

Iron-Sulfur-Thiolate Basket Clusters

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The self-assembly reaction system $\text{Fe}(\text{PEt}_3)_2(\text{SPh})_2 + (\text{Me}_3\text{Si})_2\text{S}$ in THF and the cluster expansion system $\text{Fe}(\text{PEt}_3)_2(\text{SPh})_2 + [\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ in acetonitrile afford the same cluster, $\text{Fe}_6\text{S}_6(\text{PEt}_3)_4(\text{SPh})_2$ (**1**), in 65–70% purified yield as a brown-black, air-sensitive, crystalline solid. The compounds $\text{Fe}_6\text{S}_6(\text{PEt}_3)_4(\text{SR})_2$ ($\text{R} = \text{Ph}, p\text{-C}_6\text{H}_4\text{Br}$) (**2**) were also obtained in ca. 50% yield by the reaction of (previously reported) $\text{Fe}_6\text{S}_6(\text{PEt}_3)_4\text{Cl}_2$ (**3**) and 2 equiv of NaSR in THF. Compound **2** as its 1.5 THF solvate crystallizes in orthorhombic space group *Pccn* with $a = 28.363$ (4) Å, $b = 20.996$ (4) Å, $c = 20.204$ (8) Å, and $Z = 8$. Its structure contains the $[\text{Fe}_6(\mu_4\text{-S})(\mu_3\text{-S})_4(\mu_2\text{-S})]^{2+}$ core, consisting of six nonplanar Fe_2S_2 rhombs fused in the form of a basket with an Fe–S–Fe bridge as the handle. Coordination at the Fe atoms is completed by thiolates at two sites, affording roughly tetrahedral $\text{FeS}_3(\text{SR})$ units, and by phosphine at the remaining sites to give two pairs of symmetry-related FeS_3P units under the idealized C_{2v} symmetry of the core. These sites adopt a distorted-trigonal-pyramidal arrangement. The core stereochemistry is nearly congruent with that of isoelectronic $\text{Fe}_6\text{S}_6(\text{PBU}_3)_4\text{Cl}_2$, a result consistent with the conversion of **3** to **1** and **2** by ligand substitution and the reverse transformation with benzoyl chloride, both in THF. Two sets of phosphine ^1H NMR resonances indicate retention of the basket stereochemistry in solution. These and prior results show that cluster self-assembly in a nonpolar solvent in the presence of tertiary phosphine yields a new Fe–S cluster type, $\text{Fe}_6\text{S}_6(\text{PEt}_3)_4\text{L}_2$, which is readily prepared, is stable with $\text{L} = \text{RS}^-$ and halide, and is topologically isomeric with Fe_6S_6 prismane clusters. Basket clusters are members of an extensive set of Fe–S clusters of nuclearity 2–8, the cores of most of which are convertible or interconvertible under mild conditions. The structures of this cluster set are schematically presented.

Introduction

Recent research in this laboratory has shown that, when the concept of spontaneous self-assembly of clusters is investigated with systems containing an iron(II) salt, a sulfide source, and a tertiary phosphine in a low dielectric solvent, new cluster structural types are produced.^{1–3} These clusters, distinguished principally by the topology and oxidation level of their Fe–S cores, have not been obtained by the assembly process when carried out in the absence of phosphine and in more polar solvents normally employed to produce clusters such as $[\text{Fe}_4\text{S}_4\text{L}_4]^{2+}$ ^{3–4,5} and $[\text{Fe}_6\text{S}_9(\text{SR})_2]^{4-}$ ^{6,7} Fenske and co-workers^{8–10} have obtained high-nuclearity Co–S and Ni–S clusters by similar means.

The two new cluster types prepared by the above assembly procedure, from FeCl_2 , PEt_3 , and $(\text{Me}_3\text{Si})_2\text{S}$ in THF, are $\text{Fe}_7\text{S}_6(\text{PEt}_3)_4\text{Cl}_3$ ¹ and $\text{Fe}_6\text{S}_6(\text{PEt}_3)_4\text{Cl}_2$.^{2,3} The $[\text{Fe}_7\text{S}_6]^{3+}$ core of the former has a monocapped-prismane configuration, whereas the $[\text{Fe}_6\text{S}_6]^{2+}$ core of the latter exhibits a “basket” structure. This core stereochemistry, presented in detail below, is a topological isomer of the $[\text{Fe}_6\text{S}_6]^{2+,3+}$ cores in the prismane clusters $[\text{Fe}_6\text{S}_6\text{L}_6]^{2-,3-11-13}$ ($\text{L} = \text{RS}^-, \text{RO}^-, \text{halide}$). We have also found it possible to prepare $\text{Fe}_6\text{S}_6(\text{PEt}_3)_4\text{Cl}_2$ from $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ or $[\text{Fe}_6\text{S}_6\text{Cl}_6]^{3-}$ and $\text{Fe}(\text{PEt}_3)_2\text{Cl}_2$. Inasmuch as prismane, cubane, and basket clusters are transformable into one another^{2,3,11,12} and the monocapped prismane spontaneously converts to the basket structure in solution,³ the four cluster types form a chemically integrated set. Further, there is a clear topological link between

prismane and its mono- and dicapped derivatives. The last compound has been established in the form of the stellated octahedron $[\text{Fe}_8\text{S}_6\text{I}_8]^{3-}$.¹⁴

The above structures and transformations all have been established with clusters containing chloride as the non-phosphine terminal ligand. We seek to develop further the topological relationships among Fe–S clusters, their structures, and their reactivities, with particular interest in the formation of mixed-metal clusters relevant to the native clusters of nitrogenase. Noting the substantial ligand effects on redox potentials and reactivity in the cubane^{4,15} and prismane^{11,12} series and the instability of prismane $[\text{Fe}_6\text{S}_6(\text{SR})_6]^{3-}$ with respect to cubane $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$,¹¹ we have prepared several examples of $\text{Fe}_6\text{S}_6(\text{PEt}_3)_4(\text{SR})_2$ clusters in order to assess the effects of thiolate for chloride substitution. The results of this investigation are detailed here.

Experimental Section

Preparation of Compounds. The compounds $(n\text{-Bu}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{16}$ and $\text{Fe}_6\text{S}_6(\text{PEt}_3)_4\text{Cl}_2$ ^{2,3} were prepared as previously described. NaSPh was obtained from the reaction of sodium metal and benzenethiol in methanol, and $\text{Na}(S\text{-}p\text{-C}_6\text{H}_4\text{Br})$ was prepared similarly in ether. Anhydrous FeCl_2 (Cerac, Strem) and hexamethyldisilthiane (Aldrich, Petrarch) were obtained commercially. Triethylphosphine was a gift from American Cyanamid and was purified by distillation. THF was distilled from sodium-benzophenone and stored over sodium metal. Acetonitrile was distilled from CaH_2 and stored over 4-Å molecular sieves. Solvents were thoroughly degassed before use. All operations were conducted under a pure dinitrogen atmosphere by using standard Schlenk techniques or a Vacuum Atmospheres drybox.

$\text{Fe}_6\text{S}_6(\text{PEt}_3)_4(\text{SPh})_2$ (1**).** **Method A.** A solution of $\text{Fe}(\text{PEt}_3)_2(\text{SPh})_2$ (7.9 mmol) in 80 mL of THF was prepared by the reaction of stoichiometric amounts of FeCl_2 (1.00 g), NaSPh (2.09 g), and PEt_3 (2.33 mL) over a period of 1–2 h, followed by filtration to remove NaCl . Treatment of this dark red-orange solution with 1.66 mL (7.90 mmol) of $(\text{Me}_3\text{Si})_2\text{S}$ led to a rapid color change to dark brown. The reaction mixture was stirred for 12–16 h at room temperature. Removal of solvent in vacuo yielded a black, oily residue, which was washed consecutively with hexanes, ether, and acetonitrile until colorless washes were obtained. The dark solid was recrystallized from THF–hexanes to afford 1.12 g (70%) of pure product as a brown-black, crystalline solid. ^1H NMR (CDCl_3 , 296 K): δ 11.7 (2, *o*-H), 11.5 (1, *p*-H), 4.14 (2, *m*-H), 0.22 (Me), –0.25 (Me), –5.15 (CH_2), –5.70 (CH_2). Absorption spectrum (THF; λ_{max} , nm (ϵ_{M})): 298 (34800), 400 (sh, 12000), 620 (sh, 8000). Anal. Calcd for $\text{C}_{36}\text{H}_{70}\text{Fe}_6\text{P}_4\text{S}_6$: C, 35.49; H, 5.79; Fe, 27.50; P, 10.17; S, 21.00. Found: C, 35.58; H, 5.38; Fe, 27.52; P, 10.28; S, 21.18. $\mu_{\text{eff}} = 2.88 \mu_{\text{B}}$ (CDCl_3 ,

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Table I. Crystallographic Data for $\text{Fe}_6\text{S}_6(\text{PET}_3)_4(\text{S-}p\text{-C}_6\text{H}_4\text{Br})_2 \cdot 1.5\text{THF}$

chem formula: $\text{C}_{42}\text{H}_{80}\text{Br}_2\text{Fe}_6\text{O}_{1.5}\text{P}_4\text{S}_8$	fw = 1484.37
$a = 28.363$ (4) Å	space group: <i>Pccn</i> (No. 56)
$b = 20.996$ (4) Å	$T = 192$ K
$c = 20.204$ (8) Å	$\lambda = 0.71073$ Å (Mo $K\alpha$)
$V = 12.032$ (5) Å ³	$\rho_{\text{calcd}} = 1.51$ g/cm ³
$Z = 8$	$\mu = 30.8$ cm ⁻¹
$R(F_o) = 0.0685$	$R_w(F_o) = 0.0618$

298 K), 2.72 μ_B (toluene- d_8 , 296 K).

Method B. To a solution of $\text{Fe}(\text{PET}_3)_2(\text{SPh})_2$ (9.2 mmol) in 30 mL of acetonitrile was added 5.86 g (4.60 mmol) of $(n\text{-Bu}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SPh})_4]$. The mixture was stirred for 12–16 h at room temperature. The dark solid was collected by filtration, washed with acetonitrile until the washings were colorless, and recrystallized from THF–hexanes. The pure product (2.43 g, 65%) was obtained as dark brown crystals, identical in all respects with the product of method A.

$\text{Fe}_6\text{S}_6(\text{PET}_3)_4(\text{S-}p\text{-C}_6\text{H}_4\text{Br})_2$ (2). To a solution of 1.98 g (1.90 mmol) of $\text{Fe}_6\text{S}_6(\text{PET}_3)_4\text{Cl}_2$ in 50 mL of THF was added 0.78 g (3.8 mmol) of $\text{Na}(\text{S-}p\text{-C}_6\text{H}_4\text{Br})$. The dark brown reaction mixture was stirred for 24 h at room temperature. After filtration to remove NaCl and a black solid, the volume of the filtrate was reduced in vacuo. Addition of hexanes to the solution afforded after collection 1.25 g (49%) of pure product as a brown-black crystalline solid. This material was found by ¹H NMR and crystallography to contain 1.5 molecules of THF solvate per cluster. The compound was dried in vacuo prior to elemental analysis. ¹H NMR (CDCl_3 , 296 K): δ 11.4 (2, *o*-H), 4.47 (2, *m*-H), 0.24 (Me), -0.20 (Me), -5.00 (CH_2), -5.45 (CH_2). Absorption spectrum (THF; λ_{max} , nm (ϵ_M)): 320 (sh, 38 200). Anal. Calcd for $\text{C}_{36}\text{H}_{68}\text{Br}_2\text{Fe}_6\text{P}_4\text{S}_8$: C, 31.42; H, 4.98; Fe, 24.35; P, 9.00; S, 18.64. Found: C, 32.22; H, 4.96; Fe, 24.75; P, 8.70; S, 18.76. $\mu_{\text{eff}} = 2.47 \mu_B$ (toluene- d_8 , 296 K).

Collection and Reduction of X-ray Data. Brown-black needles of $\text{Fe}_6\text{S}_6(\text{PET}_3)_4(\text{S-}p\text{-C}_6\text{H}_4\text{Br})_2 \cdot 1.5\text{THF}$ were obtained by layer diffusion of hexanes into a THF solution. A suitable crystal was mounted under dinitrogen and sealed in a glass capillary. Diffraction experiments were performed at 192 K on a Nicolet R3m/V four-circle automated diffractometer using Mo $K\alpha$ radiation and equipped with a graphite monochromator and a LT-1 low-temperature device. Crystallographic data are listed in Table I. The final orientation matrix and unit cell parameters were obtained from 25 machine-centered reflections with $20^\circ \leq 2\theta \leq 25^\circ$. Intensities of three standard reflections examined every 80 reflections showed no significant decay over the course of data collection. The data were corrected for Lorentz and polarization effects by using the program XTAPE of the SHELXTL program package.¹⁷ An empirical absorption correction was applied by using the program PSICOR. Axial photographs indicated the Laue group *mmm*. The systematic absences $0kl$ ($l = 2n + 1$), $h0l$ ($l = 2n + 1$), $hk0$ ($h + k = 2n + 1$), $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), and $00l$ ($l = 2n + 1$) uniquely determine space group *Pccn* (No. 56). Successful solution and refinement of the structure with the SHELXTL-PLUS program package¹⁷ confirmed this choice of space group.

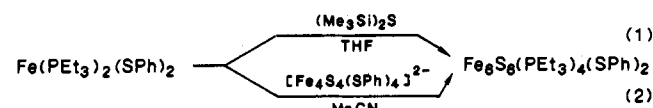
Structure Solution and Refinement. Atomic scattering factors were taken from the tabulation of Cromer and Waber.¹⁸ The structure was solved by using a combination of direct methods and Fourier techniques. Isotropic refinement of a model including the cluster and one THF solvate molecule converged at $R = 13.3\%$. Subsequent Fourier maps revealed an additional THF solvate molecule disordered about a 2-fold axis. The asymmetric unit consists of one cluster and 1.5 THF solvate molecules. Some, but not all, hydrogen atoms were located in the difference Fourier maps. In the final stages of refinement, therefore, hydrogen atoms were placed at a fixed distance of 0.96 Å from, and with thermal parameters set to 1.2 times those of, the bonded carbon atoms. Full-matrix least-squares refinement was performed with anisotropic thermal parameters on all non-carbon atoms of the cluster. Owing to limitations in the quality of data, refinement of $F_o > 3\sigma(F)$ data resulted in negative thermal motion for most of the carbon atoms and in rather high residuals (ca. 10%). All carbon atoms and solvate molecules were therefore described isotropically by using data with $F_o > 6\sigma(F)$. This approach gave improvements in residuals and standard deviations; no significant changes were observed in the structural model. Final agreement factors are listed in Table I, and positional parameters are collected in Table II.¹⁹

The compound $\text{Fe}_6\text{S}_6(\text{PET}_3)_4(\text{SPh})_2$, as obtained by layer diffusion of hexanes in THF, crystallizes in monoclinic space group $P2_1/a$ (No. 14, cell choice 3) with $a = 21.27$ (1) Å, $b = 10.428$ (3) Å, $c = 24.39$ (1) Å, $\beta = 96.20$ (4)°, and $Z = 4$. Because of poor crystal quality, diffraction data were limited and the structure, although solved, could not be satisfactorily refined. However, the determination clearly revealed the same cluster structure as for the preceding compound.

Other Physical Measurements. Strictly anaerobic conditions were employed for all measurements. Spectrophotometric, spectroscopic, and electrochemical measurements were made as described.³ Cluster magnetic moments in solution were determined by the usual NMR method²⁵ using *tert*-butyl methyl ether as the reference. Electrochemical measurements were performed in THF solutions with 0.1 M (*n*-Bu₄N)ClO₄ as supporting electrolyte and the SCE as the reference electrode.

Results and Discussion

Preparation of $\text{Fe}_6\text{S}_6(\text{PET}_3)_4(\text{SR})_2$. Reaction of equimolar quantities of $\text{Fe}(\text{PET}_3)_2(\text{SPh})_2$ and $(\text{Me}_3\text{Si})_2\text{S}$ in THF solution for a minimum of 12 h (reaction 1) afforded $\text{Fe}_6\text{S}_6(\text{PET}_3)_4(\text{SPh})_2$ in 70% purified yield. Attempts to isolate the monomeric precursor



gave only an intractable oil, necessitating in situ generation of this reactant. The compound is extremely dioxygen-sensitive and is soluble in weakly polar or nonpolar solvents but slowly decomposes in chlorinated solvents. The choice of reagents that lead to a well-defined product is quite restrictive. The use of alkanethiolates, phenoxide, arene-substituted tertiary phosphines, or phosphites failed, giving only insoluble black precipitates or intractable oils. Similarly, insoluble black materials were obtained with the arenethiolates *p*-O₂NC₆H₄S⁻ and *p*-MeOC₆H₄S⁻. An inseparable mixture of products, one of which was $\text{Fe}_6\text{S}_6(\text{PMe}_3)_4(\text{SPh})_2$ (identified by ¹H NMR, vide infra), was obtained with trimethylphosphine.

$\text{Fe}_6\text{S}_6(\text{PET}_3)_4(\text{SPh})_2$ was also obtained in 65% purified yield by reaction 2. Analogous core expansion reactions have been shown to give $\text{Fe}_6\text{S}_6(\text{PET}_3)_4\text{X}_2$ in good yield.³ These transformations underscore the stability of the basket structure, in the presence of phosphine, relative to that of the rather robust cubane core.

The clusters $\text{Fe}_6\text{S}_6(\text{PET}_3)_4(\text{SR})_2$ are also accessible by the ligand substitution reaction 3. That with $\text{R} = p\text{-C}_6\text{H}_4\text{Br}$ was obtained



in 49% yield, and the $\text{R} = \text{Ph}$ cluster was isolated in comparable yield. This method can doubtless be extended to other arenethiolate clusters. The use of several alkanethiolates resulted in the formation of intractable black solids. Reactions 2 and 3 with arenethiolates avoid the manipulation of oily initial products during workup and are to be preferred over reaction 1 in the preparation of $\text{Fe}_6\text{S}_6(\text{PET}_3)_4(\text{SR})_2$.

Structure of $\text{Fe}_6\text{S}_6(\text{PET}_3)_4(\text{S-}p\text{-C}_6\text{H}_4\text{Br})_2 \cdot 1.5\text{THF}$. Presented in Figure 1 are two views of the structure of the $\text{Fe}_6\text{S}_6\text{P}_4\text{S}_2$ portion of this cluster. Selected metric data are compiled in Table III. Ethyl and phenyl groups are unexceptional but for one methyl group, whose disorder was modeled over two positions. One THF solvate molecule was well-behaved; the other was disordered around a 2-fold axis. These aspects of the structure are not further considered. The cluster is of the basket type and, as such, resembles $\text{Fe}_6\text{S}_6(\text{PBu}_3)_4\text{Cl}_2$, whose structure has been described in some detail.^{2,3} The leading features of the structure of $\text{Fe}_6\text{S}_6(\text{PET}_3)_4(\text{S-}p\text{-C}_6\text{H}_4\text{Br})_2$ are briefly summarized.

(i) The mixed-valence $[\text{Fe}_6(\mu_4\text{-S})(\mu_3\text{-S})_4(\mu_2\text{-S})]^{2+}$ core (4 Fe(II) + 2 Fe(III)) has the basket configuration: six nonplanar Fe_2S_2 rhombs are fused to form the basket itself, and the Fe(2)–S(2)–Fe(4) portion (bond angle 74.0 (2)°) serves as the handle.

(ii) The close approach of the $\text{Fe}_6\text{S}_6\text{P}_4\text{S}_2$ portion of the structure to C_{2v} symmetry is apparent from the dimensions related under this symmetry, which are grouped accordingly in Table III, and by the mean deviation of ± 0.037 Å by the six core atoms from

(17) Nicolet XRD Corp., Madison, WI.

(18) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974.

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

Table II. Fractional Atomic Coordinates ($\times 10^4$) for $\text{Fe}_6\text{S}_6(\text{PET}_3)_4(\text{S}-p\text{-C}_6\text{H}_4\text{Br})_2 \cdot 1.5\text{THF}$

atom ^a	x/a	y/b	z/c	atom ^a	x/a	y/b	z/c
Fe(1)	6117 (1)	1987 (2)	7723 (2)	C(32)	5304 (8)	-839 (12)	8101 (11)
Fe(2)	5542 (1)	1493 (2)	8638 (1)	C(33)	5734 (8)	-510 (12)	6470 (11)
Fe(3)	5693 (1)	760 (2)	7588 (2)	C(34)	5510 (8)	-1022 (11)	6039 (10)
Fe(4)	6367 (1)	977 (2)	8468 (1)	C(35)	4886 (7)	240 (11)	6413 (10)
Fe(5)	6561 (1)	1027 (2)	7178 (2)	C(36)	5081 (7)	585 (11)	5782 (10)
Fe(6)	5215 (1)	1826 (2)	7431 (2)	C(41)	6790 (9)	-194 (13)	9560 (12)
S(1)	5525 (2)	2478 (3)	8201 (3)	C(42)	6505 (9)	-647 (13)	9239 (13)
S(2)	5995 (2)	1092 (3)	9392 (3)	C(43)	7201 (10)	1002 (14)	9753 (13)
S(3)	5005 (2)	981 (3)	8041 (3)	C(44)	7433 (11)	1598 (13)	9545 (13)
S(4)	5865 (2)	1486 (3)	6822 (3)	C(45)	7480 (13)	262 (17)	8582 (15)
S(5)	6320 (2)	177 (3)	7751 (3)	C(46)	7779 (18)	-257 (28)	8769 (26)
S(6)	6834 (2)	1683 (3)	7965 (3)	C(460)	7437 (18)	-228 (24)	8242 (23)
S(7)	7127 (2)	912 (3)	6407 (3)	C(71)	6865 (9)	374 (13)	5844 (12)
S(8)	4716 (2)	2147 (3)	6626 (3)	C(72)	6516 (8)	583 (12)	5400 (10)
P(3)	5339 (2)	-27 (3)	6983 (3)	C(73)	6321 (8)	189 (12)	4922 (11)
P(2)	5047 (2)	1737 (3)	9500 (3)	C(74)	6460 (9)	-452 (13)	4913 (13)
P(1)	6384 (2)	2894 (3)	7206 (3)	C(75)	6773 (9)	-655 (14)	5361 (12)
P(4)	6958 (2)	499 (4)	9051 (3)	C(76)	6972 (8)	-249 (12)	5828 (11)
Br(1)	6198 (1)	-1008 (2)	4281 (2)	C(81)	4225 (7)	2504 (12)	6987 (10)
Br(2)	2856 (1)	3433 (2)	7875 (2)	C(82)	4208 (8)	2741 (10)	7627 (11)
C(11)	6835 (8)	2771 (11)	6549 (10)	C(83)	3812 (7)	2994 (11)	7906 (11)
C(12)	6665 (7)	2533 (12)	5908 (10)	C(84)	3408 (8)	3052 (11)	7504 (12)
C(13)	6663 (7)	3472 (11)	7750 (10)	C(85)	3406 (9)	2839 (12)	6858 (11)
C(14)	6393 (9)	3717 (13)	8336 (11)	C(86)	3809 (8)	2577 (12)	6604 (11)
C(15)	5907 (7)	3318 (10)	6795 (10)	O(1)	1954 (8)	4039 (13)	8614 (11)
C(16)	6039 (7)	3957 (11)	6446 (11)	C(91)	1774 (12)	4584 (17)	8345 (15)
C(21)	4507 (7)	2161 (12)	9234 (10)	C(92)	1379 (11)	4502 (15)	7837 (15)
C(22)	4164 (8)	2337 (12)	9790 (11)	C(93)	1434 (11)	3809 (15)	7734 (15)
C(23)	4844 (8)	1070 (11)	9996 (10)	C(94)	1632 (12)	3561 (18)	8320 (16)
C(24)	4547 (8)	562 (12)	9610 (12)	O(2)	2500 ^b	2500 ^b	4603 (28)
C(25)	5312 (8)	2228 (11)	10129 (11)	C(95)	2869 (16)	2814 (27)	5084 (19)
C(26)	5490 (9)	2888 (12)	9924 (12)	C(96)	2376 (18)	2832 (12)	5426 (20)
C(31)	5037 (8)	-599 (11)	7500 (11)	C(96A)	2624 (18)	2168 (12)	5426 (20)

^aThe atom-labeling scheme for the cluster is given in Figure 1. That for the THF molecules of solvation is



^bFixed parameter; not refined.

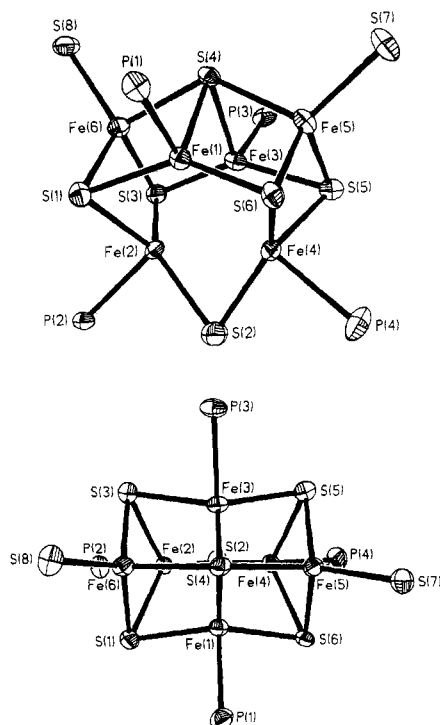


Figure 1. Two depictions of the $\text{Fe}_6\text{S}_6\text{P}_4\text{S}_2$ portion of the structure of $\text{Fe}_6\text{S}_6(\text{PET}_3)_4(\text{S}-p\text{-C}_6\text{H}_4\text{Br})_2$, showing the atom-labeling scheme and 50% probability ellipsoids. In the lower drawing the molecule is viewed down the idealized C_2 axis, through atoms S(2,4).

the 10-atom least-squares plane Fe(2,4,5,6)-S(2,4)-P(2,4)-S(7,8). The mean plane Fe(1,3)-S(2,4)-P(1,3), perpendicular to the first,

contains its four core atoms to ± 0.016 Å. The largest deviations from the idealized symmetry are found with bond angles external to the core and the attendant terminal atom deviations from the 10-atom plane (mean ± 0.157 Å).

(iii) The core exterior consists of six Fe_2S_2 rhomboidal faces and two confacial Fe_3S_3 rings in a distorted chairlike conformation. The molecule is virtually identical in this regard with $\text{Fe}_6\text{S}_6(\text{PBu}_3)_4\text{Cl}_2$, for which a detailed description of conformation and a comparison with the prismane Fe_6S_6 core have been provided.³

(iv) The Fe(5,6) S_3 (SR) sites have a distorted-tetrahedral stereochemistry with the Fe atoms displaced an average of 0.95 Å above the S_3 planes. The mean Fe-S terminal bond length of 2.255 Å is indistinguishable from those in two different salts of $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$,^{20,21} indicating an electronically delocalized structure. A localized Fe(II) or Fe(III) site would afford distances that would be at least 0.05 Å longer or shorter, respectively, than those observed.²²

(v) The $\text{Fe}_3\text{S}_3\text{P}$ sites divide into two inequivalent pairs (Fe(1,3) and Fe(2,4)) under idealized C_{2v} symmetry; their stereochemistry is unconventional. The mean displacements of Fe(1,3) and Fe(2,4) above their least-squares S_3 planes are 0.145 and 0.057 Å, respectively. The six S-Fe-S angles within rhombs, which cover the range 102.6 (2)-110.2 (2)°, are unexceptional compared to

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Table III. Selected Interatomic Distances (Å) and Angles (deg) for $\text{Fe}_6\text{S}_6(\text{PEt}_3)_4(\text{S}-p\text{-C}_6\text{H}_4\text{Br})_2 \cdot 1.5\text{THF}$

Fe(1)-Fe(2)	2.675 (4)	Fe(1)-Fe(5)	2.619 (4)	Fe(5)-S(4)	2.309 (6)	Fe(1)-S(4)	2.220 (6)
Fe(3)-Fe(2)	2.656 (4)	Fe(3)-Fe(5)	2.657 (4)	Fe(6)-S(4)	2.329 (6)	Fe(3)-S(4)	2.226 (6)
Fe(1)-Fe(4)	2.694 (5)	Fe(1)-Fe(6)	2.647 (4)	mean	2.319	mean	2.223
Fe(3)-Fe(4)	2.650 (4)	Fe(3)-Fe(6)	2.635 (4)	Fe(1)-P(1)	2.301 (7)	Fe(5)-S(7)	2.251 (7)
mean	2.669	mean	2.640	Fe(2)-P(2)	2.293 (6)	Fe(6)-S(8)	2.259 (7)
Fe(2)-Fe(6)	2.700 (4)	Fe(1)-Fe(3)	2.856 (4)	Fe(3)-P(3)	2.287 (7)	mean	2.255
Fe(4)-Fe(5)	2.665 (4)	Fe(2)-Fe(4)	2.602 (4)	Fe(4)-P(4)	2.283 (8)		
mean	2.683			mean	2.291		
Fe(1)-S(1)	2.194 (6)	Fe(2)-S(1)	2.249 (7)	S(1)...S(2)	4.004 (11)	S(1)...S(4)	3.609 (10)
Fe(1)-S(6)	2.187 (6)	Fe(2)-S(3)	2.220 (6)	S(2)...S(3)	3.923 (11)	S(3)...S(4)	3.625 (10)
Fe(3)-S(3)	2.204 (6)	Fe(4)-S(5)	2.221 (7)	S(2)...S(5)	3.941 (11)	S(4)...S(5)	3.568 (10)
Fe(3)-S(5)	2.185 (7)	Fe(4)-S(6)	2.233 (6)	S(2)...S(6)	3.938 (10)	S(4)...S(6)	3.613 (10)
mean	2.192	mean	2.231	mean	3.952	mean	3.604
Fe(6)-S(1)	2.250 (7)	Fe(2)-S(2)	2.164 (7)	S(1)...S(3)	3.487 (11)	S(1)...S(6)	4.098 (11)
Fe(6)-S(3)	2.241 (7)	Fe(4)-S(2)	2.158 (7)	S(5)...S(6)	3.509 (10)	S(3)...S(5)	4.136 (11)
Fe(5)-S(5)	2.234 (7)	mean	2.161	mean	3.498	mean	4.117
Fe(5)-S(6)	2.244 (6)						
mean	2.242						
S(2)-Fe(2)-S(3)	127.0 (3)	S(4)-Fe(1)-S(1)	109.7 (2)	P(1)-Fe(1)-S(1)	93.5 (2)	S(7)-Fe(5)-S(5)	119.5 (3)
S(2)-Fe(2)-S(1)	130.3 (3)	S(4)-Fe(1)-S(6)	110.2 (2)	P(1)-Fe(1)-S(6)	92.2 (2)	S(7)-Fe(5)-S(6)	108.0 (2)
S(2)-Fe(4)-S(5)	128.3 (3)	S(4)-Fe(3)-S(3)	109.8 (2)	P(2)-Fe(2)-S(1)	94.6 (2)	S(8)-Fe(6)-S(1)	124.1 (3)
S(2)-Fe(4)-S(6)	127.5 (3)	S(4)-Fe(3)-S(5)	108.0 (2)	P(2)-Fe(2)-S(3)	95.8 (2)	S(8)-Fe(6)-S(3)	117.7 (3)
mean	128.3	mean	109.4	P(3)-Fe(3)-S(3)	89.2 (2)	S(7)-Fe(5)-S(4e)	116.0 (2)
S(4)-Fe(5)-S(5)	103.5 (2)	S(1)-Fe(1)-S(6)	138.6 (3)	P(3)-Fe(3)-S(5)	91.9 (2)	S(8)-Fe(6)-S(4)	102.0 (2)
S(4)-Fe(5)-S(6)	105.0 (2)	S(3)-Fe(3)-S(5)	140.9 (3)	P(4)-Fe(4)-S(5)	92.7 (3)		
S(4)-Fe(6)-S(1)	104.0 (2)	mean	139.8	P(4)-Fe(4)-S(6)	95.2 (3)		
S(4)-Fe(6)-S(3)	105.0 (2)			mean	93.1		
mean	104.4			Fe(2)-S(2)-Fe(4)	74.0 (2)	Fe(1)-S(4)-Fe(3)	79.9 (2)
S(1)-Fe(2)-S(3)	102.6 (2)					Fe(5)-S(4)-Fe(6)	129.8 (3)
S(5)-Fe(4)-S(6)	104.0 (2)			Fe(1)-S(1)-Fe(2)	73.8 (2)	Fe(2)-S(1)-Fe(6)	74.5 (2)
S(5)-Fe(5)-S(6)	103.2 (2)			Fe(1)-S(6)-Fe(4)	73.9 (2)	Fe(2)-S(3)-Fe(6)	73.8 (2)
S(1)-Fe(6)-S(3)	101.9 (2)			Fe(3)-S(3)-Fe(2)	74.0 (2)	Fe(4)-S(6)-Fe(5)	73.5 (2)
mean	102.9			Fe(3)-S(5)-Fe(4)	75.1 (2)	Fe(4)-S(5)-Fe(5)	73.1 (2)
P(2)-Fe(2)-S(2)	85.2 (2)	P(1)-Fe(1)-S(4)	97.2 (2)	mean	74.2	mean	73.7
P(4)-Fe(4)-S(2)	87.8 (3)	P(3)-Fe(3)-S(4)	102.7 (2)	Fe(1)-S(1)-Fe(6)	72.7 (2)	Fe(1)-S(4)-Fe(6)	70.7 (2)
mean	86.5	mean	100.0	Fe(1)-S(6)-Fe(5)	73.9 (2)	Fe(1)-S(4)-Fe(5)	71.7 (2)
				Fe(3)-S(5)-Fe(5)	72.5 (2)	Fe(3)-S(4)-Fe(6)	71.1 (2)
				Fe(3)-S(3)-Fe(6)	73.1 (2)	Fe(3)-S(4)-Fe(5)	70.6 (2)
				mean	73.0	mean	71.0
				Fe(5)-S(7)-C(71)	102.3 (8)		
				Fe(6)-S(8)-C(81)	109.1 (7)		

the sites in (iv). However, of the 12 P-Fe-S angles, all but one occur in the 85.5 (2)-97.2 (2)° interval, and most of these are near 90°. Further, each Fe site shows exceptionally large S-Fe-S angles external to the rhombs. The two at Fe(1,3) and the four at the handle atoms Fe(2,4) average to 139.8 and 128.3°, respectively. These coordination sites may be described as distorted trigonal pyramids.

These structural results and those for $\text{Fe}_6\text{S}_6(\text{PBu}_3)_4\text{Cl}_2^{2,3}$ demonstrate that the detailed basket stereochemistry, at least at the $[\text{Fe}_6\text{S}_6]^{2+}$ oxidation level, is virtually independent of the nature of the anionic ligand. The conclusion concerning a delocalized electronic structure in (iv) is consistent with the results of Mössbauer spectroscopy, which will be reported elsewhere.²⁶ The

unusual coordination units in (v) have also been found in $\text{Fe}_7\text{S}_6(\text{PEt}_3)_4\text{Cl}_3$,¹ $\text{Fe}_6\text{S}_6(\text{PBu}_3)_4\text{Cl}_2$,^{2,3} and $\text{Co}_7\text{S}_6(\text{PPh}_3)_5\text{Cl}_2$ ⁸ and nowhere else to our knowledge. Evidently, this structure for M(II) ions with a normal tetrahedral stereochemical preference is an intrinsic property of phosphine-bound sites in baskets and in other clusters whose structures may be idealized as monocapped prisms.^{1,3} A clear coaction of this structural feature is the Fe(2)-Fe(4) distance of 2.602 (4) Å, the shortest in the molecule and one of the shortest reported in Fe-S clusters of the types summarized below. This and the other Fe-Fe distances indicate that metal-metal bonding is significant in stabilizing the basket structure.

Solution Stereochemistry. The absorption spectrum of $\text{Fe}_6\text{S}_6(\text{PEt}_3)_4(\text{SPh})_2$ is presented in Figure 2 as a simple means of identification of this compound. The spectrum of the *p*-bromobenzenethiolate cluster is similar. The ¹H NMR spectra of two clusters are shown in Figure 3. These spectra are isotropically shifted because of cluster paramagnetism; magnetic moments in toluene solution at room temperature are close to those for a *S* = 1 ground state. Signal assignments are based on relative intensities, substitution effects, and 2D-COSY experiments. The existence of one set of thiolate resonances and two sets of phosphine signals in a 2:1 intensity ratio indicates that the basket stereochemistry is retained in solution.

The clusters $\text{Fe}_6\text{S}_6(\text{PEt}_3)_4(\text{SR})_2$ in THF solutions show quasi-reversible reductions at -0.87 V (R = Ph) and -0.60 V (R = *p*-C₆H₄Br), with the latter more nearly approaching chemical reversibility. Another reduction and an oxidation, both irreversible, were observed for each cluster. When subjected to coulometric

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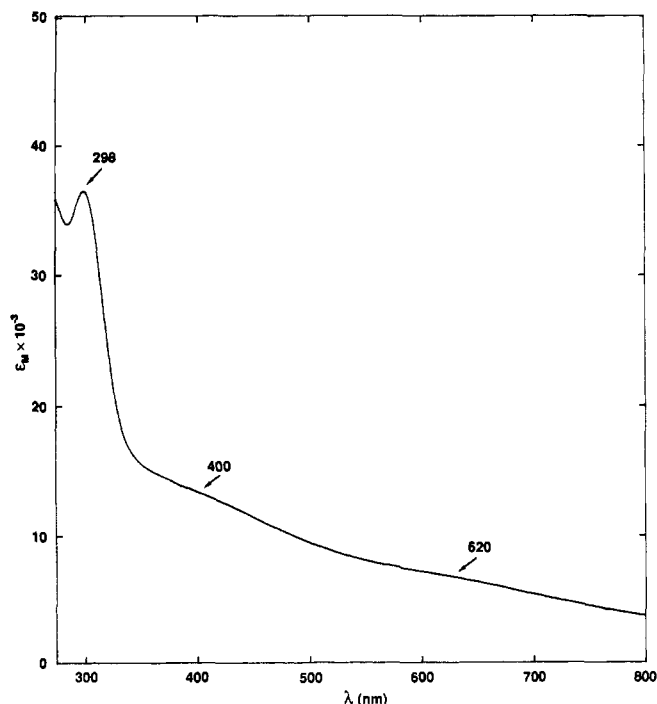


Figure 2. Absorption spectrum of $\text{Fe}_6\text{S}_6(\text{PEt}_3)_4(\text{SPh})_2$ in THF solution at 295 K.

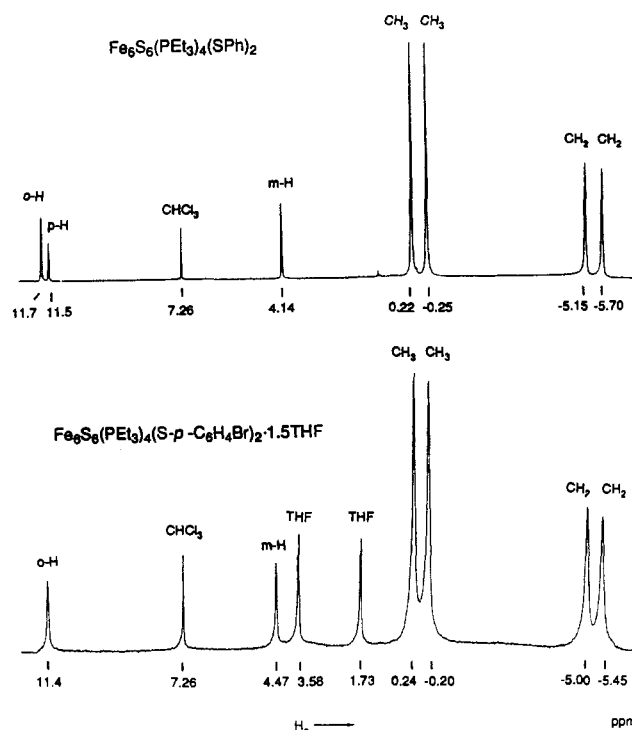
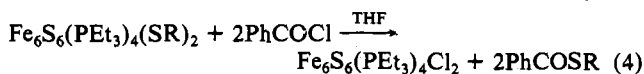


Figure 3. ^1H NMR spectra of $\text{Fe}_6\text{S}_6(\text{PEt}_3)_4(\text{SR})_2$ ($\text{R} = \text{Ph}, p\text{-C}_6\text{H}_4\text{Br}$) in CDCl_3 solutions at 296 K. Signal assignments are indicated.

oxidation or reduction, both clusters gave evidence of decomposition, and no attempt was made to isolate products.

Reactivity. The occurrence of reaction 3 demonstrates that chloride can be replaced by thiolate. The reverse transformation is effected by reaction 4. Yields for the $\text{R} = \text{Ph}$ and $p\text{-C}_6\text{H}_4\text{Br}$



clusters are comparable; that for the latter was determined as 75%. A small amount of cluster decomposition was evidenced by the formation of a black insoluble solid. These reactions are analogous to ligand substitution processes of Fe_4S_4 cubane clusters.¹⁵ Attempts to cap or otherwise cause reaction of the open face of

Table IV. Schematic Structures of Iron-Sulfur Clusters

nuclearity		ref
2		4, 27a, 28
3		29
4		4, 5, 20, 21, 23, 24, 27, 30-32
6		11-13
6		2, 3, this work
6		6, 7, 29
6		33, 34
7		1
8		14

$\text{Fe}_6\text{S}_6(\text{PEt}_3)_4(\text{SPh})_2$ with the purpose of forming mixed-metal clusters have thus far been unsuccessful with various vanadium, molybdenum, and silver reactants.

Iron-Sulfur Clusters: The Topologically Most Diverse Set. The basket clusters are the newest addition to the set of structurally characterized Fe-S clusters. With their advent and because of the lack of any comparable compilation elsewhere, we provide in Table IV a brief schematic representation of all known Fe-S cluster types. This collection does not include organometallic clusters, which in general differ from those shown by means of

their closed-shell electronic configurations and more extensive metal-metal bonding. The clusters represented contain the weak-field, anionic terminal ligands $L = RS^-$, RO^- , and halide and span the nuclearities 2-8.

It is immediately evident that prismane and basket clusters are topological isomers and that the Fe_2S_2 rhomb (albeit of varying dimensions) is the building block of all known Fe-S clusters. Indeed, the basket cluster is the only one not built up entirely by the connection of rhombs at a common point or their fusion at edges. We have previously documented¹⁻³ the conversion and/or interconversion of all clusters, except $[Fe_6S_9(SR)_2]^{4-}$, $[Fe_6S_8(PEt)_6]^{2+,+}$, and $[Fe_8S_6I_3]^{3-}$, in reactions that afford only one cluster product, often with known stoichiometry. One cluster not listed in Table IV is the trinuclear core entity $[Fe_3S_4]^{+,0}$, found in a number of proteins but not yet prepared outside a protein environment. Crystallographic results for aconitase³⁵ and a recent redetermination of the structure of *Azotobacter vinelandii* ferredoxin II³⁶ indicate a triangular Fe_3 arrangement and the voided-cubane structure $Fe_3(\mu_3-S)(\mu_2-S)_3$. These units can be reconstituted to the corresponding Fe_4S_4 cubanes,³⁷ providing another example of cluster conversion.

Summary. The following are the principal findings and conclusions from this investigation.

1. The iron-sulfur-thiolate basket clusters $Fe_6S_6(PEt_3)_4(SR)_2$ ($R = \text{arene}$) may be prepared in 65-70% purified yield by cluster self-assembly ($Fe(PEt_3)_2(SR)_2 + (Me_3Si)_2S$) or cluster expansion ($Fe(PEt_3)_2(SPh)_2 + [Fe_4S_4(SPh)_4]^{2-}$) in THF solution. The latter

process and ligand substitution (vide infra) are the preferred methods of synthesis.

2. The $[Fe_6(\mu_4-S)(\mu_3-S)_4(\mu_2-S)]^{2+}$ core of $Fe_6S_6(PEt_3)_4(S-p-C_6H_4Br)_2$ is essentially congruent with that of $Fe_6S_6(PBu_3)_4Cl_2$ and consists of six nonplanar Fe_2S_2 rhombs fused to form a basket with the bridge unit Fe-S-Fe acting as the handle.

3. Basket stereochemistry is retained in solution and is maintained in thiolate-chloride substitution reactions.

4. The baskets $Fe_6S_6(PEt_3)_4L_2$ ($L = RS^-$, halide) are the newest type of Fe-S cluster. They are topological isomers of prismane clusters and form part of a set of Fe-S clusters of nuclearities 2, 3, 4, 6, and 7 whose core structures may be converted or interconverted under mild conditions.

It is apparent that neither the coherence nor complexity of Fe-S cluster chemistry has been exhausted. For example, in this laboratory²⁶ we have characterized a basket cluster, $[Fe_6S_6(PEt_3)_6]^{+}$, lacking anionic terminal ligands, and found it to be a synthetic precursor to at least one other cluster topology. Additionally, we have identified a cluster of core composition $Fe_{18}S_{30}$ of an entirely different overall structure than has been encountered previously.³⁸ These clusters, together with the electronic properties of basket clusters, will be the subjects of subsequent reports.

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Supplementary Material Available: For $Fe_6S_6(PEt_3)_4(S-p-C_6H_4Br)_2$, a stereoview and tables of crystal data, intensity collection, and refinement parameters, atom thermal parameters, interatomic distances and angles, and calculated hydrogen atom positions (11 pages); a table of calculated and observed structure factors (51 pages). Ordering information is given on any current masthead page.

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A Triply Bridged Dinuclear Tris(bipyridine)iron(II) Complex: Synthesis and Electrochemical and Structural Studies

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A triply bridged dinuclear iron complex consisting of three bridging bis[4-(2,2'-bipyridinyl)]ethane ligands linking the two Fe(II) centers has been synthesized. An X-ray crystallographic study has confirmed the dinuclear structure. Cyclic voltammetry, differential-pulse voltammetry, and Osteryoung square-wave voltammetry studies have been conducted on the dinuclear iron complex and on the corresponding $Fe^{II}(4,4'-Me_2bpy)_3$ mononuclear complex. The electrochemistry of the dinuclear complex demonstrates that there exists significant interaction between the two iron centers. Given that the ligand bridges consist of saturated hydrocarbon linkages, through-bond interactions are not important, and thus the observed effects are purely through-space and electrostatic in nature.

Introduction

Symmetric dinuclear metal complexes have long been of interest with regard to studying phenomena associated with mixed-valence oxidation states.¹ When two redox active metal centers are linked via a bridging ligand or by a direct bond, the redox potential of one of the two centers can be influenced by the oxidation state of the other. When the bridging moiety is a single atom, a bond, or a molecule containing conjugated unsaturation, the possibility exists for charge delocalization over the two centers. In one extreme case, the second site becomes thermodynamically harder

to oxidize or reduce than the first, producing, for example, a splitting of the cyclic voltammetric waves into two separated one-electron processes. In the other extreme case, the second electron-transfer process becomes thermodynamically easier than the first, resulting in a formal two-electron process, characterized by a single cyclic voltammetric wave having a peak separation of 30 mV. On the other hand, if the valence is localized and the two sites are far apart, the cyclic voltammogram is indistin-

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