Inorg. Chem. **1992**, *31*, 957-962 **957**

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Synthesis of the Iron-Sulfur Cluster Compounds $[Fe_4S_4(MeCp)_4](PF_6)_y$ (y = 0-2). X-ray Structure Determinations of $Fe_4(\mu_3\text{-}S)_4(MeCp)_4$ and $[Fe_4(\mu_3\text{-}S)_4(MeCp)_4](PF_6)$

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Received July 2, 1991

The series of iron-sulfur cluster compounds $[Fe_4S_4(MeCp)_4](PF_6)_y$ (y = 0-2) is readily prepared by reaction of $[Fe(MeCp)_2(CO)_2]_2$ with an excess of sulfur in refluxing toluene followed by a number of suitable synthesis and purification steps. The structures of $Fe_4S_4(MeCp)_4$ and $[Fe_4S_4(MeCp)_4](PF_6)$ were determined crystallographically. $Fe_4S_4(MeCp)_4$ crystallizes in the orthorhombic system, space group *Pnma*, with cell dimensions a = 19.631 (1) Å, b = 12.453 (1) Å, c = 10.122 (1) Å, V = 2474.6 (3) Å^3, and Z = 4. Refinement of 169 parameters on 1562 "observed" reflections gave a final R value of 0.063 (R_w = 0.087). The Fe_4S_4 moiety of the structure possesses idealized (elongated) D_{2d} symmetry, which is in agreement with the qualitative Dahl bonding model. $[Fe_4S_4(MeCp)_4](PF_6)$ crystallizes in the tetragonal system, space group *I*4, with cell dimensions $a = b$ = 13.419 (3) Å, c = 7.809 (3) Å, V = 1406.3 (7) Å^3, and Z = 2. Refinement of 87 parameters on 634 "observed" reflections gave a final R value of 0.062 (R_w = 0.073). The idealized (compressed) D_{2d} symmetry of the Fe_4S_4 moiety of this structure does not agree with the Dahl model. Therefore, a slightly adjusted MO scheme is proposed, in which two energy levels are reversed.

Introduction

A well-known class of coordination cluster compounds is constituted by the compounds with the general formula $[M_4(\mu_3\text{-}A)_4(\eta^5\text{-}L)_4]^z$, where M is a d-transition metal, A an element from group 15 or 16 of the periodic system, and L a cyclopentadienyl (Cp) or a substituted cyclopentadienyl ligand (MeCp, *i*-PrCp, Me_5Cp).[1-5] The body of data available for these cluster compounds allows a systematic study of the influence of the variation of both metal ion and ligands on cluster structure and spectroscopic and redox properties. Various efforts have been put into the development of theoretical models that explain the geometry of the structure of these compounds as observed in the solid state. Two general models that account for the structural properties of the compounds are the qualitative Dahl bonding model and the model of Bottomley and Grein based on extended Huckel molecular orbital calculations.[6-8] An important parameter in these models is the number of "excess electrons" (vide infra).

In particular, X-ray crystallographic data are available for cluster compounds having 18, 19, or 20 excess electrons, among others for the series $[Fe_4S_4(Cp)_4]^z$ (z = 0, 1+, 2+)[6,9-13] and $[Fe_4Se_4(Cp)_4]^z$ (z = 0, 1+, 2+)[14,15] and for the dication $[Fe_4Te_4(Cp)_4]^{2+}$.[15] An important characteristic of these data is that an identical (idealized) cluster symmetry is observed for all compounds with the same number of excess electrons; e.g., the molecular structures of the compounds $[Fe_4(\mu_3\text{-}A)_4(Cp)_4]^0$ (A = S (two crystalline phases), Se) all display elongated D_{2d} cluster symmetry. This structural uniformity might lead to the conclusion that, to a first approach, it is the number of excess electrons that determines the cluster geometry, which is also one of the underlying thoughts of the theoretical models. Varying the μ_3-bridging ligand for instance does not bring about significant changes in cluster symmetry. In order to examine the influence of the terminal ligand L on the structural properties of the cluster compounds with 18, 19, and 20 excess electrons, we have synthesized the series of cluster compounds $[Fe_4S_4(MeCp)_4](PF_6)_y$ (y = 0-2) and structurally characterized the first two members of these series. The structural data are compared in some detail with those of the series $[Fe_4S_4(Cp)_4]^z$ (z = 0, 1+, 2+).

The spectroscopic and electrochemical properties of the compounds $[Fe_4S_4(MeCp)_4](PF_6)_y$ (y = 0-2) are described in a forthcoming paper together with the properties of the related compounds $[Fe_4S_5(MeCp)_4](PF_6)_y$ (y = 0-2) and $Fe_4S_6(MeCp)_4$.[16]

Experimental Section

General Methods. All operations and manipulations were performed under a dinitrogen atmosphere unless indicated otherwise. $[Fe(MeCp)(CO)_2]_2$ (Alfa Products), $NaBH_4$ (Merck pa), $(Bu_4N)(PF_6)$ (TBAH; Janssen Chimica pa), and NH_4PF_6 (Janssen Chimica pa) were used as received. Elemental sulfur was purified by sublimation under reduced pressure. Ferrocene (Aldrich analyzed) was sublimed before use. $[Fe(Cp)_2](PF_6)$ was prepared by bulk electrochemical oxidation of 0.05 M ferrocene in a 0.1 M solution of NH_4PF_6 in acetonitrile, followed by evaporation of the solvent, washing with water and diethyl ether, and drying under vacuo. Acetonitrile (Janssen Chimica pa) was distilled from CaH_2. Dichloromethane (Merck reinst) was washed subsequently with concentrated H_2SO_4, water, a 5% solution of Na_2CO_3 in water, and water, predried over $CaCl_2$, and distilled from CaH_2. Diethyl ether (Merck pa or Boom technical grade) was washed with a solution of 6 g of $FeSO_4$ and 6 mL of concentrated H_2SO_4 in 100 mL of water, predried over $CaCl_2$, and distilled from sodium. Hexane (Merck reinst) was washed with concentrated H_2SO_4, predried over $CaCl_2$, and distilled from sodium. Toluene (Merck pa) was distilled from sodium. Acetone (Merck pa) was used as received. All solvents were degassed before use by the pump-freeze-thaw method.

The elemental analyses of $Fe_4S_4(MeCp)_4$ and $[Fe_4S_4(MeCp)_4](PF_6)_2$ were carried out in the microanalytical department of the University of Nijmegen. The elemental analysis of $[Fe_4S_4(MeCp)_4](PF_6)$ was carried out by Analytische Laboratorien in Engelskirchen, FRG. Conductivity measurements were made with a Metrohm Model E653 conductoscope and a Philips conductance cell.

Synthesis of $[Fe_4S_4(MeCp)_4](PF_6)$. An 8.50-g sample of $[Fe(MeCp)(CO)_2]_2$ (44.5 mmol of Fe) and 2.00 g of S_8 (62.4 mmol of S) were refluxed in 200 mL of toluene for 7 h. The solution was then cooled and filtered. The filtrate was evaporated to dryness and yielded about 5 g of crude $Fe_4S_4(MeCp)_4$. This material was air-oxidized by stirring a suspension in CH_3CN in the presence of excess NH_4PF_6 for 24 h. The

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0020-1669/92/1331-0957$03.00/0

Table I. Crystal Data and Experimental Details for the X-ray Diffraction Studies of $Fe_4(\mu_3\text{-}S)_4(MeCp)_4$ and $[Fe_4(\mu_3\text{-}S)_4(MeCp)_4](PF_6)$

chem formula	$C_{24}H_{28}Fe_4S_4$	$C_{24}H_{28}F_6Fe_4PS_4$
fw	668.1	813.1
a, Å	19.631 (1)	13.419 (3)
b, Å	12.453 (1)	
c, Å	10.122 (1)	7.809 (3)
V, Å^3	2474.6 (3)	1406.3 (7)
Z	4	2
space group	*Pnma* (No. 62)	$I\bar{4}$ (No. 82)
T, °C	25	25
λ, Å	0.71073	0.71073
ρ_{calcd}, g·cm^{-3}	1.79	1.92
μ(MoKα), cm^{-1}	26.38	24.2
R	0.063	0.062
R_w^{a}	0.087	0.073

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

Table II. Fractional Positional and Thermal Parameters (Å^2) for the Fe_4S_4 moiety of $Fe_4(\mu_3\text{-}S)_4(MeCp)_4$ (with Esd's)

atom	*x*	*y*	*z*	$100U_{eq}$^{a}
Fe(1)	−0.39956 (5)	0.14513 (11)	0.36354 (10)	6.62 (4)
Fe(2)	−0.43165 (10)	0.25000	0.06362 (15)	8.35 (6)
Fe(3)	−0.53927 (8)	0.25000	0.2154 (2)	7.67 (5)
S(1)	−0.46693 (1)	0.1166 (2)	0.1876 (2)	7.82 (6)
S(2)	−0.35028 (15)	0.25000	0.2188 (3)	7.36 (7)
S(3)	−0.48597 (15)	0.25000	0.4154 (3)	7.19 (7)
C(11)	−0.3452 (5)	0.0009 (8)	0.3632 (9)	9.91 (10)
C(12)	−0.3084 (5)	0.0824 (9)	0.4303 (11)	12.10 (10)
C(13)	−0.3516 (6)	0.1078 (9)	0.5448 (9)	10.75 (10)
C(14)	−0.4068 (8)	0.0444 (11)	0.5330 (10)	16.55 (10)
C(15)	−0.4059 (7)	−0.0115 (10)	0.4275 (12)	16.46 (10)
C(111)	−0.3274 (11)	−0.0605 (11)	0.2414 (12)	27.73 (10)
C(21)	−0.3719 (6)	0.1919 (8)	−0.0915 (8)	12.39 (10)
C(22)	−0.4420 (6)	0.1577 (10)	−0.1177 (8)	12.45 (10)
C(23)	−0.4780 (10)	0.25000	−0.1309 (10)	14.36 (10)
C(211)^b	−0.3260 (12)	0.1206 (14)	−0.0789 (15)	20.52 (10)
C(31)	−0.6400 (5)	0.25000	0.2911 (12)	10.32 (10)
C(32)	−0.6305 (4)	0.3413_2 (9)	0.2096 (10)	11.26 (10)
C(33)	−0.6142 (5)	0.3077 (9)	0.0865 (10)	13.21 (10)
C(311)	−0.6611 (7)	0.25000	0.4274 (12)	12.30 (10)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j a^*_i a^*_j a_i a_j U_{ij}$. ^{b} Occupation factor 0.5.

Table III. Interatomic Distances (in Å, with Esd's) and Angles (deg, with Esd's) for the Fe_4S_4 Moiety of $Fe_4(\mu_3\text{-}S)_4(MeCp)_4$

Fe(1)–S(2)	2.188 (2)	S(1)···S(1)	3.322 (4)
Fe(1)–S(3)	2.204 (3)	S(2)···S(3)	3.325 (4)
Fe(2)–S(1)	2.194 (3)	Fe(1)–C(11)	2.089 (10)
Fe(3)–S(1)	2.204 (3)	Fe(1)–C(12)	2.067 (10)
Fe(1)–S(1)	2.246 (2)	Fe(1)–C(13)	2.114 (10)
Fe(2)–S(2)	2.240 (3)	Fe(1)–C(14)	2.130 (12)
Fe(3)–S(3)	2.279 (3)	Fe(1)–C(15)	2.059 (12)
Fe(1)–Fe(1)	2.612 (2)	Fe(2)–C(21)	2.090 (10)
Fe(2)–Fe(3)	2.612 (3)	Fe(2)–C(22)	2.176 (10)
Fe(1)···Fe(2)	3.364 (2)	Fe(2)–C(23)	2.169 (12)
Fe(1)···Fe(3)	3.388 (2)	Fe(3)–C(31)	2.121 (11)
S(1)···S(2)	2.847 (3)	Fe(3)–C(32)	2.121 (9)
S(1)···S(3)	2.866 (3)	Fe(3)–C(33)	2.094 (10)
Fe(1)–S(1)–Fe(3)	99.16 (9)	S(1)–Fe(2)–S(1′)	98.42 (8)
Fe(1)–S(1)–Fe(2)	98.51 (9)	S(1)–Fe(3)–S(1′)	97.86 (8)
Fe(1)–S(3)–Fe(3)	98.16 (3)	S(2)–Fe(1)–S(3)	98.39 (5)
Fe(1)–S(2)–Fe(2)	98.87 (3)	S(1)–Fe(1)–S(2)	79.86 (7)
Fe(1)–S(3)–Fe(1′)	72.67 (4)	S(1)–Fe(2)–S(2)	79.87 (6)
Fe(1)–S(2)–Fe(1′)	73.29 (4)	S(1)–Fe(1)–S(3)	80.17 (7)
Fe(2)–S(1)–Fe(3)	72.88 (7)	S(1)–Fe(3)–S(3)	79.48 (6)

solution was then filtered, and the filtrate was evaporated to dryness. The crude product was washed subsequently with water, methanol, and diethyl ether. The black solid thus obtained was recrystallized twice from an acetonitrile–diethyl ether mixture to give 1.5 g (17%) of pure product as black crystalline needles. $[Fe_4S_4(MeCp)_4](PF_6)$ is soluble in most organic solvents. Anal. Calcd for $[Fe_4S_4(MeCp)_4](PF_6)$: C, 35.45; H, 3.47; Fe, 27.48; S, 15.77; F, 14.02. Found: C, 35.82; H, 3.47; Fe, 24.75; S, 14.49; F, 17.1.

Synthesis of $Fe_4S_4(MeCp)_4$. A 680-mg sample (0.84 mmol) of $[Fe_4S_4(MeCp)_4](PF_6)$ was dissolved in 200 mL of acetonitrile. After addition of 42 mg (1.11 mmol) of $NaBH_4$, the solution was stirred for 6 h and then stored at −20 °C overnight. The product was collected by filtration and washed with water, methanol, and diethyl ether. A 170-mg amount (30%) of needlelike black crystals was obtained. Anal. Calcd for $Fe_4S_4(MeCp)_4$: C, 43.15; H, 4.22; S, 19.19. Found: C, 42.82; H, 4.13; S, 19.96.

Synthesis of $[Fe_4S_4(MeCp)_4](PF_6)_2$. To a solution of 360 mg (0.39 mmol) of $[Fe_4S_4(MeCp)_4](PF_6)$ in 25 mL of acetonitrile was added 122 mg (0.369 mmol) of $[Fe(Cp)_2](PF_6)$. After addition of 100 mL of diethyl ether the precipitate was collected by filtration and washed with dichloromethane and diethyl ether. The crude product was recrystallized once from acetone–diethyl ether to give 0.30 g (80%) of pure product. Anal. Calcd for $[Fe_4S_4(MeCp)_4](PF_6)_2$: C, 30.09; H, 2.95; S, 13.38. Found: C, 30.31; H, 2.75; S, 14.18.

Structure Determination of $Fe_4(\mu_3\text{-}S)_4(MeCp)_4$. A single crystal of $Fe_4(\mu_3\text{-}S)_4(MeCp)_4$ was obtained by slow diffusion of acetonitrile into a dichloromethane solution of the compound. X-ray data were measured on a Nonius CAD4 diffractometer. The unit cell dimensions were determined by least-squares refinement of the setting angles of 25 reflections in the range 15° ≤ θ ≤ 21°. The crystal data and the experimental details are listed in Table I and in Table A of the supplementary material. A profile analysis was performed on all reflections.[17,18] After absorption correction (program ABSORB[19]) and correction for Lorentz and polarization effects the equivalent reflections were averaged ($R_{av} = \sum(|F_o - F_o|)/\sum F_o = 0.049$, including all reflections). No extinction correction was applied.

The positions of the iron and sulfur atoms were found by automated vector search methods,[20] using the positional parameters of the Fe_4S_4 moiety of the compound $[Fe_4S_4(Cp)_4]Br$ as the searching fragment.[11] The positions of the carbon atoms were found with Fourier techniques. Scattering factors were taken from ref 21. The methyl group of the methylcyclopentadienyl ring bonded to Fe(2) appeared to be disordered through the crystallographic mirror plane. The positional and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares refinement on the *F* values, using SHELX.[22] The positions of the hydrogen atoms on the MeCp rings were calculated, and their isotropic temperature factors were included in the refinement. Plots were made with PLUTO[23] and ORTEP.[24] Geometrical calculations were done with PARST.[25]

Positional and thermal parameters of the atoms in the iron–sulfur moiety of $Fe_4(\mu_3\text{-}S)_4(MeCp)_4$ are given in Table II, and interatomic distances and bond angles, in Table III.

Structure Determination of $[Fe_4(\mu_3\text{-}S)_4(MeCp)_4](PF_6)$. Black prism-shaped crystals were grown from a solution of $[Fe_4(\mu_3\text{-}S)_4(MeCp)_4](PF_6)$ in a mixture of acetonitrile and diethyl ether. A single crystal with approximate dimensions of 0.15 × 0.13 × 0.09 mm was mounted on a glass fiber. X-ray data were measured on a Nonius CAD4 diffractometer. The cell dimensions were determined by least-squares refinement of the setting angles of 25 reflections in the range 12.2° ≤ θ ≤ 13.2°. The crystal data and the experimental details are listed in Table I and in Table A of the supplementary material. A profile analysis was performed on all reflections.[17,18] After correction for crystal decay and Lorentz–polarization effects, a numerical adsorption correction was applied using Gaussian integration.[19]

The positions of the iron and sulfur atoms were found by automated vector search methods,[20] using the positional parameters of the Fe_4S_4 moiety of the compound $[Fe_4S_4(Cp)_4]Br$ as the searching fragment.[11] The positions of the PF_6 anion and the carbon atoms were found from

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Table IV. Selected Fractional Positional and Thermal Parameters (Å^2) for $[Fe_4(\mu_3\text{-}S)_4(MeCp)_4](PF_6)$ (with Esd's)

atom	*x*	*y*	*z*	$100U_{eq}{}^a$
Fe	0.0761 (2)	0.0967 (2)	0.1098 (3)	8.06 (10)
S	0.0841 (3)	–0.0636 (4)	0.1624 (4)	7.8 (2)
C(1)	0.082 (3)	0.230 (2)	0.238 (5)	16 (2)
C(2)	0.113 (2)	0.161 (2)	0.347 (2)	11 (1)
C(3)	0.204 (3)	0.126 (2)	0.265 (3)	13 (1)
C(4)	0.209 (2)	0.180 (2)	0.119 (4)	15 (2)
C(5)	0.131 (3)	0.249 (2)	0.088 (3)	15 (2)
C(11)	–0.014 (2)	0.292 (3)	0.282 (4)	16 (1)
P	0.5000	0.0000	0.2500	8.5 (3)
F(1)	0.5000	0.0000	0.078 (4)	35 (3)
F(2)	0.3980 (12)	–0.041 (2)	0.2500	22 (1)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j a^*_i a^*_j a_i a_j U_{ij}$.

Table V. Selected Interatomic Distances (Å, with Esd's) and Angles (deg, with Esd's) for $[Fe_4(\mu_3\text{-}S)_4(MeCp)_4](PF_6)^a$

Fe–S	2.193 (5) [4]	Fe–C(1)	2.06 (3)
Fe–S(I)	2.234 (5) [4]	Fe–C(2)	2.10 (2)
Fe–S(II)	2.138 (4) [4]	Fe–C(3)	2.14 (3)
Fe–Fe(II)	2.898 (3) [4]	Fe–C(4)	2.11 (3)
Fe···Fe(I)	3.304 (3) [2]	Fe–C(5)	2.18 (2)
S···S(I)	2.829 (6) [2]	P–F(1)	1.34 (3)
S···S(II)	3.230 (6) [4]	P–F(2)	1.48 (2)
S–Fe–S(I)	79.5 (2) [4]	S–Fe–S(II)	96.5 (2) [4]
S(I)–Fe–S(II)	95.2 (2) [4]	Fe–S–Fe(I)	96.5 (2) [4]
Fe–S–Fe(III)	84.0 (2) [4]	Fe(I)–S–Fe(III)	83.0 (1) [4]

^{a}Symmetry: (I) $-x, -y, +z$; (II) $-y, +x, -z$; (III) $y, -x, -z$. Numbers between brackets indicate the multiplicity of the (bond) length by the S_4 symmetry.

a weighted difference Fourier map. Scattering factors were taken from ref 21. The positional and anisotropic thermal parameters of the nonhydrogen atoms were refined by full-matrix least-squares refinement on the *F* values, using SHELX.[22] The F–P–F angles were confined to 90° because of the large thermal motion of the fluorine atoms. An additional, semiempirical absorption correction was applied,[26] with correction factors in the range of 0.88–1.17. The equivalent reflections were averaged, to give 2025 reflections ($R_{av} = 0.122$) of which 634 were "observed" ($I \geq 4\sigma(I)$). The absolute configuration of the structure was confirmed by calculation of the Bijvoet coefficient, which appeared to be 1.000 (1) for the first 20 reflections.[27] The final refinement was performed with calculated hydrogen atoms (C–H = 1.00 Å) on each MeCp ring. Geometrical calculations were done with PARST.[25] Plots were made with PLUTO[23] and ORTEP.[24]

Positional and thermal parameters are given in Table IV, and selected interatomic distances and bond angles, in Table V.

The final difference electron-density Fourier map showed residual peaks up to 1.1 e·Å^{-3} in the area of the [4Fe–4S] core, which may be due to uncorrected absorption effects. One peak of 0.7 e·Å^{-3} was found near the fluorine atoms. Remaining peaks were less than 0.6 e·Å^{-3}. The P–F distances (1.34 (3) and 1.48 (2) Å) appeared to be shortened due to the large thermal motion of the PF_6 group.

Results and Discussion

Syntheses. The synthesis of the cluster compounds $[Fe_4S_4(MeCp)_4](PF_6)_y$ (y = 0–2) goes along the same principles as the synthesis of the non-methylated counterparts,[6,9,11] but due to different solubilities of products and intermediates some adjustments of the procedures were necessary.

Refluxing $[Fe(MeCp)(CO)_2]_2$ with elemental sulfur in toluene for 7 h followed by filtration and evaporation of the toluene yielded a mixture of $Fe_4S_4(MeCp)_4$, unreacted sulfur, and some unidentified material of probably polymeric nature. The presence of $Fe_4S_4(MeCp)_4$ in this mixture was established by recording a cyclic voltammogram in dichloromethane. $Fe_4S_4(MeCp)_4$ shows the same cyclic voltammetric behavior as $Fe_4S_4(Cp)_4$[28-30] but with slightly different redox potentials. Two other products of the reaction of $[Fe(MeCp)(CO)_2]_2$ with elemental suflur, $Fe_4S_5(MeCp)_4$ and $Fe_4S_6(MeCp)_4$, are only obtained when a shorter reaction time is used.[16,31] Air oxidation of a suspension of $Fe_4S_4(MeCp)_4$ in acetonitrile in the presence of NH_4PF_6 yields $[Fe_4S_4(MeCp)_4](PF_6)$. This cluster compound can more easily be purified than the neutral compound due to the higher solubility in most organic solvents. In order to determine the oxidation state of the cluster compounds, a cyclic voltammogram was routinely recorded and the equilibrium potential of the solution was compared with the location of the redox transitions. The oxidation state thus deduced was always consistent with information from spectroscopic measurements. For $[Fe_4S_4(MeCp)_4](PF_6)$, conductivity measurements in acetonitrile solutions in the concentration range 10^{-3}–10^{-2} mol dm^{-3} gave a linear Λ vs $c^{1/2}$ plot with $\Lambda_0 = 148\ \Omega^{-1}$ cm^2 mol^{-1}, a value commonly found for 1:1 electrolytes.[32] Purity of the products was checked by recording cyclic and differential pulse voltammograms and NMR spectra. Usually the voltammograms and NMR spectra did not show any impurities other than a small amount (1–3%) of either $Fe_4S_5(MeCp)_4$ or $[Fe_4S_5(MeCp)_4]^{2+}$.

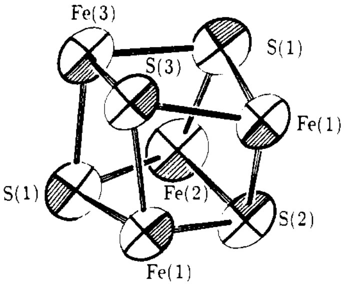

Figure 1. ORTEP drawing of the structure of $Fe_4(\mu_3\text{-}S)_4(MeCp)_4$. Iron atoms 2 and 3 and sulfur atoms 2 and 3 lie in the crystallographic mirror plane.

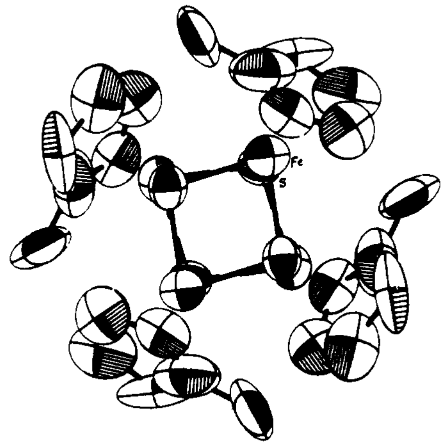

Figure 2. ORTEP drawing of the structure of $[Fe_4(\mu_3\text{-}S)_4(MeCp)_4]^+$.

Description of the Structure of $Fe_4(\mu_3\text{-}S)_4(MeCp)_4$. Crystalline $Fe_4(\mu_3\text{-}S)_4(MeCp)_4$ consists of discrete tetrameric units. No unusually short intermolecular distances were found. The molecular structure of $Fe_4(\mu_3\text{-}S)_4(MeCp)_4$ is shown in Figure 1, together with the atom-labeling scheme. The crystallographic site symmetry is C_s. An important feature of the structure is the approximate (elongated) D_{2d} geometry of the Fe_4S_4 core. There are two bonding Fe–Fe distances of 2.612 (2) and 2.612 (3) Å. One of these distances occurs in the crystallographic mirror plane, and the other occurs between the symmetry-related iron atoms 1 and 1′. The remaining four Fe–Fe distances, two of which are crystallographically independent, are nonbonding with a mean value of 3.376 Å. The six nonbonding S–S distances break down

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Table VI. X-ray Structural Data for $[Fe_4(\mu_3\text{-}A)_4(\eta^5\text{-}L)_4]^z$ Cluster Compounds

cluster	no. of excess e⁻'s	idealized sym (cryst site sym)	Fe–Fe, Å	av Fe–Fe dist, Å	ref
$Fe_4S_4(Cp)_4{}^a$	20	D_{2d} (C_2)	2.65 [2], 3.36 [4]	3.12	10
$Fe_4S_4(Cp)_4{}^b$	20	D_{2d} (C_s)	2.63 [2], 3.37 [4]	3.12	9
$[Fe_4S_4(Cp)_4]^{+c}$	19	D_2 (C_2)	2.65 [2], 3.19 [2], 3.32 [2]	3.05	11
$[Fe_4S_4(Cp)_4]^{+d}$	19	D_2 (C_2)	2.65 [2], 3.18 [2], 3.30 [2]	3.04	12
$[Fe_4S_4(Cp)_4]^{+e}$	19	C_2 (C_1)	2.64 [2] (3.19–3.31) [4]	3.04	12
	19	C_2 (C_1)	2.63 [2] (3.08–3.31) [4]	3.03	12
$[Fe_4S_4(Cp)_4]^{+a,f}$	19	D_2 (C_2)	2.66 [2], 3.19 [2], 3.30 [2]	3.05	13
$[Fe_4S_4(Cp)_4]^{+f,g}$	19	D_2 (D_2)	2.63 [2], 3.21 [2], 3.30 [2]	3.05	13
$[Fe_4S_4(Cp)_4]^{2+f}$	18	D_{2d} (S_4)	2.83 [4], 3.25 [2]	2.97	6
$Fe_4Se_4(Cp)_4$	20	D_{2d} (C_s)	2.72 [2], 3.56 [4]	3.29	14
$[Fe_4Se_4(Cp)_4]^{+h}$	19	C_2 (C_1)	2.72 [2] (3.36–3.48) [4]	3.20	15
$[Fe_4Se_4(Cp)_4]^{2+i}$	18	D_{2d} (S_4)	2.95 [4], 3.42 [2]	3.11	14
$Fe_4S_4(MeCp)_4$	20	D_{2d} (C_s)	2.61 [2], 3.36 [2], 3.39 [2]	3.12	this work
$[Fe_4S_4(MeCp)_4]^{+f}$	19	D_{2d} (S_4)	2.90 [4], 3.30 [2]	3.03	this work

[a] Monoclinic phase. [b] Orthorhombic phase. [c] Counterion Br^-. [d] Counterion $[FeCl_3(DMA)]^-$. [e] The composition of this compound is $[Fe_4S_4(Cp)_4]_2[MoOCl_4(THF)][MoOCl_4(CH_3CN)]$. The two cations are crystallographically independent. [f] Counterion PF_6^-. [g] Tetragonal phase. [h] Counterion $FeBr_4^-$. [i] Counterion unknown.

under idealized D_{2d} symmetry into four short lengths, two of which are crystallographically independent, with the mean value of 2.857 Å and two long lengths with the mean value 3.324 Å. The Fe–S distances split into a set of eight short lengths (four of which are crystallographically independent) in the range 2.188–2.204 Å and a set of four long lengths (three of which are crystallographically independent) between 2.240 and 2.279 Å. Likewise, the S–Fe–S and Fe–S–Fe angles divide into one set of four and one set of eight angles of about the same magnitude.

Description of the Structure of $[Fe_4(\mu_3\text{-}S)_4(MeCp)_4](PF_6)$. Crystalline $[Fe_4(\mu_3\text{-}S)_4(MeCp)_4](PF_6)$ consists of discrete $[Fe_4(\mu_3\text{-}S)_4(MeCp)_4]^+$ cations and PF_6 anions. Figure 2 shows the configuration of the cation, whose center is located on a crystallographic S_4 axis. The PF_6 anion is also situated on the S_4 axis. The P–F distances are smaller than normally found in comparable systems.[6] This is caused by the high degree of thermal motion of the fluorine atoms. There are no F···S distances below 4.0 Å.

The geometry of the [4Fe–4S] framework can be idealized to compressed D_{2d} symmetry, although the deviation from this symmetry is significantly greater than the experimental error. The six Fe–Fe distances divide into four short lengths of 2.898 (3) Å, and two longer lengths of 3.304 (3) Å. The six nonbonding S–S distances are separated into two shorter lengths of 2.829 (6) Å and four longer lengths of 3.230 (6) Å. The 12 Fe–S bonding distances can be divided into three sets of four lengths. The four shortest lengths of 2.138 (4) Å are parallel to the S_4 axis; the other two sets have lengths of 2.193 (5) and 2.234 (5) Å and are perpendicular to the S_4 axis. The S_4 symmetry divides the 12 Fe–S–Fe angles into three sets of four. Two sets have acute angles of 84.0 (2) and 83.0 (1)°, and one set has obtuse angles of 96.5 (2)°. The S–Fe–S angles are divided into two sets of four obtuse angles of 95.2 (2) and 96.5 (2)° and one set of four acute angles of 79.5 (2)°.

General Discussion of the Structural Data. According to the Dahl bonding model for the cluster compounds $[M_4(\mu_3\text{-}A)_4(\eta^5\text{-}L)_4]^z$, the twelve metal orbitals in excess of those needed for M–Cp and M–(μ_3-A) bonding transform under T_d symmetry into six bonding (a_1 + e + t_2) and six antibonding (t_1 + t_2) tetrametal cluster orbitals. The first 12 "excess" electrons fill the six bonding orbitals; the remaining electrons occupy antibonding orbitals. A cluster compound with 12 excess electrons is thus predicted to show idealized T_d symmetry with 6 short M–M distances and a total bond order 6. Such a geometry has indeed been found for the compounds $M_4S_4(L)_4$, where M is Cr or Mo.[3] A cluster compound with 24 excess electrons is also predicted to show idealized T_d symmetry, but with 6 long M–M distances and a total bond order 0. This prediction is compatible with the geometry observed for the cluster compound $Co_4S_4(Cp)_4$.[33] According to the Dahl model, oxidation of a cluster species with more than 12 excess electrons leads to the loss of an electron from an orbital that is antibonding with respect to the tetrametal interactions. The X-ray structural data for the compounds $[Fe_4S_4(Cp)_4]^z$ (z = 0, 1+, 2+) and $[Fe_4Se_4(Cp)_4]^z$ (z = 0, 1+, 2+) indeed show

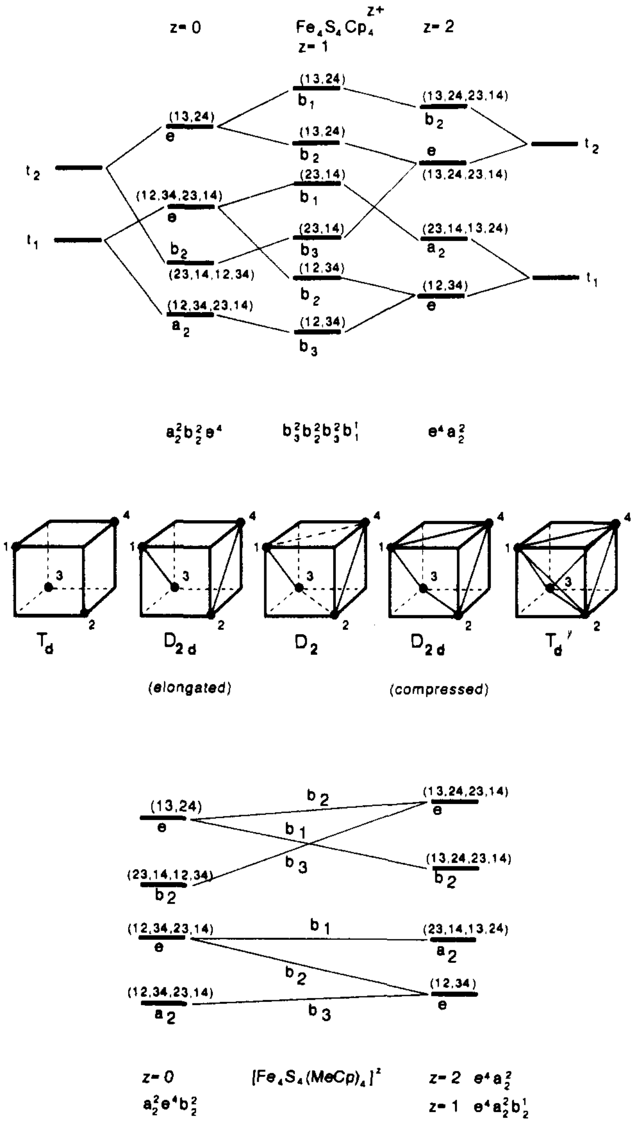

Figure 3. (a) Top: MO scheme as proposed by Dahl for the $[Fe_4S_4(Cp)_4]^z$ (z = 0, 1+, 2+) compounds. (b) Bottom: Alternative MO scheme for the $[Fe_4S_4(MeCp)_4]^z$ (z = 0, 1+, 2+) compounds.

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Table VII. Detailed Comparison of Mean Distances (Å) and Bond Angles (deg) for Iron–Sulfur Cluster Compounds[a]

	tetramer					
	$[Fe_4(\mu_3\text{-}S)_4(Cp)_4]^+$	$[Fe_4(\mu_3\text{-}S)_4(Cp)_4]^{2+}$	$[Fe_4(\mu_3\text{-}S)_4(MeCp)_4]^+$	$Fe_4(\mu_3\text{-}S)_4(Cp)_4$ (monoclinic phase)	$Fe_4(\mu_3\text{-}S)_4(Cp)_4$ (orthorhombic phase)	$Fe_4(\mu_3\text{-}S)_4(MeCp)_4$
ref	11	6	this work	10	9	this work
cryst site sym	C_2	S_4	S_4	C_2	C_s	C_s
idealized geometry of Fe_4S_4 core	D_2	D_{2d}	D_{2d}	D_{2d}	D_{2d}	D_{2d}
Fe–Fe	[1] 2.643 (4)	[4] 2.834 (3)	[4] 2.898 (3)	[2] 2.650 (6)	[2] 2.631 (2)	[2] 2.612 (3)
	[1] 2.661 (5)	[2] 3.254 (3)	[2] 3.304 (3)	[4] 3.363 (10)	[4] 3.366 (2)	[4] 3.376 (2)
	[2] 3.188 (3)					
	[2] 3.319 (3)					
S···S	[2] 2.879 (6)	[2] 2.820 (6)	[2] 2.829 (6)	[4] 2.880 (13)	[4] 2.884 (3)	[4] 2.857 (3)
	[2] 3.062 (6)	[4] 3.304 (5)	[4] 3.230 (6)	[2] 3.334 (9)	[2] 3.344 (6)	[2] 3.324 (4)
	[2] 3.389 (8)					
Fe–S	[4] 2.185 (5)	[4] 2.156 (3)	[4] 2.138 (4)	[8] 2.204 (8)	[8] 2.206 (2)	[8] 2.198 (3)
	[4] 2.212 (5)	[4] 2.204 (4)	[4] 2.193 (5)	[4] 2.250 (10)	[4] 2.256 (3)	[4] 2.253 (3)
	[4] 2.246 (5)	[4] 2.212 (4)	[4] 2.234 (5)			
Fe–S–Fe	[4] 74.2 (2)	[4] 80.9 (1)	[4] 83.0 (1)	[4] 73.9 (2)	[4] 73.3 (1)	[4] 72.9 (1)
	[4] 92.1 (2)	[4] 81.1 (1)	[4] 84.0 (2)	[8] 98.0 (3)	[8] 98.0 (1)	[8] 98.7 (1)
	[4] 96.3 (2)	[4] 94.9 (1)	[4] 96.5 (2)			
S–Fe–S	[4] 80.5 (2)	[4] 79.3 (1)	[4] 79.5 (2)	[8] 80.5 (3)	[8] 80.5 (1)	[8] 79.8 (1)
	[4] 87.5 (2)	[4] 98.3 (1)	[4] 95.2 (2)	[4] 98.2 (2)	[4] 98.7 (1)	[4] 98.3 (1)
	[4] 100.9 (2)	[4] 98.6 (1)	[4] 96.5 (2)			

[a] Standard deviations given in parentheses are mean values of the esd's of the individual distances and angles. Numbers between brackets indicate the number of times the bond occurs in the molecule.

a shortening of the average Fe–Fe distance in the order from the neutral to the dicationic cluster compound (Table VI). The same trend is observed for the newly characterized $Fe_4S_4(MeCp)_4$ and $[Fe_4S_4(MeCp)_4]^+$ cluster compounds.

Figure 3a contains an MO scheme that has been developed by Dahl and co-workers in order to rationalize the geometries observed for the $[Fe_4S_4(Cp)_4]^z$ (z = 0, 1+, 2+) compounds.[6] For $Fe_4S_4(Cp)_4$ having 20 excess electrons a Jahn–Teller distortion causes a lowering of the idealized symmetry from T_d to D_{2d} with two short and four long Fe–Fe distances. Such an idealized cluster symmetry is observed for $Fe_4S_4(Cp)_4$ in two different crystalline phases (Table VI).[9,10] For $[Fe_4S_4(Cp)_4]^+$ with 19 excess electrons a D_{2d} symmetry is not possible, because in the elongated and in the compressed D_{2d} configuration a degenerate orbital set would then be occupied by 3 electrons and 1 electron, respectively. Therefore, for the iron–sulfur cluster in the compound $[Fe_4S_4(Cp)_4]Br$, a lowering of the symmetry to D_2 is observed with two short Fe–Fe distances of 2.65 Å (formal bond order 1), two intermediate Fe–Fe distances of 3.19 Å (formal bond order 0.25), and two long Fe–Fe distances of 3.32 Å.[11]

Other X-ray crystallographic data that are available for cluster compounds with 19 and 20 excess electrons are consistent with this MO scheme. The idealized elongated D_{2d} symmetry observed for $Fe_4S_4(Cp)_4$ is also a feature of the other structures that have been determined so far for cluster compounds having 20 excess electrons, i.e. $Fe_4Se_4(Cp)_4$,[14] $Ru_4S_4(MeCp)_4$,[34] $Co_4P_4(Cp)_4$,[35] $Co_4P_4(Me_5Cp)_4$,[36] and $Co_4Sb_4(Cp)_4$.[36] Since the publication of the first X-ray crystal and molecular structure of $[Fe_4S_4(Cp)_4]^+$, four X-ray structure determinations of this cation with other counterions have been carried out. Dupré has determined the X-ray crystallographic structures of $[Fe_4S_4(Cp)_4][FeCl_3(DMA)]$ and $[Fe_4S_4(Cp)_4]_2[MoOCl_4(THF)][MoOCl_4(CH_3CN)]$.[12] The iron–sulfur cluster in $[Fe_4S_4(Cp)_4][FeCl_3(DMA)]$ also has idealized D_2 symmetry. The two crystallographic independent [4Fe–4S] units of $[Fe_4S_4(Cp)_4]_2[MoOCl_4(THF)][MoOCl_4(CH_3CN)]$ both have the lower idealized C_2 symmetry, which can be explained by the occurrence of anisotropic steric effects.[6] Shimoi et al. have performed the X-ray crystal structure determinations of $[Fe_4S_4(Cp)_4](PF_6)$ in two different crystalline phases.[13] The iron–sulfur cluster in the monoclinic phase has crystallographically imposed C_2 symmetry, which can be idealized to D_2 symmetry. For the tetragonal phase a compressed D_{2d} symmetry was found for the iron–sulfur cluster, which is incompatible with the MO model of Dahl, that predicts D_2 symmetry due to a Jahn–Teller distortion. To escape from this incompatibility, the authors have interpreted the apparent D_{2d} symmetry as being the result of the disordered packing of two enantiomeric structures with D_2 symmetry. A close comparison of the data for the six $[Fe_4S_4(Cp)_4]^+$ structures reveals that there are always two short Fe–Fe distances. These two short distances are in all cases equal within 0.02 Å, and their average falls in the narrow range 2.63–2.65 Å (Table VI). The structural differences are therefore merely reflected in the four long Fe–Fe distances.

In Table VII the structural data for $Fe_4S_4(MeCp)_4$ and $[Fe_4S_4(MeCp)_4]^+$ are compared with structural data for the cluster compounds $[Fe_4S_4(Cp)_4]^z$ (z = 0, 1+, 2+). The overall structure of $Fe_4S_4(MeCp)_4$ is very similar to the structures of $Fe_4S_4(Cp)_4$. The iron–sulfur cluster of $[Fe_4S_4(MeCp)_4]^+$ has idealized D_{2d} symmetry with four short and two long Fe–Fe distances and therefore bears more resemblance to the structure of $[Fe_4S_4(Cp)_4]^{2+}$ than to the structure of $[Fe_4S_4(Cp)_4]^+$.[37] On the basis of our data, we consider the possibility that we have a similar disorder problem as supposed by Shimoi et al. for the tetragonal phase of $[Fe_4S_4(Cp)_4](PF_6)$ (vide supra) as very unlikely. Although in $[Fe_4S_4(MeCp)_4]^+$ all thermal parameters are rather large, they are not clearly anisotropic and the shapes and orientations of the thermal ellipsoids for the Fe and S atoms do not show any evidence of a crystal disorder. If the data of Shimoi are interpreted as originating from a D_{2d} iron–sulfur cluster, bond distances and angles can be calculated from their positional parameters, which are surprisingly close to these for the $[Fe_4S_4(MeCp)_4]^+$ ion. The geometries of these clusters could therefore be the same. The energies of the D_2 and D_{2d} structures could be not far apart, the actual structure being determined by crystal packing forces or slightly different electronic or steric properties of Cp and MeCp.

In the case of D_{2d} symmetry, the structure of $[Fe_4S_4(MeCp)_4](PF_6)$ cannot be explained by the MO scheme developed

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(35) Simon, G. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1973**, *95*, 2175.

(36) Johnson, R. E. Ph.D. Thesis, University of Wisconsin—Madison, 1981.

(37) In fact this strong resemblance caused some doubts whether the structure obtained really belongs to the compound $[Fe_4S_4(MeCp)_4](PF_6)$. In order to take away these doubts, we have crystallized another batch of $[Fe_4S_4(MeCp)_4](PF_6)$ and determined the X-ray crystal structure of a crystal that was representative for the bulk of the material. The structure obtained (with a final R value of 0.08) was indeed identical with the initial result.

for the $[Fe_4S_4(Cp)_4]^z$ compounds (Figure 3a). We therefore propose a small adjustment of this scheme.

The geometries observed for the iron-sulfur clusters in $Fe_4S_4(MeCp)_4$ and $[Fe_4S_4(MeCp)_4](PF_6)$ can again be understood by a qualitative MO scheme (Figure 3b), if it is assumed that in comparison with the $[Fe_4S_4(Cp)_4]^z$ compounds the e and b_2 levels have been reversed. This could be caused by a slightly different mixing up of the antibonding tetrairon cluster orbitals and the iron-cyclopentadienyl orbitals. Interchanging the e and b_2 levels does not affect the symmetries predicted for the neutral and the dicationic cluster species. It does have consequences, however, for the monocation. Since both in the compressed and in the elongated D_{2d} configuration, the partially occupied orbitals are nondegenerate, no symmetry lowering due to the Jahn-Teller effect occurs. Apparently the compressed form is energetically the most stable. In comparison with $[Fe_4S_4(MeCp)_4]^{2+}$ the additional electron occupies a b_2 orbital, which has antibonding character with respect to the interactions between the pairs of irons 1 and 3, 2 and 4, 2 and 3, and 1 and 4 (denoted as (13,24,23,14) in Figure 3. Therefore these four Fe-Fe distances are longer in $[Fe_4S_4(MeCp)_4]^+$ than in $[Fe_4S_4(Cp)_4]^{2+}$ (2.90 and 2.83 Å, respectively).

In summary, the X-ray structure determinations of $Fe_4S_4(MeCp)_4$ and $[Fe_4S_4(MeCp)_4](PF_6)$ have yielded some interesting new data. The limited number of X-ray structures for cluster compounds with 19 excess electrons has been extended. It appears that the geometries of these compounds are not only determined by the number of excess electrons but also by quite subtle differences in the electronic structure of the terminal ligand. After a small adjustment the qualitative MO scheme proposed by Dahl's group can be used to describe the bonding in the $[Fe_4S_4(MeCp)_4]^z$ compounds.

A similar effect has recently been reported for $Co_3S_2Cp^n$ clusters, which for $n = 0$ and $n = +1$ show slightly different structures when Cp is substituted by MeCp.[38]

Acknowledgment. We thank W. P. Bosman for valuable assistance with the X-ray work. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO) and by the Centre National de la Recherche Scientifique-DRCI.

Supplementary Material Available: Tables A-D, listing crystallographic data and experimental details, atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, and anisotropic thermal parameters for $Fe_4S_4(MeCp)_4$ and $[Fe_4S_4(MeCp)_4](PF_6)$ (6 pages); tables of calculated and observed structure factors (25 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Inorganic Chemistry and Crystallography, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands, and Département de Recherche Fondamentale sur la Matière Condensée, Service d'Etudes des Systèmes Moléculaires, Centre d'Etudes Nucléaires, 85X 38041 Grenoble Cedex, France

Synthesis and Characterization of the Iron-Sulfur Cluster Compounds $[Fe_4S_5(MeCp)_4](PF_6)_y$ (y = 0-2). X-ray Structure Determination of $[Fe_4S_5(MeCp)_4](PF_6)$

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Received July 2, 1991

The series of iron-sulfur cluster compounds $[Fe_4S_5(MeCp)_4](PF_6)_y$ (y = 0-2) is readily prepared by reaction of $[Fe(MeCp)(CO)_2]_2$ with an excess of sulfur in refluxing toluene followed by a number of suitable synthesis and purification steps. The structure of $[Fe_4S_5(MeCp)_4](PF_6)$ was determined crystallographically. $[Fe_4S_5(MeCp)_4](PF_6)$ crystallizes in the triclinic system, space group $P\bar{1}$, with cell dimensions a = 9.876 (1) Å, b = 10.683 (1) Å, c = 14.642 (1) Å, α = 87.86 (3)°, β = 108.67 (2)°, γ = 90.66 (2)°, V = 1462.4 (5) Å^3, and Z = 2. Refinement of 388 parameters on 5127 "observed" reflections gave a final R value of 0.054 (R_w = 0.078). The structure consists of an asymmetric Fe_4S_5 core with each iron involved in three Fe-S bonds. The disulfur group in the iron-sulfur core is μ_3-bonded with one sulfur atom coordinating to two iron atoms and the other sulfur atom to a third iron atom. This coordination mode differs from coordination mode of the S_2 group in the related compound $[Fe_4S_5(Cp)_4][MoOCl_4(THF)]$, which is side-on bonded to one iron atom and end-on bonded to two iron atoms. From ^1H NMR spectra recorded at several temperatures in the range 208-302 K and ^1H COSY spectra recorded at 208 K it is concluded that in acetone-d_6 solution the iron-sulfur core of the $[Fe_4S_5(MeCp)_4]^{2+}$ ion is rigid with the disulfur group coordinating two neighboring iron atoms in an equivalent way and a third iron atom in a unique way. The ^1H NMR spectrum of $[Fe_4S_5(MeCp)_4]^0$ recorded in $CDCl_3$ at 319 K indicates that the iron-sulfur cluster is fluxional with the S_2 group rotating around a pseudo-3-fold axis. The electrochemical behavior of the compounds $[Fe_4S_4(MeCp)_4](PF_6)$, $[Fe_4S_5(MeCp)_4](PF_6)_2$, and $Fe_4S_6(MeCp)_4$ is very similar to the electrochemical behavior of the related compounds $[Fe_4S_4(Cp)_4](PF_6)$, $[Fe_4S_5(Cp)_4](PF_6)_2$, and $Fe_4S_6(Cp)_4$. As expected because of the electron-releasing properties of the methyl groups, the redox potentials have shifted slightly in negative direction.

Introduction

The structural properties of the compounds $[M_4(\mu_3\text{-}A)_4(\eta^5\text{-}L)_4]$, where M is a d-transition metal, A an element from group 15 or 16 of the periodic table, and L a cyclopentadienyl (Cp) or a substituted cyclopentadienyl ligand (MeCp, *i*-PrCp, Me_5Cp), have been extensively studied.[1-5] The central theme in these studies is the relation between structure and electron count.[6-8] The related compounds $[Fe_4S_5(Cp)_4]^z$ (z = 0, 1+, 2+) and $Fe_4S_6(Cp)_4$ also possesses a number of interesting structural properties in the solid state as well as in solution.[9-13] In these compounds both μ_3-

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