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Sterically Encumbered Iron(II) Thiolate Complexes: Synthesis and Structure of Trigonal Planar $[\mathrm{Fe(SR)_3}]^-$ (R = 2,4,6-t-$\mathrm{Bu_3C_6H_2}$) and Mössbauer Spectra of Two- and Three-Coordinate Complexes

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The synthesis and structural characterization of three compounds containing three-coordinate Fe(II) and stabilized by sterically encumbered thiolate ligands are reported. Reaction of $[\mathrm{Fe_2(SC_6H_2\text{-}2,4,6\text{-}}t\text{-}\mathrm{Bu_3)_4}]$ (**3**) with $\mathrm{LiSC_6H_2\text{-}2,4,6\text{-}}t\text{-}\mathrm{Bu_3}$ in ether/THF/hexane afforded $[\mathrm{Li(THF)_2(\mathbf{5})]\cdot 0.5C_6H_{14}}$ ($\mathbf{5} = [\mathrm{Fe(SC_6H_2\text{-}2,4,6\text{-}}t\text{-}\mathrm{Bu_3)_3}]^-$). Addition of $\mathrm{Ph_4PCl}$ to a reaction mixture in toluene followed by recrystallization of the product from acetonitrile yielded $\mathrm{(Ph_4P)[\mathbf{5}]\cdot 2MeCN\cdot C_7H_8}$. The compound $[\mathrm{Fe_3(SC_6H_2\text{-}2,4,6\text{-}}i\text{-}\mathrm{Pr_3)_4(N(SiMe_3)_2)_2}]$ (**6**) was prepared by the reaction of $[\mathrm{Fe(N(SiMe_3)_2)_2}]$ with the thiol in toluene. $[\mathrm{Li(THF)_2(\mathbf{5})]\cdot 0.5C_6H_{14}}$ crystallizes in monoclinic space group $P2_1/c$ with $a = 9.809(2)$ Å, $b = 22.507(5)$ Å, $c = 29.553(5)$ Å, $\beta = 95.72(2)°$, and $Z = 4$ (130 K). $\mathrm{(Ph_4P)[\mathbf{5}]\cdot 2MeCN\cdot C_7H_8}$ was obtained in monoclinic space group $P2_1$ with $a = 17.538(5)$ Å, $b = 14.912(4)$ Å, $c = 17.608(5)$ Å, $\beta = 115.71(3)°$, and $Z = 2$ (143 K). These compounds contain the first example of mononuclear Fe(II) in a close approach to a trigonal planar [**5**] or a distorted trigonal planar $[\mathrm{Li(THF)_2(\mathbf{5})}]$ sulfur coordination environment. In the $\mathrm{Ph_4P}$ salt, [**5**] exhibits the mean values Fe−S = 2.274(9) Å and S−Fe−S = 120(3)°, while in $[\mathrm{Li(THF)_2(\mathbf{5})}]$ the $\mathrm{Li^+}$ ion bridges two sulfur atoms, causing a lengthening (0.06−0.07 Å) of the Fe−S bridged bond lengths and constriction of the bridged S−Fe−S angle (92.2(1)°). Compound **6** crystallizes in $P2_1/c$ with $a = 14.521(5)$ Å, $b = 41.60(2)$ Å, $c = 14.241(4)$ Å, $\beta = 100.42(2)°$, and $Z = 4$ (130 K). The structure has a linear $\mathrm{Fe_3(\mu_2\text{-}SR)_4}$ fragment with an almost linear $\mathrm{Fe_3}$ array involving the central Fe(II) atom in a severely distorted tetrahedral environment; the terminal Fe(II) atoms are three-coordinate and planar with terminal $\mathrm{N(SiMe_3)_2}$ ligands. Complex **5** expands the family of homoleptic molecular Fe(II) thiolates to five structural types; complexes **5** and **6** with two previously reported species of the type $[\mathrm{Fe_2(SR)_4}]$ constitute the known examples of three-coordinate $\mathrm{Fe^{II}}$ with partial or complete sulfur ligation. The zero-field Mössbauer spectra of examples of the five types of homoleptic Fe(II) thiolates are reported together with several tetrahedral complexes having $\mathrm{Fe^{II}}$−S/SR coordination in order to determine what structural distinctions could be made from isomer shifts and quadrupole splittings. From the limited data set, it is tentatively concluded that trigonal planar $\mathrm{Fe^{II}(SR)_3}$ can be distinguished from tetrahedral $\mathrm{Fe^{II}(SR)_4}$ and $\mathrm{Fe^{II}}$−S/SR units on the basis of its smaller quadrupole splitting (0.81 mm/s for **5** at 4.2−100 K).

Introduction

The synthesis and spectroscopy of iron−thiolate complexes have been extensively studied, in large measure because of the ubiquitous presence of iron−sulfur coordination in a wide variety of proteins and enzymes.[2] For example, the complexes $[\mathrm{Fe(SR)_4}]^{-,2-}$ are informative synthetic analogues of the coordination units in oxidized and reduced rubredoxins.[3−7] To date, the vast majority of native coordination sites contain tetrahedral Fe(II,III) with exclusive cysteinyl (rubredoxins) or sulfido/cysteinyl binding. One remarkable exception is the distorted trigonal Fe−sulfido coordination which defines the geometry of six of the seven Fe atoms in the FeMo cofactor of nitrogenase.[8] Given this precedent, it is perhaps not implausible that other stereochemically unusual biological Fe−S coordination sites will be discovered in as yet uncharacterized metallobiomolecules.

The family of homoleptic molecular iron thiolates is currently composed of the types $[\mathrm{Fe^{II}(SR)_2}]$,[9] $[\mathrm{Fe^{II}(SR)_4}]^{2-}$,[3,4,6,10,11] $[\mathrm{Fe^{III}(SR)_4}]^-$,[3,5,12] $[\mathrm{Fe^{II}_2(SR)_4}]$,[13,14] $[\mathrm{Fe^{III}_2(SR)_8}]^{2-}$,[15] $[\mathrm{Fe^{II}_2(SR)_6}]^{2-}$,[16,17] and $[\mathrm{Fe^{II}_4(SR)_{10}}]^{2-}$.[16,18] Of these, all but two contain Fe(II), all but $[\mathrm{Fe(SR)_2}]$, $[\mathrm{Fe_2(SR)_4}]$, and $[\mathrm{Fe_2(SR)_8}]^{2-}$

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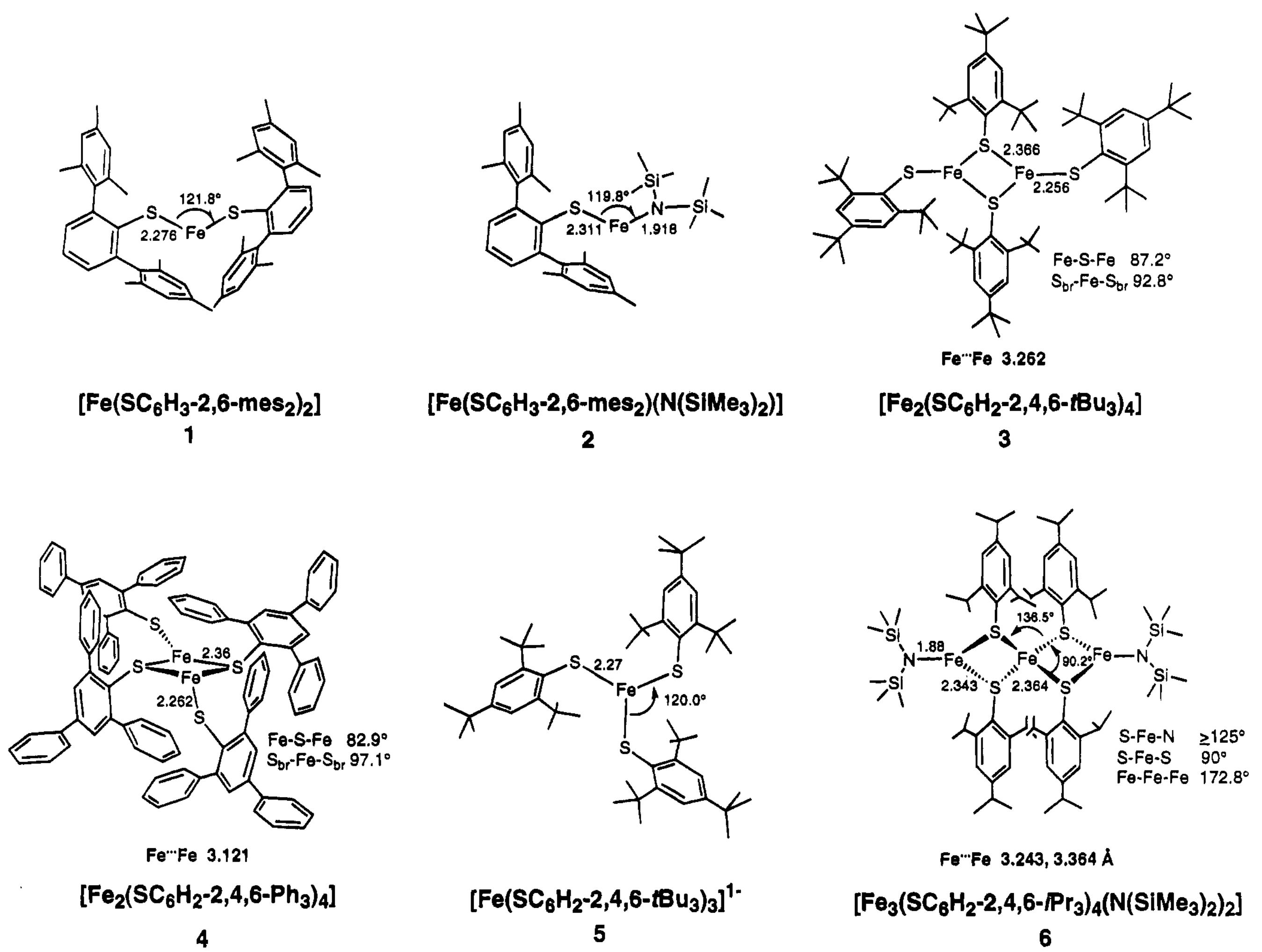

$[Fe(SC_6H_3\text{-}2,6\text{-}mes_2)_2]$
1

$[Fe(SC_6H_3\text{-}2,6\text{-}mes_2)(N(SiMe_3)_2)]$
2

$[Fe_2(SC_6H_2\text{-}2,4,6\text{-}tBu_3)_4]$
3

$[Fe_2(SC_6H_2\text{-}2,4,6\text{-}Ph_3)_4]$
4

$[Fe(SC_6H_2\text{-}2,4,6\text{-}tBu_3)_3]^{1-}$
5

$[Fe_3(SC_6H_2\text{-}2,4,6\text{-}iPr_3)_4(N(SiMe_3)_2)_2]$
6

Figure 1. Schematic structures of two-coordinate (**1**, **2**)[9] and three-coordinate (**3**,[13] **4**,[14] **5**, **6**) Fe(II) thiolate complexes. Selected bond distances (Å) and angles are indicated.

exhibit tetrahedral coordination, and all bi- and tetranuclear species are antiferromagnetically coupled. The binuclear Fe(III) complex is five-coordinate and is known only with chelating dithiolates. In the foregoing context, we have become interested in Fe−thiolate species with low coordination numbers. As shown in Figure 1, such complexes can be realized by employing 2,6-di- and 2,4,6-trisubstituted benzenethiolate ligands with exceptional steric demands, such that no combination of terminal and bridging interactions involving thiolate ligands alone permits an $Fe(SR)_4$ coordination unit.[19] Thus, complexes **1** and **2** are nominally two-coordinate but include weak interactions with adjacent phenyl rings at Fe−C distances of *ca.* 2.5 Å.[9] Complexes **3** and **4** are centrosymmetric with planar Fe_2S_2 rhombs; their Fe(II) atoms are three-coordinate with relatively close Fe···H and Fe···C interactions, exhibit irregular bond angles (93−138° (**3**), 97−130° (**4**)), and are displaced from their S_3 planes by 0.297 Å (**3**) and 0.471 Å (**4**).

Here we augment the series of low-coordinate Fe(II) thiolates with the synthesis and structure of a new type, $[Fe(SR)_3]^-$, stabilized by a sterically encumbering ligand. Also reported is a similarly stabilized trinuclear complex of the type $[Fe_3(SR)_4(N(SiMe_3)_2)_2]$. Of the various spectroscopic properties of mono- and polynuclear Fe−SR and Fe−S/SR complexes, isomer shifts (δ) and quadrupole splittings (ΔE_Q) of ^{57}Fe Mössbauer spectra are particularly effective in deducing oxidation states. This is especially so for the cuboidal $[Fe_3S_4]$ and cubane-type $[Fe_4S_4]$ and heterometal $[MFe_3S_4]$ clusters,[20] which are often electronically delocalized but display a linear relationship between (mean) Fe oxidation state and isomer shift.[21] Further, oxidation states of protein coordination sites have on occasion been determined by comparison of Mössbauer parameters with those of synthetic compounds with defined oxidation states. In view of the absence of such parameters for low-coordinate Fe(II) in a sulfur environment, we have determined the zero-field Mössbauer spectra of complexes **1**−**5** (Figure 1) and report the results here.

Experimental Section

Preparation of Compounds. All reactions were performed under a pure dinitrogen atmosphere using either modified Schlenk techniques or a Vacuum Atmospheres HE 43-2 drybox. The solvents *n*-hexane and THF were freshly distilled from a Na/K alloy; acetonitrile was dried over CaH_2. All solvents were twice-degassed before use. Commercial Ph_4PCl was dried at 0.01 mmHg/100 °C for 24 h. The compounds $[Fe(SC_6H_3\text{-}2,6\text{-}Mes_2)_2]$[9] (Mes = mesityl), $[Fe(SC_6H_3\text{-}2,6\text{-}$

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Table 1. Crystallographic Data

	[Li(THF)$_2$(**5**)]·0.5C$_6$H$_{14}$	(Ph$_4$P)[**5**]·2MeCN·C$_7$H$_8$	**6**
formula	C$_{65}$H$_{110}$FeLiO$_2$S$_3$	C$_{89}$H$_{121}$FeN$_2$PS$_3$	C$_{72}$H$_{128}$Fe$_3$N$_2$S$_4$Si$_4$
fw	1082.5	1401.9	1429.9
color, habit	yellow plates	yellow blocks	dark red parallelpipeds
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1$	$P2_1/c$
a, Å	9.809(2)	17.538(5)	14.521(5)
b, Å	22.507(5)	14.912(4)	41.60(2)
c, Å	29.553(5)	17.608(5)	14.241(4)
β, deg	95.72(2)	115.71(3)	100.42(2)
V, Å^3	6492(4)	4149(3)	8462(6)
Z	4	2	4
temp, K	130	143	130
radiation	Cu Kα (λ = 1.541 78 Å)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
cryst dimens, mm	0.08 × 0.15 × 0.80	0.64 × 0.5 × 0.46	0.15 × 0.25 × 0.40
d_{calc}, g cm^{-3}	1.104	1.117	1.122
μ, mm^{-1}	3.046	0.32	5.798
no. of obsd rflcns	3797 ($I > 3.5\sigma(I)$)	7411 ($I > 2\sigma(I)$)	5937 ($I > 2\sigma(I)$)
R, R_w[a]	0.095, 0.097	0.056, 0.063	0.048, 0.048

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o|^2 - |F_c|^2)/\sum w|F_o|^2]^{1/2}$.

Table 2. Selected Atom Coordinates (×10^4)

atom	x	y	z
	[Li(THF)$_2$(**5**)]·0.5C$_6$H$_{14}$		
Fe	2345(2)	1403(1)	1960(1)
S(1)	3746(3)	2100(2)	2304(1)
S(2)	1684(3)	994(1)	1254(1)
S(3)	1609(3)	569(1)	2337(1)
Li	1395(22)	−48(10)	1617(7)
O(1)	19(9)	−384(4)	1184(3)
O(2)	2813(8)	−655(4)	1785(3)
C(1)	3280(12)	2807(6)	2023(4)
C(19)	2415(12)	1314(5)	773(4)
C(37)	638(11)	803(5)	2769(4)
	(Ph$_4$P)[**5**]·2MeCN·C$_7$H$_8$		
Fe(1)	8135(1)	0	1429(1)
S(1)	9568(1)	72(1)	2067(1)
S(2)	7367(1)	12(1)	2187(1)
S(3)	7507(1)	−39(1)	−11(1)
C(1)	10079(3)	53(4)	3204(3)
C(19)	6244(3)	−5(5)	1554(3)
C(37)	8230(3)	−34(4)	−479(2)
P(1)	6449(1)	1096(1)	4890(1)
C(55)	6387(3)	570(4)	5783(3)
C(61)	5494(3)	875(4)	3953(3)
C(67)	7343(3)	637(4)	4781(3)
C(73)	6561(3)	2288(4)	5078(3)
	Complex **6**		
Fe(1)	4203(1)	3823(1)	6597(1)
Fe(2)	2325(1)	3845(1)	4972(1)
Fe(3)	383(1)	3767(1)	3297(1)
S(1)	3003(1)	4202(1)	6190(1)
S(2)	3580(1)	3476(1)	5352(1)
S(3)	1028(1)	3500(1)	4717(1)
S(4)	1597(1)	4145(1)	3612(1)
N(1)	5270(3)	3739(1)	7545(3)
N(2)	−659(3)	3631(1)	2400(3)
C(1)	2358(4)	4328(1)	7081(4)
C(16)	4269(4)	3373(1)	4468(4)
C(31)	346(4)	3409(1)	5606(4)
C(46)	239(4)	4238(1)	2744(4)

Mes$_2$)(N(SiMe$_3$)$_2$)],[9] [Fe$_2$(SC$_6$H$_2$-2,4,6-t-Bu$_3$)$_4$],[13] [Fe$_2$(SC$_6$H$_2$-2,4,6-Ph$_3$)$_4$,[14] (Et$_4$N)$_2$[Fe(SEt)$_4$],[10] (Pr$_4$N)[Fe(SEt)$_4$],[12] (Et$_4$N)$_2$[Fe$_2$(SEt)$_6$],[16] and (Me$_4$N)$_2$[Fe$_4$(SEt)$_{10}$][16] were prepared as described.

[Li(THF)$_2$Fe(SC$_6$H$_2$-2,4,6-t-Bu$_3$)$_3$]·0.5C$_6$H$_{14}$. A solution of 2,4,6-t-Bu$_3$C$_6$H$_2$SH[22] (0.56 g, 2.00 mmol) in a mixture of diethyl ether (20 mL) and THF (5 mL) was cooled in an ice bath. It was treated with 1.25 mL (2.00 mmol) of a 1.6 M solution of n-BuLi in hexane and stirred for 2 h at ambient temperature. A solution of [Fe$_2$(SC$_6$H$_2$-2,4,6-t-Bu$_3$)$_4$] (1.22 g, 2.00 mmol) in diethyl ether (20 mL) was added dropwise to the solution of the lithium thiolate. The red-brown reaction mixture was stirred for 18 h, during which the color became dark yellow. The solvents were removed under reduced pressure, the residue was extracted with n-hexane (50 mL), and the extract was filtered. Reduction of the filtrate volume to *ca.* 15 mL and storage of the solution at −20 °C resulted in the separation of the product as extremely moisture- and dioxygen-sensitive yellow needles (0.89 g, 43%). Mp: dec >100 °C to a dark brown solid which melts at 185 °C. Magnetic moment: $\mu_{\text{eff}} = 4.80\,\mu_B$ (298 K). IR spectrum (Nujol): 1588 m, 1258 m, 1238 m, 1208 m, 1180 w, 1152 w, 1060 w, br, 1032 st, 1028 sh, 872 st, 800 w, br, 749 m, 720 st, 642 w, 603 w, 408 w, 376 m, 334 w cm^{-1}. Anal. Calcd for C$_{65}$H$_{110}$FeLiO$_2$S$_3$: C, 72.12; H, 10.24. Found: C, 72.46; H, 10.53. The compound was additionally characterized by an X-ray structure determination.

(Ph$_4$P)[Fe(SC$_6$H$_2$-2,4,6-t-Bu$_3$)$_3$]·2MeCN·C$_7$H$_8$. A solution of 2,4,6-t-Bu$_3$C$_6$H$_2$SH[22] (0.56 g, 2.00 mmol) in toluene (20 mL) was treated with 1.25 mL (2.00 mmol) of a 1.6 M solution of n-BuLi in hexane and stirred for 2 h at ambient temperature. The pale yellow solution was added dropwise to a solution of [Fe$_2$(SC$_6$H$_2$-2,4,6-t-Bu$_3$)$_4$] (1.22 g, 2.00 mmol) in toluene (20 mL). The mixture was stirred for 2 h and added to a suspension of Ph$_4$PCl (0.75 g, 2.00 mmol) in toluene (20 mL). The mixture was stirred overnight to give a dark yellow precipitate which was almost completely redissolved by the addition of *ca.* 10 mL of acetonitrile. The cloudy solution was filtered through a Celite-padded frit and concentrated to *ca.* 30 mL. Storage of the filtrate at −20 °C overnight afforded the product as yellow crystals (1.06 g, 49%). Mp: dec >95 °C to a dark brown oil. Magnetic moment: $\mu_{\text{eff}} = 5.05\,\mu_B$ (298 K). IR (Nujol): 1585 w, 1348 m, 1335 sh, 1309 w, 1278 w, 1258 w, 1235 m, 1206 m, 1102 s, 1030 s, 990 m, 872 m, 752 m, 748 m, 722 s, 686 st, 522 s, 356 m cm^{-1}. Anal. Calcd for C$_{89}$H$_{121}$FeN$_2$PS$_3$: C, 76.25; H, 8.70; N, 2.00. Found: C, 76.41; H, 8.51; N, 1.96. The compound was additionally characterized by an X-ray structure determination.

[Fe$_3$(SC$_6$H$_2$-2,4,6-i-Pr$_3$)$_4$(N(SiMe$_3$)$_2$)$_2$]. To a solution of 2,4,6-i-Pr$_3$C$_6$H$_2$SH[23] (0.96 g, 4.00 mmol) in toluene (20 mL) was added dropwise 2.05 mL of 1.47 M solution of [Fe(N(SiMe$_3$)$_2$)$_2$][19a] in hexane. The solution immediately became red-brown and was stirred for 18 h. Hexane (5 mL) was added, and the solution was filtered. Storage of the filtrate at −20 °C for several days caused separation of the product as dark red, almost black, crystals (0.51 g, 36%). Magnetic moment: $\mu_{\text{eff}} = 6.15\,\mu_B$. IR (Nujol): 1592 m, 1560 m, 1248 m, 1162 m, 1151 m, 1100 m, 1050 sh, 1055 s, 1030 s, 955 w, 936 m, 920 w, 872 s, 839 w, 749 m, 648 m, 635 m, 518 w, 455 w, 410 w, 387 w, 300 s. Anal. Calcd for C$_{72}$H$_{128}$Fe$_3$N$_2$S$_4$Si$_4$: C, 60.47; H, 9.04; N, 1.96. Found: C, 60.81; H, 8.91; N, 1.91. The compound was additionally characterized by an X-ray structure determination.

X-ray Crystallographic Studies. X-ray-quality crystals were grown from hexane/THF ([Li(THF)$_2$Fe(SC$_6$H$_2$-2,4,6-t-Bu$_3$)$_3$]·0.5C$_6$H$_{14}$) and

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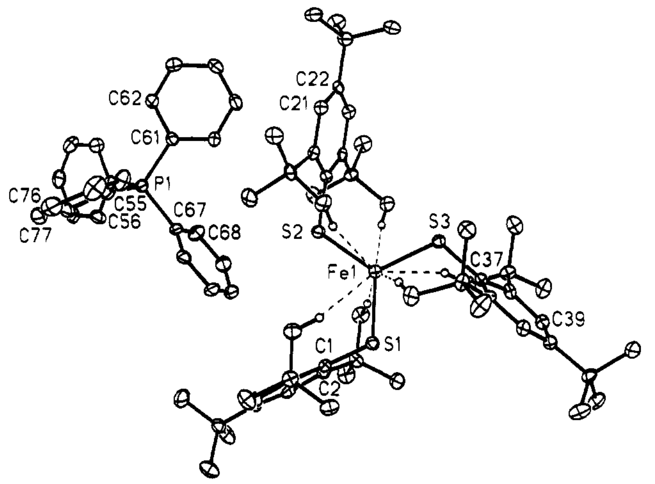

Figure 2. Structure of $(Ph_4P)[5]$ as the bis(acetonitrile)−mono(toluene) solvate, showing 30% thermal ellipsoids and the atom-labeling scheme.

acetonitrile/toluene ($(Ph_4P)[Fe(SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_3]\cdot 2MeCN\cdot C_7H_8$) solutions. Suitable crystals of $[Fe_3(SC_6H_2\text{-}2,4,6\text{-}i\text{-}Pr_3)_4(N(SiMe_3)_2)]$ were obtained from the preparative crystallization. Crystals were removed from Schlenk tubes and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in a low-temperature nitrogen stream, as described.[24] The data for $[Li(THF)_2Fe(SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_3]\cdot 0.5C_6H_{14}$ were collected at 130 K using a Siemens P4R4 diffractometer equipped with a rotating Cu anode (50 kV, 300 mA) X-ray source and a locally modified LT-2 low-temperature device. X-ray data for $(Ph_4P)[Fe(SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_3]\cdot 2MeCN\cdot C_7H_8$ and $[Fe_3(SC_6H_2\text{-}2,4,6\text{-}Ph_3)_4(N(SiMe_3)_2)_2]$ were collected at 147 and 130 K, respectively, with a Siemens R3m/V diffractometer using graphite-monochromatized Mo Kα radiation and an Enraf-Nonius universal temperature device. Crystal data are given in Table 1. Calculations were carried out with the SHELXTL-PLUS program system installed on a MicroVax station 3200. Scattering factors and the correction for anomalous scattering were those provided by the program. Absorption corrections were applied using the program XABS.[25] The structures were solved by Patterson synthesis; missing atoms were located in subsequent difference Fourier maps and included in the least-squares refinements. Hydrogen atoms were included by use of a riding model with C−H distances of 0.96 Å and fixed isotropic parameters $U_H = 0.05$ Å^2. In $(Ph_4P)[Fe(SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_3]\cdot 2MeCN\cdot C_7H_8$ and $[Fe_3(SC_6H_2\text{-}2,4,6\text{-}Ph_3)_4(N(SiMe_3)_2)_2]$ all non-hydrogen atoms except those of solvate molecules were refined with anisotropic thermal parameters, whereas the Fe and S atoms were refined anisotropically in the case of $[Li(THF)_2Fe[SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_3]\cdot 0.5C_6H_{14}$. Final *R* factors are included in Table 1, and positional coordinates for selected atoms are provided in Table 2.[26]

Other Physical Measurements. All measurements were made under strictly anaerobic conditions. Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer PE-1430 spectrophotometer. Magnetic measurements were carried out at room temperature with a Johnson-Mathey magnetic susceptibility balance. Mössbauer spectroscopic data were collected on a modified Ranger MS-1500 spectrometer equipped with an external VT-1200L velocity transducer and a PA-1200 krypton proportional counter and operated in the constant-acceleration mode. The source was ^{57}Co diffused in a Rh matrix. Low-temperature data were obtained with use of a Janis Model 8DT superVaritemp dewar fitted with Mylar windows. Freshly powdered samples were prepared anaerobically; 20−50 mg quantities were loaded in Delrin sample cups and sealed with silicone grease. Data were analyzed and fitted to Lorentzian or Voigt line shapes using WMOSS software (WEB Research Co., Endina, MN). Isomer shifts are quoted relative to Fe metal at 298 K.

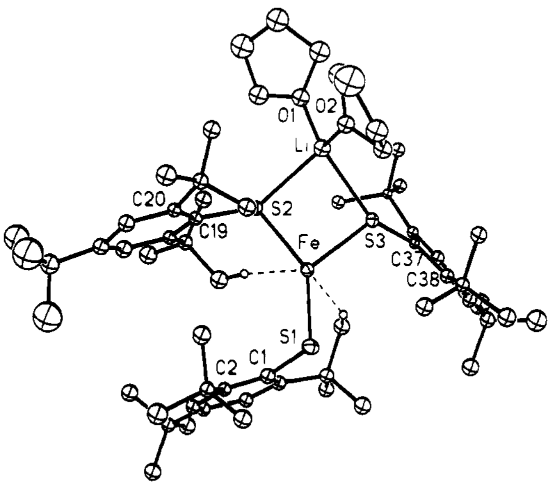

Figure 3. Structure of $[Li(THF)_2(\mathbf{5})]$ as its *n*-hexane hemisolvate, showing 30% thermal ellipsoids and the atom-labeling scheme.

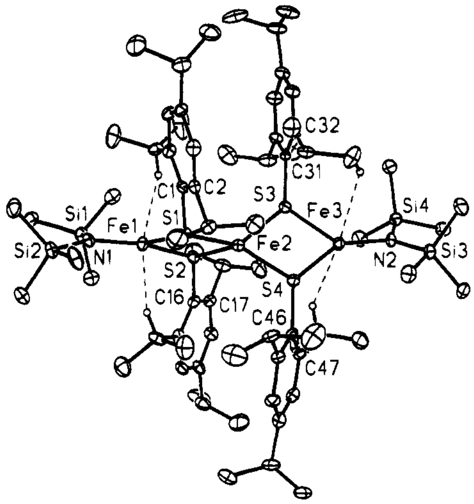

Figure 4. Structure of **6**, showing 30% thermal ellipsoids and the atom-labeling scheme.

Results and Discussion

The following complexes are of primary interest in this investigation:

$[Fe(SC_6H_3\text{-}2,6\text{-}Mes_2)_2]$	**1**
$[Fe(SC_6H_3\text{-}2,6\text{-}Mes_2)(N(SiMe_3)_2)]$	**2**
$[Fe_2(SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_4]$	**3**
$[Fe_2(SC_6H_2\text{-}2,4,6\text{-}Ph_3)_4]$	**4**
$[Fe(SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_3]^-$	**5**
$[Fe_3(SC_6H_2\text{-}2,4,6\text{-}i\text{-}Pr_3)_4(N(SiMe_3)_2)_2]$	**6**

The preparations and structures of complexes **1**−**4** have been described previously.[9,13,14]

Synthesis. The synthesis of the two compounds containing anionic complex **5** involves the simple bridge cleavage reaction (1) (R = $2,4,6\text{-}t\text{-}Bu_3C_6H_2$), during which the dark red color of

$$[Fe_2(SR)_4] + 2RS^- \rightarrow 2[Fe(SR)_3]^- \qquad (1)$$

the binuclear complex changes to deep yellow upon addition of the lithium thiolate. Complex **5** may be crystallized as a contact ion pair with $Li(THF)_2^+$ or in discrete form as the Ph_4P^+ salt. Reaction 1 is one of only two reactions known to interconvert homoleptic Fe(II) thiolate complexes.[27] It is precedented by the addition of lithium amides or alkoxides to

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(24) Hope, H. *Prog. Inorg. Chem.* **1994**, *41*, 1.

(25) Moezzi, B. Ph.D. Dissertation, University of California, Davis, 1987.

(26) See paragraph at the end of this article concerning supplementary material.

(27) The other:[16] $3[Fe_2(SR)_6]^{2-} \rightleftharpoons 2[Fe(SR)_4]^{2-} + [Fe_4(SR)_{10}]^{2-}$.

Table 3. Selected Bond Distances (Å) and Angles (deg)

	$[Li(THF)_2(\mathbf{5})]\cdot 0.5C_6H_{14}$		
Fe−S(1)	2.259(4)	S(1)−Fe−S(2)	141.7(1)
Fe−S(2)	2.315(4)	S(1)−Fe−S(3)	123.2(1)
Fe−S(3)	2.334(4)	S(2)−Fe−S(3)	92.2(1)
Li−S(2)	2.606(23)	Fe−S(1)−C(1)	106.6(4)
Li−S(3)	2.535(22)	Fe−S(2)−C(19)	117.0(4)
Li−O(1)	1.918(22)	Li−S(2)−C(19)	138.7(6)
Li−O(2)	1.978(23)	Li−S(2)−Fe	91.1(5)
S(1)−C(1)	1.831(13)	Fe−S(3)−C(37)	109.5(4)
S(2)−C(19)	1.804(12)	Li−S(3)−C(37)	141.5(6)
S(3)−C(37)	1.811(11)	Li−S(3)−Fe	92.5(5)
		S(2)−Li−S(3)	81.3(7)
		O(1)−Li−O(2)	109.0(11)
	$(Ph_4P)[\mathbf{5}]\cdot 2MeCN\cdot C_7H_8$		
Fe(1)−S(1)	2.267(1)	S(1)−Fe(1)−S(2)	121.4(1)
Fe(1)−S(2)	2.271(2)	S(1)−Fe(1)−S(3)	116.6(1)
Fe(1)−S(3)	2.285(1)	S(2)−Fe(1)−S(3)	121.9(1)
S(1)−C(1)	1.805(4)	Fe(1)−S(1)−C(1)	117.3(2)
S(2)−C(19)	1.794(4)	Fe(1)−S(2)−C(19)	114.0(2)
S(3)−C(37)	1.788(5)	Fe(1)−S(3)−C(37)	114.5(11)
		C(55)−P(1)−C(61)	109.7(3)
P(1)−C(55)	1.801(6)	C(55)−P(1)−C(67)	108.2(3)
P(1)−C(61)	1.799(4)	C(55)−P(1)−C(73)	108.2(3)
P(1)−C(67)	1.796(6)	C(61)−P(1)−C(67)	109.9(3)
P(1)−C(73)	1.803(6)	C(61)−P(1)−C(73)	109.5(3)
		C(67)−P(1)−C(73)	111.3(3)
	Complex **6**		
Fe(2)−S(1)	2.360(2)	S(1)−Fe(1)−S(2)	93.4(1)
Fe(2)−S(2)	2.369(2)	N(1)−Fe(1)−S(1)	140.9(2)
Fe(2)−S(3)	2.343(2)	N(1)−Fe(1)−S(2)	125.5(2)
Fe(2)−S(4)	2.383(2)	S(3)−Fe(3)−S(4)	89.0(1)
Fe(1)−S(1)	2.343(2)	N(2)−Fe(3)−S(3)	126.1(2)
Fe(1)−S(2)	2.338(2)	N(2)−Fe(3)−S(4)	144.7(2)
Fe(3)−S(3)	2.348(2)	S(1)−Fe(2)−S(2)	92.2(1)
Fe(3)−S(4)	2.343(2)	S(3)−Fe(2)−S(4)	88.2(1)
Fe(1)−Fe(2)	3.568	S(1)−Fe(2)−S(3)	135.7(1)
Fe(3)−Fe(2)	3.352	S(2)−Fe(2)−S(4)	137.3(1)
Fe(1)−N(1)	1.895(4)	Fe(1)−S(1)−Fe(2)	87.2(1)
Fe(3)−N(2)	1.882(4)	Fe(1)−S(1)−C(1)	118.9(2)
N(1)−Si(1)	1.715(5)	Fe(2)−S(1)−C(1)	120.2(2)
N(1)−Si(2)	1.729(5)	Si(1)−N(1)−Si(2)	126.1(3)
N(2)−Si(3)	1.730(5)		
N(2)−Si(4)	1.722(5)		

low-coordinate metal amides to give three-coordinate products.[28] Trinuclear complex **6** was prepared by reaction 2. Initially it

$$3[Fe(N(SiMe_3)_2)_2] + 4RSH \rightarrow [Fe_3(SR)_4(N(SiMe_3)_2)_2] + 4(Me_3Si)_2NH \quad (2)$$

was hoped to obtain a homoleptic product of formula $[Fe(SR)_2]_n$ ($n \geq 2$) by using an exact 2:1 mole ratio of thiol to amide. However, increasing this ratio to as much as 2.5:1 and employment of prolonged reaction times at reflux temperature did not afford an isolable product other than **6**.

Structures. For the three compounds in Table 1, structures are set out in Figures 2−4 and important bond distances and angles are contained in Table 3.

Complex 5. This species has been crystallized as two salts, neither of which has any imposed symmetry. In $(Ph_4P)[\mathbf{5}]\cdot 2MeCN\cdot C_7H_8$, the Fe(II) atom exhibits slightly distorted trigonal planar geometry with idealized C_{3h} symmetry for the $Fe(SC_{ipso})_3$ array (Figure 2). The ranges of Fe−S distances and S−Fe−S angles are 2.267(1)−2.285(1) Å and 116.6(1)−121.9(1)°, respectively. In the Ph_4P^+ counterion, the C−P−C angles are within 1.6° of the tetrahedral value and the P−C bond distances average to 1.800(3) Å. In $[Li(THF)_2(\mathbf{5})]\cdot 0.5C_6H_{14}$, the trigonal planar stereochemistry of complex **5** is significantly distorted by a bridging lithium ion (Figure 3). The bridged S(2)−Fe−S(3) angle is constricted to 92.2(1)° compared to the nonbridged angles S(1)−Fe(2)−S(3) = 123.2(1)° and S(1)−Fe(2)−S(3) = 141.7(1)° and the mean value of 119(3)° in the Ph_4P^+ salt, where **5** is unbridged. The bridged Fe−S bonds are substantially longer (mean 2.324 Å) than the unbridged bond length (2.259(4) Å). The interligand angle sum at the Fe(II) atom is 357.1°, indicating a slight deviation from planar coordination. Distorted tetrahedral coordination at Li^+ is completed by two THF molecules.

Complex 6. The structure of this molecule features an almost linear array of three Fe(II) atoms (Fe(1)−Fe(2)−Fe(3) = 172.8(1)°) with unequal Fe−Fe separations of 3.243(1) and 3.364(1) Å (Figure 4). Central Fe(2) is coordinated in a distorted tetrahedral manner by four thiolate groups, each of which bridges to outer Fe(1) or Fe(3). Coordination of each of the latter atoms is completed by a terminal amide ligand, generating distorted trigonal planar geometry. The mean bridging and terminal Fe−S distances are 2.36(1) and 2.343(5) Å, respectively. The structure core is composed of two Fe_2S_2 rhombs sharing a common vertex and forming a dihedral angle between mean planes of 62.3°. Severe distortion from idealized tetrahedral stereochemistry at the vertex atom is further emphasized by a mean S−Fe(2)−S ring angle of 90.2° and the external angles S(1)−Fe(2)−S(4) = 137.3(1)° and S(1)−Fe(2)−S(3) = 135.7(1)°. Distortions from trigonal stereochemistry at Fe(1,3) are made evident by internal ring angles near 90° and N−Fe−S angles in the range 125.5(2)−144.7(2)°. The stereochemistry at ligand atoms N(1,2) is planar. The two Si_2N planes are somewhat twisted out of the immediately adjacent FeS_2 planes, the dihedral angles being 23.8 and 25.9° for planes joined by Fe(1)−N(1) and Fe(3)−N(2) bonds, respectively.

Comparative Structures. Complex **5** is the first characterized example of a $[Fe(SR)_3]^-$ species; **3**,[13] **4**,[14] and **5** constitute the known set of structurally defined molecules containing three-coordinate Fe(II) bound entirely by thiolate. No such homoleptic Fe(III) complexes have been reported. Three-coordinate iron (of uncertain oxidation state) bound by bridging sulfide ligands has been established in the FeMo-cofactor cluster of nitrogenase.[8] The Fe−S bond lengths in **5** and its lithium-bridged version are similar to terminal bond lengths observed in binuclear **3** (2.256(3) Å) and **4** (2.262(3) Å); these values are shorter than the range of Fe−S bridging distances (2.337(3)−2.387(3) Å) in **3** and **4**. In $[Li(THF)_2(\mathbf{5})]$, bridging Li−S distances are longer than in previously reported lithium thiolates;[29] Li−O bond lengths are within the range of values found for four-coordinate Li^+ with THF ligands.[30] Thus the structural parameters indicate that the bridging thiolates are bound more strongly to the Fe(II) center than to Li^+. Accordingly, $[Li(THF)_2(\mathbf{5})]$ may be viewed as a contact ion pair between solvated Li^+ and **5** rather than an adduct of neutral $Fe(SR)_2$ and LiSR. This view is supported by the independent existence of **5** in its crystalline Ph_4P^+ solvate salt. Closely related to **5** are the compounds $[M(SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_3]$ (M = Al, Ga, In).[31] As for **5**, their MS_3 central portions are neither exactly planar (deviations of M by <0.1 Å from the S_3 planes) nor exactly trigonal (S−M−S range of 115−126°). These compounds do differ noticeably from **5** in that their Fe−S−C angles are *ca.*

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Table 4. Probable Fe−S Stretching Frequencies (cm^{-1}) in Two- and Three-Coordinate Iron(II) Thiolate Complexes

$[Fe(SC_6H_3\text{-}2,6\text{-}Mes_2)_2]$	**1**	368
$[Fe(SC_6H_3\text{-}2,6\text{-}Mes_2)(N(SiMe_3)_2)]$	**2**	370
$[Fe_2(SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_4]$	**3**	370
$[Fe_2(SC_6H_2\text{-}2,4,6\text{-}Ph_3)_4]$	**4**	386
$(Ph_4P)[Fe(SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_3]^a$	**5**	356
$[Li(THF)_2Fe(SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_3]^b$	**5**	376, 334 (br)
$[Fe_3(SC_6H_3\text{-}2,4,6\text{-}i\text{-}Pr_3)_4(N(SiMe_3)_2)_2]$	**6**	387 (br), 300 (br)

[a] $0.5C_6H_{14}$ solvate. [b] $2MeCN{\cdot}C_7H_8$ solvate.

15° larger than mean value of the former (115(1)°); the cause of this difference does not relate to the radii of M[31b] and is otherwise unclear.

The unusual trinuclear species **6** was obtained during attempts to synthesize a homoleptic complex of the $2,4,6\text{-}i\text{-}Pr_3C_6H_2S^-$ ligand. The nearly linear trinuclear array is precedented in the complexes $[Zn_3(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_4(CH_2(SiMe_3)_2)_2]$,[32] $[Zn_3(SC_6H_2\text{-}2,4,6\text{-}i\text{-}Pr)_4(N(SiMe_3)_2)_2]$,[33] and $[Mn_3(NHC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_4(N(SiMe_3)_2)_2]$.[34] A linear core is also found in $[Fe_3(SPh)_6(CO)_6]$, but in this molecule the Fe(II) atoms are six-coordinate.[35] The magnetic moment $\mu_{Fe} = 3.55\ \mu_B$ of **6** at room temperature is indicative of antiferromagnetic coupling.

Fe⋯H Interactions. Given the low coordination numbers in the series **1**−**6**, we have examined each complex for agostic interactions, which would partially allay the electron deficiency at the Fe(II) sites. Calculated hydrogen atom positions have been used in each case; all interactions are intramolecular and involve *ortho* substituents. In the Ph_4P^+ salt of **5**, the shortest interaction is Fe⋯H(10a) (2.74 Å) involving the S(1) ligand. In $[Li(THF)_2(\textbf{5})]$, the closest approach is Fe⋯H(12c) = 2.34 Å (ligand S(1)). Turning to **6**, we find Fe(1)⋯H(13a) = 2.42 Å (ligand S(1)) and Fe(1)⋯H(28a) = 2.37 Å (ligand S(2)). There are no Fe(3)⋯H distances shorter than 2.58 Å.

The closest Fe⋯H interaction in complexes **5** and **6** (2.34 Å) is thus well in excess of the sum of covalent radii of Fe(II) and hydrogen (*ca.* 1.7 Å). Furthermore, there is no clear evidence of structural distortion in these complexes that could be ascribed to agostic interactions. Marginal agostic interactions in **3** and isostructural $[Co_2(SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_4]$[13] are indicated by M⋯H distances as low as *ca.* 1.8 Å; the effect is absent in isostructural $[Mn_2(SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_4]$,[13] where the shortest such distance is 2.36 Å. Relatively close M⋯C separations of *ca.* 2.5 Å involving adjacent phenyl groups occur in **1**, **2**, and **4**. In summary, no M⋯H or M⋯C interaction in **1**−**6** can be construed as coordinative, and the description of the complexes as two- or three-coordinate is valid.

Fe−S Stretching Frequencies. Examination of IR spectra below 450 cm^{-1} reveals features that are attributable to Fe−S stretches. Bands so assigned for compounds **1**−**6** are collected in Table 4. The spectrum of **5** as the Ph_4P^+ salt is characterized by a single medium-intensity feature at 356 cm^{-1}. (In idealized C_{3h} symmetry the FeS_3 stretching modes are A′ (Raman) and E′ (IR and Raman). This value may be compared with those for the structurally related set $[M(SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_3]$ with M = Al (547 cm^{-1}) and Ga (398 cm^{-1})[31a] and for various $[Fe(SR)_4]^-$ complexes (*ca.* 300−380 cm^{-1}).[7] For $[Li(THF)_2(\textbf{5})]$, bands are observed at 408, 376, and 334 cm^{-1}; it appears likely that at least the two lower frequency absorptions are Fe−S stretches, consistent with reduced symmetry of the bridged anion. The spectrum of **6** has two low-frequency bands (386, 300 cm^{-1}); the 300 cm^{-1} absorption is quite broad and may include bridging Fe−S vibrations. As shown by detailed work on Fe(III)−thiolate species, features described as Fe−S stretches are presumably coupled to C−S vibrations.[7]

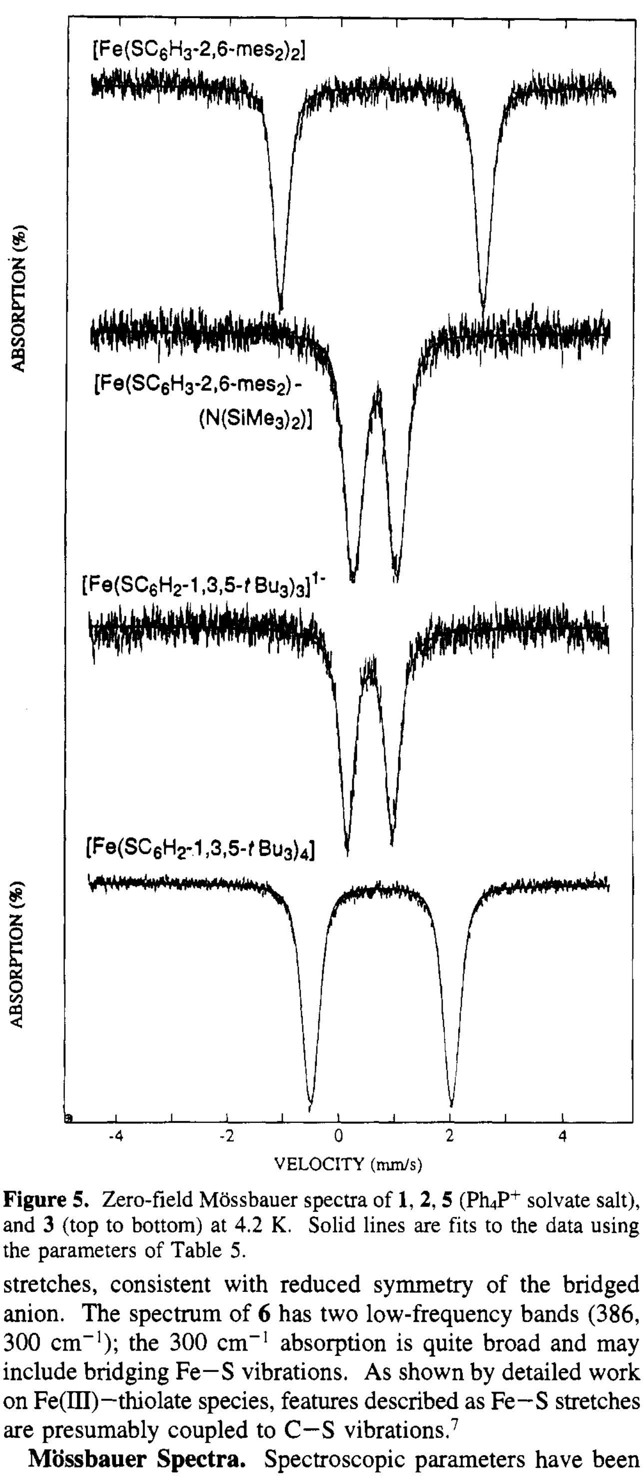

Figure 5. Zero-field Mössbauer spectra of **1**, **2**, **5** (Ph_4P^+ solvate salt), and **3** (top to bottom) at 4.2 K. Solid lines are fits to the data using the parameters of Table 5.

Mössbauer Spectra. Spectroscopic parameters have been determined for a number of synthetic tetrahedral Fe^{II}−S/SR complexes[3,4,36] and for protein-bound centers including reduced rubredoxin and polynuclear units.[20,37−39] All protein iron sites are tetrahedral except for the trigonally coordinated $Fe(\mu_3\text{-}S)_2(\mu_2\text{-}S)$ sites of uncertain oxidation state in nitrogenase.[8,40] In such cases, isomer shifts $\delta \approx 0.60-0.75$ mm/s and quadrupole

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Table 5. Mössbauer Parameters for Two-, Three, and Four-Coordinate Fe(II,III)−Thiolate Complexes

complex	CN[a]	T, K	mm/s δ	 ΔE_Q	 Γ
$[Fe(SC_6H_3\text{-}2,6\text{-}Mes_2)_2]$ (**1**)	2	4.2	0.75	3.64	0.21
		100	0.74	2.91	0.33
$[Fe(SC_6H_3\text{-}2,6\text{-}Mes_2)(N(SiMe_3)_2)]$ (**2**)	2	4.2	0.66	0.79	0.36
$[Fe_2(SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_4)]$ (**3**)	3	4.2	0.78	2.53	0.27, 0.28
		100	0.77	2.49	0.39
$[Fe_2(SC_6H_2\text{-}2,4,6\text{-}Ph_3)_4]$ (**4**)	3	4.2	0.77	2.28	0.54
$[Fe(SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_3]^-$ (**5**)[b]	3	4.2	0.57	0.81	0.22
		100	0.53	0.81	0.42
$[Fe(SEt)_4]^-$	4	4.2	0.25	0.62	0.67
$[Fe(SEt)_4]^{2-}$	4	4.2	0.74	3.50	0.32, 0.31
$[Fe(SPh)_4]^{2-}$ [c]	4	4.2	0.66	3.24	
		77	0.64	3.24	
$[Fe_2(SEt)_6]^{2-}$	4	4.2	0.70	3.25	0.37, 0.41
		100	0.67	2.97	0.44, 0.48
$[Fe_4(SEt)_{10}]^{2-}$	4	4.2	0.72	3.29	0.49, 0.52
		100	0.71	3.28	0.49, 0.55
$[Fe_4(SPh)_{10}]^{2-}$	4	4.2	0.74	3.12	0.62, 0.61
		100	0.73	3.12	0.60, 0.57

[a] Coordination number. [b] Ph_4P^+ solvate salt. [c] Data from ref 36a.

splittings $\Delta E_Q \approx 3-4$ mm/s at 4.2 K. For iron proteins, Mössbauer parameters in these ranges, sometimes augmented by magnetically perturbed spectra, are considered diagnostic for tetrahedral Fe^{II}−S/S·Cys sites such as those in reduced rubredoxins. In the present work, we have sought to determine whether zero-field parameters can distinguish nonlinear two-coordinate and the (approximately) trigonal planar coordination modes ($Fe(SR)_3$, $Fe(SR)(\mu\text{-}SR)_2$) from each other and from tetrahedral $Fe(SR)_4$ and Fe−S/SR units.

In the case of high-spin Fe(II) systems, the spin degeneracy of the ground state quintet is fully removed by spin−orbit coupling and in the absence of an applied magnetic field the expectation value is $\langle\vec{S}\rangle = 0$ for the ground term. Consequently, the zero-field Mössbauer spectrum consists of a simple quadrupole doublet. The data in Table 5 include examples of all known types of homoleptic tetrahedral Fe(II) thiolates; parameters fall into the foregoing ranges and reveal no dependence on the exact mode of coordination ($Fe(SR)_4$, $Fe(SR)_2(\mu_2\text{-}SR)_2$, $Fe(SR)(\mu_2\text{-}SR)_3$, or alkane- vs arenethiolate ligands. As is well known and seen here by comparison of $[Fe(SEt)_4]^{2-,-}$, high-spin tetrahedral Fe^{III}−S/SR is distinguished by its much smaller isomer shift and quadrupole splitting.

Complexes **1**−**5** (Figure 1) were examined by zero-field Mössbauer spectroscopy at 4.2 and 100 K. All complexes have homoleptic thiolate coordination except for **2**, which carries one thiolate and one amidate ligand. Spectra were fit using one iron site, consistent with the mononuclear nature of **1**, **2**, and **5** and the crystallographically imposed inversion symmetry of dimers **3** and **4**. Quadrupole doublets were constrained to have equal line widths; however, unconstrained fits gave somewhat better results for **3**. Zero-field spectra for complexes **1**−**3** and **5** are set out in Figure 5; variant quadrupole splittings are immediately apparent. Parameters used in the spectral fits are collected in Table 5. High-temperature (100 K) data for **2** and **4** were not collected. The broad asymmetric quadrupole doublet observed for **4** reflects incipient paramagnetic broadening which causes a relatively large line width (0.54 mm/s) relative to the other compounds (0.21−0.39 mm/s at 4.2 K).

Isomer shifts for all the complexes range between 0.53 and 0.78 mm/s at 4.2 K and are consistent with high-spin Fe(II). Among the homoleptic complexes, it is immediately evident on the basis of both isomer shift (0.57 mm/s) and quadrupole splitting (0.81 mm/s) that mononuclear **5** is distinguishable from bridged **3** and **4** and from tetrahedral $Fe(SR)_4$, and that nonlinear two-coordinate **1** has the largest quadrupole splitting (3.64 mm/s) but not a distinctive isomer shift (0.75 mm/s). (It is unclear why nonlinear **2** has a much smaller splitting (0.79 mm/s).[41]) Complex **5** was examined as its Ph_4P^+ solvate salt, in which it approaches idealized trigonal symmetry to an extent far greater than do the coordination units in **3** and **4**. Under idealized C_{3h} symmetry, the probable ground state electron configuration is $(a')^2(e'')^2(e')^2$, consistent with a relatively small quadrupole splitting.

Although the number of examples is limited at this stage, we tentatively conclude that trigonal planar $Fe^{II}(SR)_3$ can be distinguished from tetrahedral $Fe^{II}(SR)_4(e^3t_2^3)$ and related tetrahedral Fe^{II}−S/SR units on the basis of quadrupole splitting. In the dithionite-reduced state (M^N, $S = {}^3/_2$) of nitrogenase from *Clostridium pasteurianum*, $\delta = 0.41$ mm/s and $\Delta E_Q \approx 0.8$ mm/s. In the fixing state (M^R), δ increases to 0.46 mm/s and $\Delta E_Q \approx 0.9-1.3$ mm/s.[40] These data are averages over the six three-coordinate Fe atoms and the one tetrahedral $Fe(\mu_3\text{-}S)_3$(S·Cys) site in the $MoFe_7S_9$ cofactor cluster, at least for the M^N state. Coordination numbers in the fixing or reduced state are unknown. We note that the localized Fe(II) sites in two protein-bound $[ZnFe_3S_4]^+$ clusters have $\delta = 0.62$ mm/s and $\Delta E_Q \approx 2.7-2.9$ mm/s at 50 K.[39] These values arise from a site, $Fe(\mu_3\text{-}S)_3$(S·Cys), which contains more sulfide ligation than any other localized Fe−S/S·Cys biological coordination unit; they fall in the range of those for reduced rubredoxins, especially when the temperature dependence of ΔE_Q is taken into account.[39b] To the extent that these results can be extended to three-coordinate sites, the mean iron oxidation state in the M^N state has substantial ferric character, especially if $\delta \approx 0.2-0.3$ mm/s is taken as the lower limit for Fe^{3+}. The comparison is

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(41) The spectrum of trinuclear mixed-ligand complex **6** at 4.2 K is broadened by relaxation effects. The spectrum at 100 K is better resolved, but no satisfactory fit was found with parameters internally consistent with those for **1**−**5**.

inexact, but it is the only one currently available. Where there is a more extensive database, Mössbauer parameters can be applied with greater certainty, as in the recent identification of unbridged and bridged tetrahedral $Fe^{II}(S\cdot Cys)_4$ sites in Fe(II)-reconstituted metallothioneins.[38]

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Supplementary Material Available: Crystallographic data for the compounds in Table 1, including tables of crystal data, details of data collection, thermal and positional parameters, bond distances and angles, and calculated hydrogen atom positions (35 pages). Ordering information is given on any current masthead page. Listings of observed and calculated structure factors are available from the authors.

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