Terminal Ligand Assignments Based on Trends in Metal−Ligand Bond Lengths of Cubane-Type $[Fe_4S_4]^{2+,+}$ Clusters

B. M. Segal, H. R. Hoveyda, and R. H. Holm

Department of Chemistry and Chemical Biology,
Harvard University, Cambridge, Massachusetts 02138

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Introduction

As part of our recent investigations of the synthesis and properties of polycubane $[Fe_4S_4]_n$[1−3] and dicubanoid $[Fe_4S_5]_2$[4] clusters, the self-condensation reactions of the functionalized cluster $[Fe_4S_4(SH)_4]^{2-}$ were examined.[5] From spectroscopic data, the doubly bridged tricubane $[(Fe_4S_4)_3(SH)_8(\mu_2\text{-}S)_2]^{8-}$ was concluded to be the principal condensation product in solution. The initial cluster was first prepared in an apparently serendipitous reaction of $[CpFe(CO)_2I]$ and H_2S, and was isolated as the Ph_4P^+ salt.[6] The compound was identified by an X-ray structure determination, which revealed an imposed C_2 axis and unexceptional bond distances and angles. The two independent Fe−SH bond lengths average to 2.262 Å.[6] Subsequently, we prepared $(Ph_4P)_2[Fe_4S_4(SH)_4]$ in 83% yield by the reaction of $[Fe_4S_4(SEt)_4]^{2-}$ with H_2S and identified the compound by a total elemental analysis and the −SH resonance at 47.6 ppm in acetonitrile.[7] In later work, $(Pr_4P)_2[Fe_4S_4(SH)_4]$ was obtained in 92% yield by the same reaction, and was also identified by a total analysis and ^{1}H NMR.[5]

As a means of further characterization, $(Pr_4P)_2[Fe_4S_4(SH)_4]$ was recrystallized from a 1,2-dichloroethane solution into which THF was introduced by vapor diffusion. The structure of the crystalline material so obtained was determined by X-ray diffraction, which revealed the standard cubane-type geometry with normal bond distances and angles, no imposed symmetry, and a mean apparent Fe−SH bond length of 2.211(7) Å when averaged over the two crystallographically independent clusters (range 2.197(2)−2.214(2) Å). In the report of these results,[5] we noted the ca. 0.05 Å difference in terminal ligand bond lengths between the Ph_4P^+ and Pr_4N^+ compounds but were unable to account for it. The reason has now emerged in the context of (i) bond length differences involving the same ligand in clusters of different oxidation state and (ii) bond length differences for ligands not necessarily distinguishable by X-ray diffraction in clusters of the same oxidation state.

Experimental Section

Preparation of Compounds. All manipulations were performed under a pure dinitrogen atmosphere using standard glovebox and Schlenk techniques. Solvents were dried and degassed prior to use. The compounds $[Fe(PEt_3)_2Cl_2]$[8] and $(Pr_4N)_2[Fe_4S_4(SH)_4]$[5] were prepared by literature procedures. Commercial samples of Et_4NSH (Strem) and Na_2S (Strem) were used without further purification.

$(Pr_4N)_2[Fe_4S_4Cl_4]$. The compound $(Pr_4N)_2[Fe_4S_4(SH)_4]$ (0.200 g, 0.233 mmol) was stirred with 20 mL of 1,2-dichloroethane at room temperature for 15 min. The deep brown solution was filtered. The filtrate was placed in a vapor diffusion system with 30 mL of THF, and diffusion was allowed to occur slowly over a period of 8 days until the solution was nearly colorless. The product was collected by filtration as 0.171 g (85%) of a black microcrystalline solid. Anal. Calcd for $C_{24}H_{56}Cl_4Fe_4N_2S_4$: C, 33.28; H, 6.52; Cl, 16.37; Fe, 25.79; N, 3.23; S, 14.81. Found: C, 33.26; H, 6.60; Cl, 16.31; Fe, 25.88; N, 3.16; S, 14.75.

$(Et_4N)_3[Fe_4S_4(SH)_4]\cdot Et_4NCl$. To a stirred solution of 2.00 g (5.51 mmol) of $[Fe(PEt_3)_2Cl_2]$ in 40 mL of THF was added 1.59 g (9.74 mmol) of Et_4NSH and 0.430 g (5.51 mmol) of Na_2S. A dark brown-black solution and a colorless precipitate formed immediately. After the reaction mixture was stirred for 30 min, a black precipitate separated; stirring was continued overnight. The black solid was collected by filtration, washed with THF (3 × 10 mL), and extracted with 60 mL of acetonitrile. The solution was filtered through a plug of Celite to remove NaCl and other insoluble material. The brownish-black filtrate was layered with 60 mL of THF and allowed to stand at −20 °C overnight. The solid was isolated by filtration, washed with THF (3 × 5 mL), and dried in vacuo to afford the product as 0.265 g (18%) of black block-shaped crystals. Anal. Calcd for $C_{32}H_{84}ClFe_4N_4S_4$: C, 36.94; H, 8.14; Cl, 3.41; Fe, 21.47; N, 5.39; S, 24.65. Found: C, 37.05; H, 8.23; Cl, 3.42; Fe, 21.34; N, 5.52; S, 24.56.

X-ray Structure Determination. Suitable crystals of $(Et_4N)_3[Fe_4S_4(SH)_4]\cdot Et_4NCl$ were selected from the solid that crystallized from acetonitrile/THF, coated with Apiezon L grease, and attached to a glass fiber. The crystals were transferred to a Siemens SMART CCD diffractometer system and cooled in a dinitrogen stream. The raw intensity data were converted (including corrections for background and Lorentz and polarization effects) to structure factor amplitudes and their esd's using the program SAINT of SHELXTL PLUS. An absorption correction was applied using SADABS. Space group assignment was based on analysis of systematic absences, *E* statistics, and successful refinement of the structure. The structure was solved by direct methods with the aid of successive difference Fourier maps using the SHELXS program and refined by the least-squares method on F^2 using SHELXL, incorporated in the SHELXTL PLUS software package. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2× that of the attached carbon atom (1.5× for methyl and sulfur hydrogen atoms). Electron density found near each terminal sulfur atom was refined isotropically as a hydrogen atom. The asymmetric unit consists of one cation, one-fourth cluster anion, and one-fourth chloride ion. In the last cycles of the refinement, all parameters shifted by less than 1% of their esd's, and the final difference Fourier maps showed no significant electron density. Crystallographic data are listed in Table 1.[9]

Other Physical Measurements. ^{1}H NMR spectra were recorded on a Bruker AM-500 spectrometer. Cyclic voltammetry measurements were performed on a PAR model 263 potentiostat/galvanostat using a Pt working electrode. The supporting electrolyte was 0.1 M $(Bu_4N)(PF_6)$. Potentials are referenced to the SCE. EPR spectra were recorded on a Bruker ESP 300-E spectrometer operating at X-band frequencies.

Results and Discussion

The argument for the identity of the compound whose structure was initially attributed to $(Pr_4P)_2[Fe_4S_4(SH)_4]$[5] rests in part on terminal metal−ligand bond lengths. Presented in

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(9) See paragraph at the end of this article concerning available Supporting Information.

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Table 1. Crystallographic Data[a] for $(Et_4N)_3[Fe_4S_4(SH)_4]\cdot Et_4NCl$

empirical formula	$C_{32}H_{84}ClFe_4N_4S_8$
fw	1040.36
T, K	213
crystal system	tetragonal
space group	$P\bar{4}2_1c$
Z	2
a, Å	12.4914(4)
c, Å	16.2238(8)
V, Å^3	2531.5(2)
d_{calc}, g/cm^3	1.364
*wR*2,[b] *R*1[c]	0.0973, 0.0549

[a] Obtained with graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

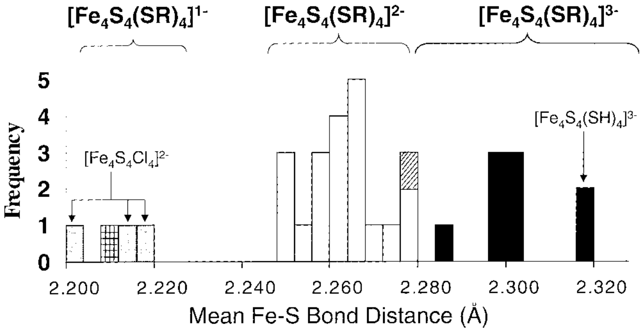

Figure 1. Frequency of mean values of Fe−SR bond distances (R = H, alkyl, aryl) in $[Fe_4S_4(SR)_4]^{-,2-,3-}$ clusters as determined from 30 crystal structure determinations.[6,9−11] Also included are mean Fe−Cl bond lengths from three determinations. The cross-shaded area immediately preceding 2.280 Å refers to $(Et_4N)_3[Fe_4S_4(SC_6H_{11})_4]\cdot 4MeCN$ (2.277 Å),[11f] which overlaps with the $[Fe_4S_4(SR)_4]^{2-}$ regime. The entry $[Fe_4S_4(SH)_4]^{3-}$ is from this work.

Figure 1 is a frequency plot of *mean* Fe−SR bond lengths for the clusters $[Fe_4S_4(SR)_4]^z$, $z = 1-$ (1),[10] $2-$ (20),[11] and $3-$ (10).[12] The numbers in parentheses refer to the number of structure determinations of each oxidation state; the structures of several clusters have been determined more than once as different salts or at different temperatures. The plot does not include mixed ligand clusters, and does not account for differences in temperature nor differing standard deviations from the mean. It is well recognized that the bond lengths increase with decreasing core oxidation state, $[Fe_4S_4]^{3+}$ ($Fe^{2.75+}$) < $[Fe_4S_4]^{2+}$ ($Fe^{2.50+}$) < $[Fe_4S_4]^{+}$ ($Fe^{2.25+}$), i.e., as the ferrous character increases. The Shannon radii of tetrahedral Fe(III) and Fe(II) are 0.63 and 0.77 Å,[13] respectively. The $[Fe_4S_4(SR)_4]^-$ regime is clearly demarcated at 2.21 Å, but thus far there is only one example. The $[Fe_4S_4(SR)_4]^{2-}$ regime extends from 2.25 to 2.28 Å, and that of $[Fe_4S_4(SR)_4]^{3-}$ at distances longer than 2.28 Å. As noted in Figure 1, there is a single intrusion of the latter cluster type into the $[Fe_4S_4(SR)_4]^{2-}$ range, at the long end.

The compound $(Ph_4P)_2[Fe_4S_4(SH)_4]$ was prepared by Müller et al.[6] in 35% yield by the aerobic reaction of $[CpFe(CO)_2I]$ and H_2S in the presence of Ph_4PBr in a DMF/MeOH/Et_3N reaction system. Mössbauer parameters are normal for the $[Fe_4S_4]^{2+}$ oxidation level and an Fe−S(H) vibration was assigned at 342 cm^{-1}. The compound was described as characterized by elemental analysis (results not given).[6] While any bromide and/or iodide terminal ligands would not have been crystallographically mistaken for sulfur, we simply note that the mean Fe−SH distance of 2.262 Å is inconsistent with $[Fe_4S_4Br_4]^{2-}$ (2.339(9)-2.342 Å)[14] and $[Fe_4S_4I_4]^{2-}$ (2.52(3), 2.542(9) Å),[15] for which mean values are indicated. With reference to Figure 1, $[Fe_4S_4(SH)_4]^{2-}$ falls in the middle of the $[Fe_4S_4(SR)_4]^{2-}$ regime. By this criterion, the compound is correctly formulated.

After the structure of the compound described as $(Pr_4P)_2[Fe_4S_4(SH)_4]$ was published,[5] we were made aware of a reaction unknown to us; viz., replacement of thiolate ligands by chloride when cubane-type Fe_4S_4 clusters are placed in dichloromethane or 1,2-dichloroethane solvents.[16,17] We had observed two previous instances where chloride was apparently abstracted from solvent in reactions of iron−sulfur clusters: (i) the formation of $[Fe_4S_4(LS_3)Cl]^{2-}$ in ca. 20% yield in the reaction of $[Fe_4S_4(SMe)_4]^{2-}$ with the trithiol ligand LS_3 in acetonitrile−chloroform;[18] (ii) the conversion of $[Fe_8S_8(P(C_6H_{11})_3)_8]$ to $[Fe_8S_6Cl_4(P(C_6H_{11})_3)_4]$ (17% yield) in neat chloroform over 2 h.[2] Because we normally manipulate Fe_4S_4 cluster salts in the solvents acetonitrile, DMF, and Me_2SO, we previously observed only the one incident (i) of thiolate/chloride replacement in chlorinated solvents and none in solvents less reactive than chloroform.

To simulate closely the earlier crystallization conditions[5] (from which no crystals remained), THF was introduced by vapor diffusion into a 1,2-dichloroethane solution of $(Pr_4N)_2[Fe_4S_4(SH)_4]$ over a period of 8 days. In three attempts, we did not obtain crystals of adequate diffraction quality, but we did isolate as a black microcrystalline solid a pure compound

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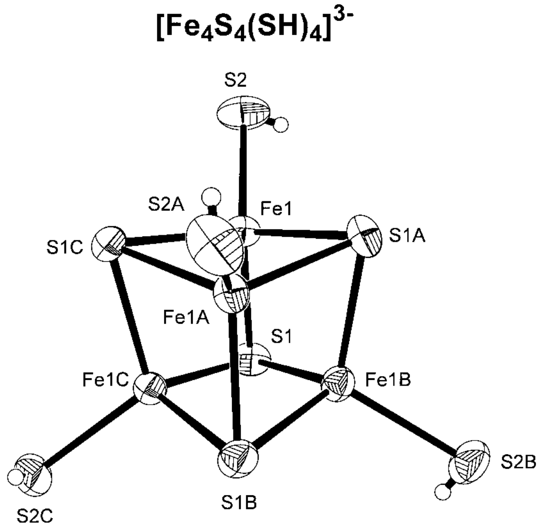

Figure 2. Structure of $[Fe_4S_4(SH)_4]^{3-}$, showing 50% thermal ellipsoids and the atom labeling scheme. Lettered and unlettered atoms are related by symmetry operations; an imposed $\bar{4}$ axis bisects the faces Fe(1,1A)S(1A,1C) and Fe(1B,1C)S(1,1B).

whose total elemental analysis requires the formulation $(Pr_4N)_2[Fe_4S_4Cl_4]$. The precision of this analysis is such as not to not permit a mixed chloride/hydrosulfide ligand set.

Because structural information is available for only one cluster having terminal Fe−SH bonds, we undertook the synthesis of another but in a more reduced oxidation state to examine its coherence with the distance range of thiolate-ligated clusters in Figure 1. The reducing reaction system $[Fe(PEt_3)_2Cl_2]$/Et_4NSH/Na_2S in THF was found to afford the compound $(Et_4N)_3[Fe_4S_4(SH)_4]\cdot Et_4NCl$ in modest (18%) but highly reproducible yield. The product requires a net oxidation of iron; the electron acceptor has not been identified but may be hydrosulfide. (Any all-ferrous cluster that might have been formed is expected to have a $[Fe_4S_4(SH)_4]^{3-/4-}$ potential near −1.9 V and is presumably too strong a reductant to exist under these reaction conditions.) The structure of the cluster is set out in Figure 2. An analytical sample was taken from the same crystal batch as the X-ray crystal. A total elemental analysis confirmed the composition.

The structure of $[Fe_4S_4(SH)_4]^{3-}$ has crystallographically imposed S_4 symmetry, with a $\bar{4}$ axis passing through the upper and lower rhombic faces of the $[Fe_4S_4]^+$ core (Figure 2). On the basis of the imposed symmetry, this cluster most closely resembles that in $(Me_4N)_3[Fe_4S_4(SEt)_4]$.[12d] Metric data are collected in Table 2; bond distances and angles are normal for this oxidation state.[12] However, the structure is somewhat unusual because the three independent Fe−S core distances are indistinguishable and average to 2.309(1) Å. Structure determinations of reduced clusters have shown that the $[Fe_4S_4]^+$ core can assume a variety of distortions from idealized T_d symmetry. These are apparently set by the crystalline environment, and generally result in some inequalities in Fe−S core bond lengths. Except for the most recent determination,[12h] the structures of $[Fe_4S_4(SR)_4]^{3-}$ clusters have been summarized.[12g] The Fe−SH bond distance of 2.317(2) Å lies at the long end of the $[Fe_4S_4(SR)_4]^{3-}$ regime (Figure 1). This cluster has been additionally characterized by electrochemistry and EPR. For the couple $[Fe_4S_4(SH)_4]^{2-,3-}$, $E_{1/2} = -1.08$ V in acetonitrile, identical to the value obtained with $[Fe_4S_4(SH)_4]^{2-}$.[5] The EPR spectrum in Figure 3 displays an $S = {}^1/_2$ rhombic pattern centered at $g = 1.92$ and at lower field a broad feature near $g = 5.3$ and associated with $S = {}^3/_2$. Spectra of this type have been encountered before in reduced protein-bound clusters and synthetic $[Fe_4S_4(SR)_4]^{3-}$ species.[12fg] As in those cases, $[Fe_4S_4(SH)_4]^{3-}$ in frozen DMF solution exists as a physical mixture of spin states. As yet, no systematic correlation has emerged between cluster structure and ground spin state.[12g,h]

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(Et_4N)_3[Fe_4S_4(SH)_4]\cdot Et_4NCl$[a]

Fe(1)−S(1)	2.309(1)
Fe(1)−S(1)A	2.310(1)
Fe(1)−S(1)C	2.309(2)
Fe(1)−S(2)	2.317(2)
Fe(1)−Fe(1)A	2.764(1)
Fe(1)−Fe(1)B	2.764(1)
Fe(1)−Fe(1)C	2.764(1)
S(1)−Fe(1)−S(1)A	104.33(5)
S(1)C−Fe(1)−S(1)	104.24(4)
S(1)C−Fe(1)−S(1)A	104.33(5)
S(1)−Fe(1)−S(2)	115.04(6)
S(1)A−Fe(1)−S(2)	114.05(6)
S(1)C−Fe(1)−S(2)	113.64(6)
Fe(1)A−Fe(1)−Fe(1)C	59.99(1)
Fe(1)B−Fe(1)−Fe(1)A	60.02(3)
Fe(1)B−Fe(1)−Fe(1)C	59.99(1)
Fe(1)−S(1)−Fe(1)B	73.51(4)
Fe(1)C−S(1)−Fe(1)	73.56(4)
Fe(1)C−S(1)−Fe(1)B	73.51(5)

[a] Symmetry transformations used to generate equivalent atoms: A, $-y + 1, x, -z + 2$; B, $y, -x + 1, -x + 1, -z + 2$; C, $-x + 1, -y + 1, z$.

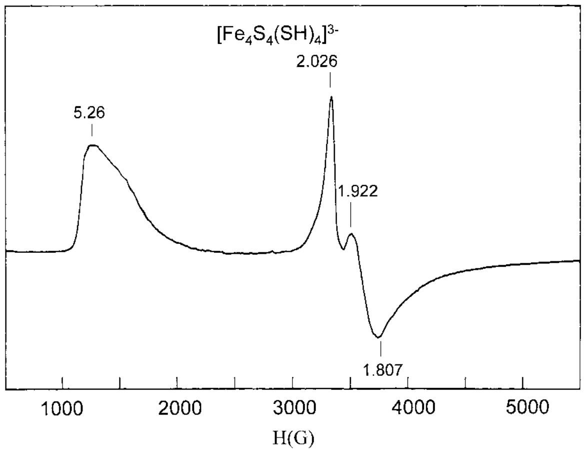

Figure 3. EPR spectrum of $[Fe_4S_4(SH)_4]^{3-}$ in DMF solution at 4.2 K; selected g values are indicated.

From two examples, we conclude that terminal Fe−SH bond lengths in $[Fe_4S_4]^{2+,+}$ clusters are not significantly different from those of alkyl- and arenethiolate ligands in the same cluster oxidation state. As seen in Figure 1, Fe−Cl distances in $[Fe_4S_4Cl_4]^{2-}$ are relatively short, in the 2.20−2.22 range[19] which encompasses the mean value of the terminal ligand bond length (2.211(7) Å) in the structure attributed to $(Pr_4N)_2[Fe_4S_4(SH)_4]$.[5] It is now apparent, from the foregoing chemical and structural evidence, that this structure is actually that of $(Pr_4N)_2[Fe_4S_4Cl_4]$. Sulfur and chlorine are not easily distinguished by X-ray diffraction; a hydrosulfide ligand could be identified with certainty by this technique if its associated hydrogen atom density were detected. The data set previously refined as

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$(Pr_4N)_2[Fe_4S_4(SH)_4]$ was refined again but with chloride terminal ligands. This refinement lowered the final R1 value to 5.81% (from 6.13%);[9] bond distances and angles of the two independent cluster anions were nearly identical with those from the previous refinement. The Fe−Cl distances ranged from 2.197(2) to 2.213(2) Å for the two anions, with a mean value of 2.208(5) Å. The compound $(Pr_4N)_2[Fe_4S_4(SH)_4]$ is authentic, but after exposure to chlorinated solvents for a sufficient period it undergoes ligand substitution with solvent chloride, presumably liberated by nucleophilic attack of coordinated hydrosulfide. At the time of its report,[5] we did not refine the structure with an alternative terminal ligand.

The differences in bond lengths observed here with clusters are consistent with those for mononuclear tetrahedral complexes of Fe(III,II). We quote several mean values from some of the more precise structures available. In two $[FeCl_4]^-$ compounds, the bond lengths are 2.196(9)[20a] and 2.185(2) Å,[20b] while in three $[Fe(SR)_4]^-$ complexes, the range 2.264(1)−2.297(6) Å is found.[21] Similarly, the bond length in $(Me_4N)_2[FeCl_4]$ is 2.292(2) Å,[22] compared to the near-identical values of several $[Fe(SR)_4]^{2-}$ complexes, which average to 2.34 Å.[23,24] The differences in chloride and thiolate bond distances for Fe(II) are ca. 0.04−0.11 Å, and for Fe(III) ca. 0.05 Å is found. The complexes $[Fe(SH)_4]^{-,2-}$ are unknown. Thus, while chloride and hydosulfide ligands may not be distinguishable by X-ray diffraction, the evidence presented here shows that in mononuclear complexes and clusters with tetrahedral metal sites, these ligands are distinguishable by bond lengths, at least when bound to Fe(III) or Fe(II) or an intermediate oxidation state.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $(Pr_4N)_2[Fe_4S_4Cl_4]$ and $(Et_4N)_3[Fe_4S_4(SH)_4]\cdot Et_4NCl$, including tables of crystal and intensity collection data, positional and thermal parameters, and interatomic distances and angles, are available on the Internet only. A table of iron−sulfur bond lengths and their mean values in the clusters $[Fe_4S_4(SR)_4]^{-,2-,3-}$ is also available (1 page). Access and ordering information is given on any current masthead page.

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