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A Novel Iron–Sulfur–Thiolate Basket Cluster: Synthesis, Structure, and Properties of $Fe_6S_5(\mu\text{-SPh})(P\text{-}n\text{-Bu}_3)_4(SPh)_2$

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A new iron–sulfur compound $Fe_6S_5(\mu\text{-SPh})(P\text{-}n\text{-Bu}_3)_4(SPh)_2$ (**1**) synthesized by the reaction of $Fe(P\text{-}n\text{-Bu}_3)_2(SPh)_2$ and $(n\text{-Bu}_4N)_2[Fe_4S_4(SPh)_4]$ in MeCN/THF has been characterized by elemental analyses and spectroscopic methods. The crystal and molecular structure of **1** was determined by X-ray diffraction data using a CAD-4 diffractometer. The compound crystallizes in the triclinic space group $P\bar{1}$, $a = 11.877$ (3) Å, $b = 14.302$ (3) Å, $c = 24.920$ (2) Å, $\alpha = 94.844$ (4)°, $\beta = 96.587$ (4)°, $\gamma = 100.443$ (3)°, $V = 4111.7$ (3) Å^3, $Z = 2$, and R (R_w) = 0.077 (0.066) for 6042 reflections ($I > 3\sigma(I)$). It is a six-Fe cluster with the core $(Fe_6S_5{}^*S)^+$ consisting of six Fe_2S_2 units fused in the form of a basket by sharing edges. All six iron atoms are tetrahedrally coordinated and the formal oxidation level is five Fe(II) + one Fe(III). The electrochemical behavior of the compound in $CHCl_3$ was investigated. The reactivities and ^1H NMR and EPR spectra are also discussed.

Introduction

Iron–sulfur proteins have been extensively investigated in the last 20 years. The preparation of $[Fe_4S_4(SCH_2Ph)_4]^{2-}$, the first synthetic analogue for the active center of 4Fe-4S protein, was accomplished in 1972.[1] Following reports of the syntheses and characterization of mono-, di-, tri-, and tetranuclear Fe–S complexes,[2,3] there appeared many works on six-Fe[4-15] and eight-Fe[16] compounds. Holm has reported $Fe_6S_6(P\text{-}n\text{-Bu}_3)_4Cl_2$ (**2**)[17] and $[Fe_6S_6(PEt_3)_4(S\text{-}p\text{-}C_6H_4Br)_2]\cdot 1.5THF$ (**3**)[18] with a $[Fe_6(\mu_4\text{-}S^*)(\mu_3\text{-}S^*)_4(\mu_2\text{-}S^*)]^{2+}$ (S* indicates inorganic sulfur atom) core, which is interesting due to its basketlike configuration. Here we report the synthesis, structure, ^1H NMR spectrum, cyclic voltammogram, and reactivities of yet another six-Fe cluster containing a $[Fe_6(\mu_4\text{-}S^*)(\mu_3\text{-}S^*)_4(\mu_2\text{-}S)]^{1+}$ core.

Experimental Section

Materials. The compound $(n\text{-Bu}_4N)_2[Fe_4S_4(SPh)_4]$ was prepared as described in the literature.[19] NaSPh was obtained from the reaction of sodium metal and thiophenol in methanol. Anhydrous $FeCl_2$ and $n\text{-Bu}_3P$ were purchased from Fluka. All solvents were dried, distilled, and degassed before use. All syntheses were carried out under a dry dinitrogen atmosphere using conventional Schlenk-ware techniques. Other operations were performed in a Vac-Atmosphere MO-4O-2H drybox.

Physical Measurements. ^1H NMR spectra were obtained on a Varian FT-80A spectrometer in $CDCl_3$ at ambient temperature with TMS as internal standard and upfield chemical shifts taken as negative. EPR spectra were measured on a Bruker ER-420 spectrometer using X-band radiation ($\nu = 9435.8$ MHz) at 77 K. IR spectra were obtained on a Perkin-Elmer 577 spectrophotometer for the compound as KBr pellets. Cyclic voltammetry was performed in a three-electrode cell with both Pt working and auxiliary electrodes and a SCE reference electrode on a DHZ-1 instrument equipped with a X-Y recorder. The solutions in $CHCl_3$ contained 0.1 M $n\text{-Bu}_4NBF_4$ as supporting electrolyte, and the scan rate was 100 mV/s.

Table I. Crystallographic Data and Refinement Parameters for $Fe_6S_5(\mu\text{-SPh})(P\text{-}n\text{-Bu}_3)_4(SPh)_2$

formula	$C_{66}H_{123}Fe_6P_4S_8$
M_r	1632.2
cryst dimens, mm^3	0.30 × 0.35 × 0.40
a, Å	11.877 (3)
b, Å	14.302 (3)
c, Å	24.920 (2)
α, deg	94.844 (4)
β, deg	96.587 (4)
γ, deg	100.443 (3)
V, Å^3	4111.7 (3)
Z	2
d_c, g/cm^3	1.318
T, K	293
μ, cm^{-1}	13.4
scan speed, deg/min	2-7
no. of unique data ($I \geq 3\sigma(I)$)	6042
no. of variables	757
R (R_w), %	7.7 (6.6)

Synthesis. A mixture of 2.4 g (19 mmol) of $FeCl_2$, 5.0 g (38 mmol) of NaSPh, and 7.3 g (9 mL, 38 mmol) of $n\text{-Bu}_3P$ in 120 mL of CH_3CN was stirred for 11 h at room temperature, resulting in a clear brown-orange solution of $Fe(P\text{-}n\text{-Bu}_3)_2(SPh)_2$ (19 mmol). After filtration, 5 g (4 mmol) of $(n\text{-Bu}_4N)_2[Fe_4S_4(SPh)_4]$ was added to the filtrate, and the reaction mixture was stirred at 50 °C for 6 h. The solution was again filtered, and the filtrate was evaporated to dryness. The residue was recrystallized from THF/CH_3CN. After 1 week at 4 °C, dark brown crystals (1.0 g, 25%) of the title compound were collected by filtration, washed with CH_3CN, and dried in vacuo. $\delta(^1H)$ ($CDCl_3$), ppm: 11.02 (o-Ht + p-Ht), 9.88 (o-Hb + p-Hb), 4.75 (m-Ht), 4.33 (m-Hb), −4.77 and −5.10 (CH_2–P), 1.2 and 0.6 ($CH_2CH_2CH_3$). Anal. Calcd for $C_{66}H_{123}Fe_6P_4S_8$: C, 48.57; H, 7.60; Fe, 20.53; P, 7.59; S, 15.71. Found: C, 48.23; H, 7.35; Fe, 20.29; P, 8.00; S, 15.15.

Conversion of $Fe_6S_5(\mu\text{-SPh})(P\text{-}n\text{-Bu}_3)_4(SPh)_2$ (1) to $Fe_6S_6(P\text{-}n\text{-Bu}_3)_4Cl_2$ (2). To the stirred solution of 1.0 g (0.61 mmol) of $Fe_6S_5(\mu\text{-SPh})(P\text{-}n\text{-Bu}_3)_4(SPh)_2$ in 15 mL of THF was added 2.44 mmol of CH_3COCl or PhCOCl. The solution developed a dark brown color with a purplish cast. After 1 h, 30 mL of acetonitrile was added, causing the product to separate as black needle crystals (0.60 g, 70%), which were collected by filtration, washed with CH_3CN (10 mL), and dried in vacuo. $\delta(^1H)$ ($CDCl_3$), ppm: −7.61 and −6.52 (CH_2P), 0.72 and 1.25 ($CH_3CH_2CH_2$). Anal. Calcd for $C_{48}H_{108}Cl_2Fe_6P_4S_6$: C, 40.96; H, 7.73; Cl, 5.04; Fe, 23.81; P, 8.80; S, 13.67. Found: C, 40.79; H, 8.21; Cl, 4.89; Fe, 23.19; P, 8.36; S, 14.23.

Determination of Crystal Structure. A black prismlike single crystal of **1** with dimensions 0.3 × 0.35 × 0.40 mm was obtained from THF/

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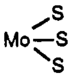
Table II. Atomic Coordinates and Thermal Parameters

atom	x	y	z	B_{eq}, Å^2
Fe(1)	−0.1254 (1)	0.9652 (1)	0.22040 (7)	3.66 (4)
Fe(2)	0.0532 (1)	1.0970 (1)	0.20110 (7)	3.78 (4)
Fe(3)	0.1108 (1)	0.9652 (1)	0.26669 (7)	3.88 (4)
Fe(4)	−0.0075 (1)	1.0948 (1)	0.30317 (7)	3.86 (4)
Fe(5)	−0.0681 (2)	0.9116 (1)	0.31767 (8)	4.47 (4)
Fe(6)	0.0347 (1)	0.9167 (1)	0.16255 (7)	3.99 (4)
S(1)	−0.0896 (3)	1.0128 (2)	0.1420 (1)	4.17 (8)
S(2)	0.0346 (3)	1.2219 (2)	0.2576 (1)	5.14 (9)
S(3)	0.1971 (3)	1.0208 (2)	0.2000 (1)	4.24 (8)
S(4)	−0.0338 (3)	0.8459 (2)	0.2349 (1)	4.33 (8)
S(5)	0.0993 (3)	1.0124 (2)	0.3510 (1)	4.38 (8)
S(6)	−0.1853 (3)	1.0141 (2)	0.2958 (1)	4.43 (8)
S(11)	0.0859 (3)	0.8229 (3)	0.0963 (2)	6.09 (9)
S(12)	−0.1537 (4)	0.8041 (3)	0.3684 (2)	7.40 (9)
P(1)	−0.3109 (3)	0.8957 (3)	0.1883 (2)	4.72 (9)
P(2)	0.1126 (3)	1.1943 (3)	0.1358 (2)	4.84 (9)
P(3)	0.2564 (3)	0.8871 (2)	0.2902 (2)	4.80 (9)
P(4)	−0.0343 (3)	1.1898 (3)	0.3784 (2)	5.60 (9)
C(1)	0.169 (1)	1.299 (1)	0.2796 (7)	7.5 (5)
C(2)	0.271 (2)	1.261 (1)	0.2957 (7)	8.6 (5)
C(3)	0.373 (2)	1.323 (1)	0.3113 (9)	11.2 (6)
C(4)	0.379 (2)	1.418 (1)	0.3124 (9)	13.1 (7)
C(5)	0.284 (2)	1.458 (1)	0.2966 (9)	12.5 (7)
C(6)	0.179 (2)	1.397 (1)	0.2804 (7)	9.3 (6)
C(11)	−0.020 (1)	0.723 (1)	0.0738 (5)	5.3 (3)
C(12)	−0.115 (1)	0.693 (1)	0.0986 (7)	7.8 (5)
C(13)	−0.194 (2)	0.612 (1)	0.0801 (8)	9.8 (6)
C(14)	−0.187 (2)	0.560 (1)	0.0343 (8)	10.0 (6)
C(15)	−0.094 (2)	0.585 (1)	0.0079 (7)	10.3 (6)
C(16)	−0.010 (2)	0.665 (1)	0.0272 (6)	8.0 (5)
C(21)	−0.073 (1)	0.713 (1)	0.3730 (6)	6.1 (4)
C(22)	−0.056 (1)	0.658 (1)	0.3250 (7)	7.6 (5)
C(23)	0.002 (1)	0.585 (1)	0.3297 (8)	8.9 (5)
C(24)	0.042 (2)	0.562 (1)	0.3812 (9)	11.8 (7)
C(25)	0.026 (2)	0.615 (1)	0.4241 (8)	12.7 (7)
C(26)	−0.034 (2)	0.688 (1)	0.4215 (7)	9.5 (6)
C(1a)	−0.342 (1)	0.841 (1)	0.1167 (5)	5.3 (4)
C(1b)	−0.465 (1)	0.794 (1)	0.0966 (7)	7.4 (5)
C(1c)	−0.481 (2)	0.755 (1)	0.0383 (8)	10.4 (6)
C(1d)	−0.601 (1)	0.710 (1)	0.0175 (9)	7.3 (8)
C(2a)	−0.380 (1)	0.802 (1)	0.2276 (5)	5.2 (3)
C(2b)	−0.334 (1)	0.712 (1)	0.2230 (6)	6.7 (4)
C(2c)	−0.398 (1)	0.636 (1)	0.2535 (9)	10.3 (6)
C(2d)	−0.353 (1)	0.545 (1)	0.2459 (9)	12.9 (7)
C(3a)	−0.408 (1)	0.982 (1)	0.1911 (6)	5.7 (4)
C(3b)	−0.384 (1)	1.067 (1)	0.1578 (7)	8.2 (5)
C(3c)	−0.457 (1)	1.137 (1)	0.1641 (8)	9.2 (5)
C(3d)	−0.434 (2)	1.193 (1)	0.2189 (9)	12.2 (7)
C(4a)	0.114 (1)	1.136 (1)	0.0664 (5)	6.6 (4)
C(4b)	0.209 (1)	1.080 (1)	0.0628 (6)	6.8 (4)
C(4c)	0.201 (1)	1.032 (1)	0.0083 (7)	8.8 (5)
C(4d)	0.297 (2)	0.975 (1)	0.0018 (6)	9.8 (6)
C(5a)	0.023 (1)	1.290 (1)	0.1263 (7)	7.7 (4)
C(5b)	−0.098 (1)	1.256 (1)	0.1167 (8)	8.9 (5)
C(5c)	−0.164 (1)	1.336 (1)	0.1129 (9)	11.5 (6)
C(5d)	−0.164 (2)	1.396 (2)	0.1660 (9)	9.3 (8)
C(6a)	0.260 (1)	1.267 (1)	0.1524 (6)	5.8 (4)
C(6b)	0.301 (1)	1.334 (1)	0.1118 (7)	6.9 (4)
C(6c)	0.415 (1)	1.394 (1)	0.1320 (8)	9.7 (6)
C(6d)	0.458 (2)	1.465 (1)	0.0945 (9)	11.7 (6)
C(7a)	0.289 (1)	0.804 (1)	0.2354 (6)	6.0 (4)
C(7b)	0.199 (1)	0.712 (1)	0.2195 (6)	5.6 (4)
C(7c)	0.235 (1)	0.651 (1)	0.1763 (7)	7.8 (5)
C(7d)	0.151 (2)	0.566 (1)	0.1569 (8)	10.1 (6)
C(8a)	0.400 (1)	0.969 (1)	0.3064 (6)	5.5 (4)
C(8b)	0.408 (1)	1.037 (1)	0.3571 (7)	6.6 (4)
C(8c)	0.521 (1)	1.098 (1)	0.3716 (7)	8.4 (5)
C(8d)	0.528 (1)	1.164 (1)	0.4222 (8)	10.3 (6)
C(9a)	0.245 (1)	0.819 (1)	0.3494 (6)	5.8 (4)
C(9b)	0.344 (1)	0.768 (1)	0.3616 (7)	8.6 (5)
C(9c)	0.342 (2)	0.731 (1)	0.4151 (9)	13.2 (7)
C(9d)	0.437 (1)	0.680 (1)	0.4294 (9)	11.5 (8)
C(10a)	0.087 (1)	1.289 (1)	0.4075 (8)	10.4 (6)
C(10b)	0.187 (2)	1.259 (1)	0.4309 (9)	12.5 (7)
C(10c)	0.291 (2)	1.347 (2)	0.4538 (9)	11.3 (7)
C(10d)	0.392 (2)	1.316 (1)	0.4758 (9)	10.1 (9)
C(11a)	−0.155 (1)	1.256 (1)	0.3566 (7)	9.3 (5)
C(11b)	−0.177 (2)	1.327 (1)	0.3954 (9)	12.3 (7)
C(11c)	−0.271 (2)	1.375 (1)	0.3648 (9)	10.8 (8)
C(11d)	−0.298 (2)	1.446 (1)	0.4046 (9)	9.3 (9)
C(12a)	−0.062 (2)	1.128 (1)	0.4413 (6)	8.9 (5)
C(12b)	−0.167 (2)	1.064 (1)	0.4399 (8)	10.2 (6)
C(12c)	−0.182 (2)	1.024 (1)	0.4936 (7)	11.3 (6)
C(12d)	−0.279 (2)	0.956 (1)	0.4892 (9)	8.6 (7)

CH_3CN. The intensity data were collected on Enraf-Nonius CAD-4 diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Accurate cell dimensions were derived from 24 reflections measured at $14 < \theta < 15.5°$ with ω–2θ scan mode as shown in Table I together with other crystallographic data and refinement parameters. Three standard reflections were monitored every 300 reflections, and no drop-off in intensities was observed. The intensities were corrected for Lorentz polarization and empirical absorption. A total of 10365 reflections were collected up to $2\theta = 45°$, of which 6042 with $I > 3\sigma(I)$ were used for structure analysis and refinement by a SDP program package on a VAX/785 computer. The structure was solved by direct methods, and the coordinates of 18 non-hydrogen atoms of the molecule were obtained from the E map, while the other non-hydrogen atoms were located from the following difference Fourier syntheses procedures. All of the non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. The hydrogen atoms were introduced at their calculated positions (C–H fixed at 1.00 Å) with isotropic thermal parameters. The final R (R_w) factor was 0.077 (0.060). The atomic coordinates with their thermal parameters are listed in Table II.

Results and Discussion

Preparation and Reactivities of $Fe_6S_5(\mu\text{-SPh})(P\text{-}n\text{-}Bu_3)_4(SPh)_2$. The title compound was prepared by the reaction of $Fe(P\text{-}n\text{-}Bu_3)_2(SPh)_2$ and $[n\text{-}Bu_4N]_2[Fe_4S_4(SPh)_4]$ in CH_3CN/THF at 50 °C. The pure product was obtained in 25% yield as dark brown crystals. The compound is soluble in weakly polar or nonpolar organic solvents and very sensitive to air even in the solid state. Compared with the reported methods of synthesis[17,18] of compounds with a $[Fe_6S^*_6]$ core, the large excess of $Fe(P\text{-}n\text{-}Bu_3)_2(SPh)_2$ present in this preparation could be the source of the μ_2-SPh bridge. The choice of reagents that lead to a well-defined product is also quite limited, since compounds like **1** with a $[Fe_6S_5{}^*S]$ core cannot be obtained with p-methyl- or p-chlorothiophenolate. All attempts to react **1** with molybdenum compounds of low, medium or high oxidation states led to decomposition. The only exception was the reaction in the presence of $Mo(CO)_3(CH_3CN)_3$, where no reaction occurred and **1** was recovered. As large S–Fe–S angles result in relatively long S···S distances (3.84–4.11 Å) in both planes S(1)S(2)S(6) and S(3)-S(2)S(5), the Mo atom in various oxidation states of molybdenum compounds is unable to reach suitable distances to connect itself with these S atoms to give a



unit as in the case of the prismatic $[Fe_6S_6X_6]^{3-}$ (X = Cl, Br),[20] which has the corresponding S···S distances of 3.59–3.63 Å and reacts with $Mo(CO)_3(CH_3CN)_3$ to form the cluster $[Fe_6S_6X_6\{Mo(CO)_3\}_2]^{3-}$. It is worthy of note that when cluster compound **1** reacted with CH_3COCl (or PhCOCl), compound **2** with the $Fe_6S_6{}^*$ core was obtained, which had been identified by elemental analysis and X-ray diffraction data. ^1H NMR measurements also revealed the conversion of compound **1** to **2** by acyl chlorides (vide infra). This result demonstrates that, with the substitution of terminal –SPh groups by chloride ions, the bridging thiophenolate

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Table III. Selected Bond Lengths (Å) for $Fe_6S_5(\mu\text{-}SPh)(P\text{-}n\text{-}Bu_3)_4(SPh)_2$

Fe(1)-Fe(2)	2.682 (3)	Fe(4)-Fe(6)	2.179 (5)
Fe(1)-Fe(4)	2.713 (4)	Fe(4)-P(4)	2.349 (6)
Fe(1)-Fe(5)	2.661 (4)	Fe(5)-S(4)	2.289 (5)
Fe(1)-Fe(6)	2.671 (4)	Fe(5)-S(5)	2.275 (4)
Fe(1)-S(1)	2.189 (5)	Fe(5)-S(6)	2.269 (6)
Fe(1)-S(4)	2.219 (5)	Fe(5)-S(7)	2.248 (6)
Fe(1)-S(6)	2.185 (5)	Fe(6)-S(1)	2.251 (5)
Fe(1)-P(1)	2.282 (5)	Fe(6)-S(3)	2.281 (4)
Fe(2)-Fe(3)	2.711 (4)	Fe(6)-S(4)	2.305 (5)
Fe(2)-Fe(4)	2.710 (4)	Fe(6)-S(8)	2.248 (6)
Fe(2)-Fe(6)	2.637 (3)	S(2)-C(1)	1.724 (7)
Fe(2)-S(1)	2.217 (4)	S(1)-S(2)	3.928 (6)
Fe(2)-S(2)	2.230 (5)	S(1)-S(3)	3.540 (6)
Fe(2)-S(3)	2.185 (5)	S(1)-S(4)	3.573 (7)
Fe(2)-P(2)	2.340 (6)	S(1)-S(6)	4.114 (7)
Fe(3)-Fe(4)	2.674 (4)	S(2)-S(3)	3.973 (7)
Fe(3)-Fe(5)	2.625 (4)	S(2)-S(5)	4.066 (7)
Fe(3)-Fe(6)	2.629 (3)	S(2)-S(6)	3.841 (6)
Fe(3)-S(3)	2.178 (5)	S(3)-S(4)	3.603 (6)
Fe(3)-S(4)	2.182 (4)	S(3)-S(5)	4.055 (7)
Fe(3)-S(5)	2.188 (6)	S(4)-S(5)	3.591 (6)
Fe(3)-P(3)	2.299 (6)	S(4)-S(6)	3.590 (7)
Fe(4)-Fe(5)	2.655 (3)	S(5)-S(6)	3.521 (7)
Fe(4)-S(2)	2.237 (5)	Fe(1)-Fe(3)	2.898 (3)
Fe(4)-S(5)	2.212 (5)		

Table IV. Selected Bond Angles (deg) for $Fe_6S_5(\mu\text{-}SPh)(P\text{-}n\text{-}Bu_3)_4(SPh)_2$

S(2)-Fe(2)-S(3)	128.3 (2)	S(4)-Fe(1)-S(1)	108.4 (3)
S(2)-Fe(2)-S(1)	124.1 (3)	S(4)-Fe(1)-S(6)	109.2 (3)
S(2)-Fe(4)-S(5)	132.2 (2)	S(4)-Fe(3)-S(3)	111.4 (2)
S(2)-Fe(4)-S(6)	120.9 (3)	S(4)-Fe(3)-S(5)	110.5 (2)
S(1)-Fe(2)-S(3)	107.2 (2)	S(4)-Fe(5)-S(5)	103.8 (2)
S(5)-Fe(4)-S(6)	106.6 (2)	S(4)-Fe(5)-S(6)	103.9 (2)
S(5)-Fe(5)-S(6)	101.6 (2)	S(4)-Fe(6)-S(1)	103.3 (2)
S(1)-Fe(6)-S(3)	102.7 (2)	S(4)-Fe(6)-S(3)	103.5 (2)
Fe(1)-S(1)-Fe(2)	75.0 (2)	Fe(2)-S(1)-Fe(6)	72.3 (2)
Fe(1)-S(6)-Fe(4)	76.9 (2)	Fe(2)-S(3)-Fe(6)	72.3 (1)
Fe(3)-S(3)-Fe(2)	76.8 (2)	Fe(4)-S(6)-Fe(5)	73.2 (2)
Fe(3)-S(5)-Fe(4)	74.8 (2)	Fe(4)-S(5)-Fe(5)	72.5 (2)
Fe(1)-S(1)-Fe(6)	73.9 (2)	Fe(1)-S(4)-Fe(6)	72.3 (2)
Fe(1)-S(6)-Fe(5)	73.3 (2)	Fe(1)-S(4)-Fe(5)	72.4 (2)
Fe(3)-S(5)-Fe(5)	72.1 (1)	Fe(3)-S(4)-Fe(6)	71.7 (2)
Fe(3)-S(3)-Fe(6)	72.2 (1)	Fe(3)-S(4)-Fe(5)	71.9 (1)
Fe(1)-S(4)-Fe(3)	84.4 (2)	Fe(2)-S(2)-Fe(4)	74.8 (2)
Fe(5)-S(4)-Fe(6)	131.6 (3)	Fe(2)-S(2)-C(1)	109.3 (2)
P(1)-Fe(1)-S(1)	93.2 (2)	Fe(4)-S(2)-C(1)	115.9 (8)
P(1)-Fe(1)-S(6)	88.7 (2)	P(3)-Fe(3)-S(3)	90.7 (2)
P(2)-Fe(2)-S(1)	90.7 (2)	P(3)-Fe(3)-S(5)	91.9 (2)
P(2)-Fe(2)-S(3)	92.0 (2)	P(4)-Fe(4)-S(5)	93.2 (2)
S(7)-Fe(5)-S(5)	121.1 (3)	P(4)-Fe(4)-S(6)	91.7 (2)
S(7)-Fe(5)-S(6)	110.9 (2)	S(8)-Fe(6)-S(1)	119.9 (3)
P(2)-Fe(2)-S(2)	92.0 (2)	S(8)-Fe(6)-S(3)	107.4 (2)
P(4)-Fe(4)-S(2)	91.5 (2)	S(7)-Fe(5)-S(4)	113.6 (3)
P(1)-Fe(1)-S(4)	106.1 (2)	S(8)-Fe(6)-S(4)	118.0 (2)
P(3)-Fe(3)-S(4)	102.2 (2)		

group was substituted by a sulfide ion.

Structure of $Fe_6S_5(\mu\text{-}SPh)(P\text{-}n\text{-}Bu_3)_4(SPh)_2$. Selected atomic distances and bond angles of compound **1** are listed in Tables III and IV, respectively. Figure 1 shows the ORTEP drawing of compound **1** where the carbon atoms of terminal thiophenolates and of tri-*n*-butylphosphine ligands except the α-carbons have been omitted for clearance. There is one molecule of **1** in an asymmetric unit. The molecule has its basket built of six edge-sharing nonplanar Fe_2S_2 rhombs and is bridged at its handle by a thiophenolate group. It can also be regarded as being composed of two incomplete cubane-like fragments $[Fe_4S_3]$ (Fe(1,2,3,6)-S(1,3,4) and Fe(1,3,4,5)-S(4,5,6)) sharing two edges Fe(1)-S(4) and Fe(3)-S(4) to form the basket. There exists in the core an approximate C_{2v} symmetry so that the C_2 axis coincides with the S(2)-S(4) vector. The skeleton geometry of this compound is quite similar to that of compound **2** or **3**. Compared to the latter, **1** differs in the handle of the basket where the μ_2-thiophenolato bridge replaces the inorganic sulfur bridge of **2** or **3**. The core $[Fe_6(\mu_4\text{-}S^*)(\mu_3\text{-}S^*)_4(\mu\text{-}SPh)]^{2+}$ in the title compound formally contains five Fe(II) + one Fe(III), while the core in compound **2** or **3** contains iron atoms at oxidation level four Fe(II) + two Fe(III).[17,18] The average Fe⋯Fe distance within the six Fe_2S_2 rhombs is 2.647 Å, nearly comparable to those in **2** or **3**, while those across the symmetry axis are 2.898 (3) Å (Fe(1)-Fe(3)) and 2.710 (4) Å (Fe(2)-Fe(4)), much longer than those in the latter (**2**, 2.835 and 2.655 Å; **3**, 2.856 and 2.602 Å). The mean Fe-μ_2-S distance of 2.234 Å and mean Fe(2,4)-P(2,4) distance of 2.345 Å are the longest for compound **1** when compared with those for **2** (2.168 and 2.315 Å) and **3** (2.161 and 2.288 Å). It is possible that the extra electron of **1** is at the handle of the basket as revealed by Mössbauer measurements.[21]

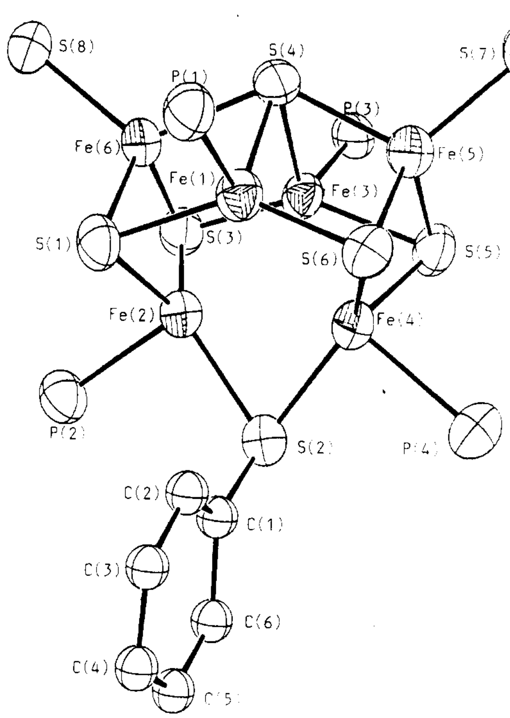

Figure 1. Structure of $Fe_6S_5(\mu\text{-}SPh)(P\text{-}n\text{-}Bu_3)_4(SPh)_2$ with carbon atoms on phosphino and terminal thiophenolato ligands omitted for clearance.

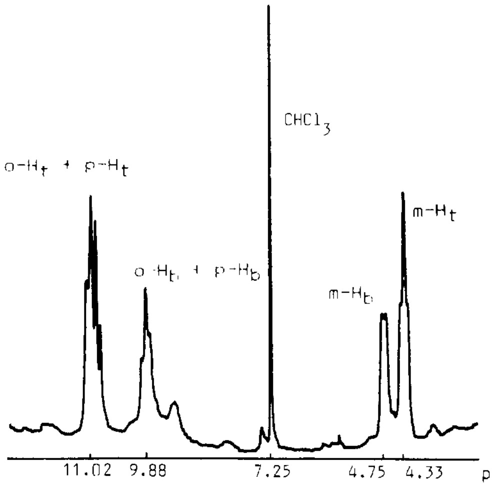

Figure 2. ^1H NMR spectrum of $Fe_6S_5(\mu\text{-}SPh)(P\text{-}n\text{-}Bu_3)_4(SPh)_2$ in $CDCl_3$ at ambient temperature. Signal assignments are indicated for downfield shifts only.

Electrochemical Behavior. Cyclic voltammetric measurements showed that compound **1** undergoes quasi-reversible one-electron oxidation at +0.12 V and reduction at -0.14 V. We conclude, therefore, that this compound is more sensitive to air than com-

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(21) Preliminary ^{57}Fe Mössbauer measurement of **1** at 77 K showed two doublets of 2:1 intensity ratio with IS (ΔE_q) = 0.53 (0.78) mm/s and 0.34 (0.78) mm/s, respectively, vs α-Fe.

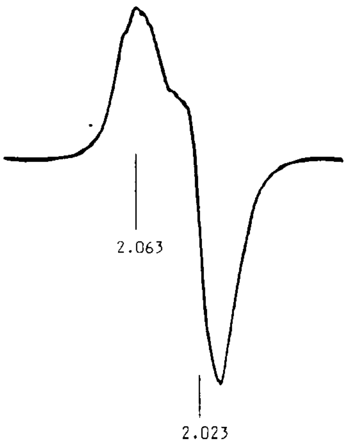

Figure 3. EPR powder spectrum of $Fe_6S_5(\mu\text{-SPh})(P\text{-}n\text{-}Bu_3)_4(SPh)_2$ at 77 K.

pounds $[Fe_6S_6(PEt_3)_4(SR)_2]$ in which quasi-reversible reductions at more negative values (−0.87 V for R = Ph and −0.60 V for R = $p\text{-}C_6H_4Br$) were observed that more nearly approach chemical reversibility.[18]

^{1}H NMR. The downfield ^{1}H NMR spectrum of **1** in $CDCl_3$ at room temperature is shown in Figure 2. The line widths of protons are broadened and isotropically shifted due to the paramagnetic nature of the iron atoms. Comparison with cluster **3** showed that two types of thiophenolato ligands are present in compound **1**, two as terminal ligands and one as a bridge. On the other hand, with one additional electron for the iron atoms in compound **1**, the isotropic shifts of protons decreased as compared to **3**, substantiating the decreased paramagnetic nature of **1**, which agrees well with the result of the EPR study ($S = {}^1/_2$). When **1** is converted to **2** by reacting it with acylchloride, all the absorptions downfield for the thiophenolate protons disappeared, including the bridging thiophenolate protons, with only the *n*-butyl protons remaining upfield (see Experimental Section).

EPR. The EPR spectrum of cluster **1** was measured at 77 K and is shown in Figure 3. It exhibits a strong axial symmetry with the two components at $g = 2.063$ and $g = 2.023$. This observation is consistent with a polynuclear system $[Fe_6S_5{}^*S]^+$ where the metal ions are antiferromagnetically coupled to yield a ground state spin of $S = {}^1/_2$ as in the $[Fe_6S_6]^{3+}$ cluster core.[9] The $S = {}^1/_2$ ground state in the former occurred from the combination of formal integral oxidation states one Fe(III) + five Fe(II) where one high-spin ferric ion ($3d^5$, $S = {}^5/_2$) and five high-spin ferrous ions ($3d^6$, $S = 2$) couple with one another to give the $S = {}^1/_2$ ground state.

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Supplementary Material Available: Tables of atomic positional and thermal parameters, bond distances and bond angles, and calculated hydrogen atom positions for $Fe_6S_5(\mu\text{-SPh})(P\text{-}n\text{-}Bu_3)_4(SPh)_2$ (9 pages); a listing of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

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A Unique Bromo- and Thioether-Bridged Tetranuclear Mixed-Valence Copper(I)–Copper(II) Compound with the N,S-Donor Ligand 4-((Ethylthio)methyl)-5-methylimidazole

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The mixed-valence compound tribromo{4-((ethylthio)methyl)-5-methylimidazole}copper(II)copper(I), $Cu_2(C_7H_{12}N_2S)Br_3$, forms spontaneously from an ethanol solution of copper(II) bromide and the ligand. The complex crystallizes as dark brown needles in the monoclinic space group $I2/a$: $a = 13.6953$ (15) Å, $b = 12.4347$ (5) Å, $c = 15.7589$ (7) Å, $\beta = 91.960$ (11)°, $Z = 8$, $R = 0.038$, and $R_w = 0.045$ for 1902 observed reflections. Each copper(II) ion is surrounded by a nitrogen atom at 1.964 (5) Å, a thioether sulfur at 2.350 (2) Å, and two bromide ions at 2.439 (1) and 2.394 (1) Å, in a square-planar geometry. The copper(I) ion is surrounded by three bromide ions at 2.360 (1), 2.483 (1), and 2.573 (1) Å and one thioether sulfur at 2.321 (2) Å in a distorted tetrahedral geometry. The dinuclear asymmetric unit is held together by a double bromide bridge between the Cu(I) and Cu(II) ion; the third bromide is terminally bonded to the Cu(I) at 2.360 (1) Å. The Cu(I) ion in each asymmetric unit is connected to the Cu(II) ion in another dinuclear unit through the bridging thioether sulfur of the ligand, thereby forming a unique tetranuclear species. The bromide, which is terminally bonded to the Cu(I), is a distance of 3.073 (1) Å from the nearest Cu(II), which is regarded as semicoordinating. Through this bond all tetranuclear species are bromide bridged to one another, forming a polymer with the copper(II) in a square-pyramidal environment. In confirmation of its mixed-valence nature, the title compound undergoes one-electron oxidation as well as one-electron reduction in DMSO at rather positive, coincident potential values ($E^{\circ\prime} = +0.19$ V vs SCE). X-ray, electrochemical, and EPR techniques point to an electron-localized $Cu^{II}Cu^{I}$ species.

Introduction

The couple Cu(II)–Cu(I) plays a central role in biological electron-transfer processes, since copper ions are integral parts of the active sites of many proteins involved in redox processes.[1,2] The architecture of the active site determines the specific function: a distorted tetrahedral N_2SS^* environment in the (blue) type I copper proteins like plastocyanin[3] and azurin[4] for electron transfer; a dinuclear $(N_3Cu)_2$ site in heamocyanin[5] (type III) for dioxygen

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