RuX_2(\text{bidentate})_2]$. In general, symmetrical bidentates have been employed as ligands,[2,3] although an investigation of the stereochemistry of trans complexes derived from 1,2-bis(methylphenylphosphino)ethane has been carried out by Horner and co-workers.[4] We have emphasized elsewhere[5,6] the value of using dissymmetric bidentates in their different stereoisomeric forms as probes for investigating the

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