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Supplementary Material Available: Tables of structure factor amplitudes (24 pages). See any current masthead page for ordering instructions.

References and Notes

(1) P.L. thanks the Program for Cultural Exchange between the United States of America and Spain for financial aid during a leave of absence from the University of Zaragoza.
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A Synthetic Tetranuclear Iron–Sulfur Complex with Ionized Side Chains: The Crystal Structure of $(Fe_4S_4(S(CH_2)_2COO)_4)^{6-}\cdot(Na_5\cdot N(C_4H_9)_4)^{6+}\cdot 5C_5H_9NO$

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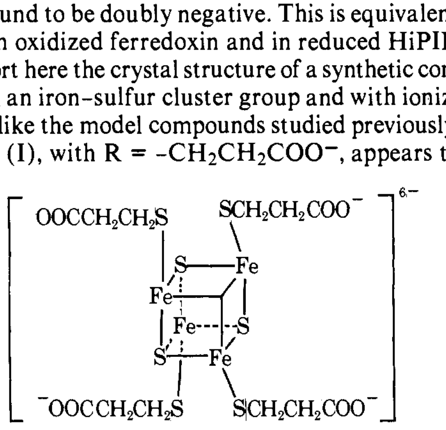
Abstract: The structure of a synthetic tetranuclear iron–sulfur complex, a model for the active site of ferredoxins, has been determined by x-ray crystallographic techniques. The contents of the asymmetric unit of the crystal consist of one hexanegative anion $(Fe_4S_4(S(CH_2)_2COO)_4)^{6-}$, and six cations (one $N(C_4H_9)_4^+$ and five Na^+). There are also five molecules of *N*-methylpyrrolidone (C_5H_9NO) of crystallization. The unit cell dimensions are a = 21.088 (7) Å, b = 31.178 (10) Å, c = 11.703 (4) Å, β = 92.63 (2)° and the space group is $P2_1/a$. The structure was refined for 17 005 independent data of which 8284 were greater than $2.5\sigma(I)$. The final R value was 0.066 for observed data. The method of preparation is described. This compound is unique among model compounds prepared so far because of its solubility in water. The half-wave potential of the compound is −0.58 V (vs. standard hydrogen electrode), a value similar to the reduction potential of a natural ferredoxin (−0.53 to −0.58 V). The iron-sulfur cluster is a distorted cube, squashed by 0.04 Å in one direction. The side chains of the cluster extend in a direction parallel to the b axis toward a column of sodium cations which extends in the c direction throughout the crystal. The oxygen atoms of *N*-methylpyrrolidone molecules take part in the coordination around sodium atoms. Clusters in adjacent unit cells pack 11.7 Å apart (c axis) with a tetrabutylammonium ion between two such clusters. There appears to be some interaction between the hydrophobic chains of the cation and some of the sulfur atoms of the cluster compound.

Nonheme iron–sulfur proteins are found in many bacterial, plant, and animal cells and act as electron carriers in these systems. Many such proteins contain an Fe_4S_4* cluster,[3] shaped approximately as a distorted cube with iron and sulfur atoms at alternate corners.[4]

Our knowledge of the Fe_4S_4* clusters comes from structural studies of both proteins containing such clusters and from similar studies of model compounds. Proteins which contain these clusters and that have been studied by x-ray crystallographic techniques include the ferredoxin from *P. aerogenes*[5] (two Fe_4S_4* clusters per molecule) and the high-potential iron-sulfur protein (HiPIP) from *Chromatium*[6] (one Fe_4S_4* cluster per molecule). However, in order to obtain high resolution data on bond lengths and angles, some model compounds with the formulas $[Fe_4S_4(SR)_4]^{2-}$ have been prepared by Holm and studied chemically and crystallographically.[7-9] In these model compounds, where R = $-CH_2C_6H_5$[7,8] or $-C_6H_5$[9], the dimensions of the cube-like cluster have been determined.

The electric charge of the cluster (equivalent to $2Fe^{2+}$ and $2Fe^{3+}$ for the iron atoms) has also been established (from a count of the cations present) in these model compounds, a situation not yet possible for the proteins which have been studied to lower resolution. The charge on the $Fe_4S_4{}^*(SR)_4$ group is found to be doubly negative. This is equivalent to the situation in oxidized ferredoxin and in reduced HiPIP.[10]

We report here the crystal structure of a synthetic compound containing an iron-sulfur cluster group and with ionized side chains (unlike the model compounds studied previously). This compound (I), with R = $-CH_2CH_2COO^-$, appears to be an extremely useful model for the active site of ferredoxins[11] since it is water soluble (unlike previously reported model compounds), and hence can be studied in aqueous solution. It is also of interest because it has a reversible half-wave potential in the physiological range. This study was undertaken in order to determine the dimensions of the box, the conformation of the side chains, the charge on the box, and the mode of molecular packing.



I

Experimental Section

A. Synthesis of $[Fe_4S_4(SCH_2CH_2COO)_4]^{6-}$. All manipulations were carried out under a blanket of nitrogen using standard Schlenk techniques.[12] Nitrogen degassed reagent grade solvents were used with no attempts being made to remove trace amounts of water. Sodium and iron analyses were carried out (by Sue Wilson, Santa Barbara laboratory) using atomic absorption spectroscopy.

To sodium methoxide (8.11 g, 150 mmol) dissolved in 100 mL of methanol was added β-mercaptopropionic acid (7.97 g, 75 mmol) with stirring. Anhydrous ferric chloride (4.05 g, 25 mmol) dissolved in 75 mL of methanol was then added dropwise via an equal pressure dropping funnel over a period of 25 min.[13] The solution turned violet at first then rapidly evolved into a brilliant deep green slurry. A solution of sodium hydrogen sulfide was prepared by dissolving sodium methoxide (1.35 g, 25 mmol) in 70 mL of methanol and bubbling in H_2S until no further absorption occurred. Nitrogen was then bubbled through for 10 min to remove excess H_2S then a further measure of sodium methoxide (1.35 g, 25 mmol) was added to prepare a solution of anhydrous sodium sulfide. This solution was added to the green slurry to give a black solution with some black precipitate. To the black solution was added tetrabutylammonium bromide (5.0 g) and the mixture refluxed for several hours. The solvent was removed, in vacuo, to give a gray powder. The powder was stirred with 50 mL of methanol then 50 mL of *N*-methylpyrrolidone was added and, after 10 min, the mixture was filtered. This was repeated with a further 20 mL of methanol and 20 mL of *N*-methylpyrrolidone. The two filtrates were combined, and a further 100 mL of *N*-methylpyrrolidone was added. After standing for a day, large clusters of deep black needles (contaminated with a small amount of white, fluffy material) had formed. A second crop was obtained by treating the residue again with methanol and *N*-methylpyrrolidone. Total yield was 8.74 g (81.3%). Anal. Calcd for $C_{53}H_{97}N_6O_{13}Fe_4S_8Na_5$: Fe, 13.78; Na, 7.09. Found: Fe, 13.0; Na, 7.0.

Measured values of some properties of this compound, including the pK_a, the half-wave potential, and the kinetics of ligand exchange have already been published.[11] The electronic spectrum is shown in Figure 1.[14]

B. Crystal Data. The purest crystals were grown by triturating the gray powder described above with eight 50-mL portions of ethanol to give a brown solution. All of the solvent was removed in vacuo at room temperature. The brown residue was dissolved in 10 mL of methanol then 25 mL of *N*-methylpyrrolidone was added. Upon overnight standing black rods were obtained which were quite hygroscopic and sensitive to oxygen. Therefore single crystals were cut to shape and sealed, under argon, in dried capillaries.

Unit cell dimensions are a = 21.088 (7) Å, b = 31.178 (10) Å, c = 11.703 (4) Å, β = 92.63 (2)°, and V = 7686 (3) Å^3, and the space group is $P2_1/a$. The density, obtained by flotation in a mixture of ethylene bromide and hexane, was difficult to obtain, probably because of the natures of the various components of the crystal, but lay in the range 1.42–1.55 g cm^{-3}. This corresponded to a formula weight of 1640–1790 for the contents of the asymmetric unit.

Three-dimensional x-ray intensity data were collected on a Syntex $P\bar{1}$ automated diffractometer with the ω scan technique and Mo Kα radiation using a highly oriented graphite crystal monochromator. Independent reflections were scanned (17 005) (out to θ = 55°) of which 8284 had intensity (I) greater than $2.5\sigma(I)$, where $\sigma(I)$ was derived from counting statistics. There was no falloff in intensity as a function of time. Lorentz and polarization corrections were applied, and an empirical absorption correction was made[15] (μ = 10.62 cm^{-1}). Values of $\sigma(F)$ were determined as $\sigma(F) = (F/2)\{(\sigma^2(I)/I^2) + \delta^2\}^{1/2}$ where δ is an instrumental uncertainty determined from the variation of the intensities of three periodically monitored standard reflections (δ = 0.032).

The structure was solved by finding the orientation and positions of the $Fe_4S_4{}^*$ box from the Patterson map and then the remaining atoms of the structure by use of successive Fourier maps. The entire contents of the unit cell were revealed in this way. It was found that the asymmetric unit contains one $Fe_4S_4(S(CH_2)_2COO)_4{}^{6-}$ ion, five sodium ions, one tetrabutylammonium cation, and five *N*-methylpyrrolidone molecules of crystallization. This corresponds to an asymmetric unit cell content of $Fe_4Na_5S_8O_{13}N_6C_{53}H_{97}$, corresponding to a formula weight of 1621.25 and a calculated density of 1.41 g cm^{-3}. The structure may then be described[16] as sodium tetrabutylammonium tetrakis(β-mercaptopropionatoiron sulfide)-*N*-methylpyrrolidone solvate.

The structure was refined by successive least-squares cycles[17] to an R value of 0.066 for the "observed data" (i.e., data with $I > 2.5\sigma(I)$). Because of the size of the unit cell contents it was necessary to refine the structure in portions. Most of the hydrogen atoms were found from difference maps and their positions were refined. The weights of the reflections during refinement were $1/[\sigma^2(F)]$ with zero weight for those reflections below the threshold value ($I < 2.5\sigma(I)$). The quantity minimized in the least-squares calculations was $\Sigma\omega\{|F_o| - |F_c|\}^2$. Scattering factors used were listed values.[18,19] Other programs used were part of the CRYSNET system.[20]

A list of positional and averaged thermal parameters is given in Table I. Individual anisotropic factors are listed in the microfilm edition of this journal (Table I). A table of observed and calculated structure factors may be obtained from the authors on request.

Results and Discussion

1. Dimensions of the Box. In the compound I studied it was found that the distances between iron and sulfur atoms agree very well with those found in other synthetic compounds and that the cluster is "squashed" to the extent of approximately 0.04 Å in the b direction, as shown in Figure 2a and Table II. Dimensions are compared with those in other synthetic compounds[7-9,21,22] in Table II. The sulfur and iron tetrahedra are nearly regular, as shown in Figure 2b although, as expected from the squashing of the box, the distances Fe(1)···Fe(4) and Fe(2)···Fe(3) are longer than the others. A general view of the entire cluster ion is shown in Figure 3. Distances and angles and planarities of groups in the cluster are given in the microfilm edition (Table 2).

It has been shown,[23,24] from x-ray crystallographic studies of difference Fourier maps between oxidized and reduced *Chromatium* high potential iron protein (HiPIP) that the reduced $Fe_4S_4{}^*$ cluster shrinks slightly, particularly in one direction, upon oxidation. Listed bond lengths and angles for oxidized and reduced HiPIP are given in Table II. In the cluster studied here the measured direction of contraction of the cluster is perpendicular to the column of sodium cations in the crystal and is in the direction of extension of the side chains, as shown in Figure 1. This shrinkage of the box in one

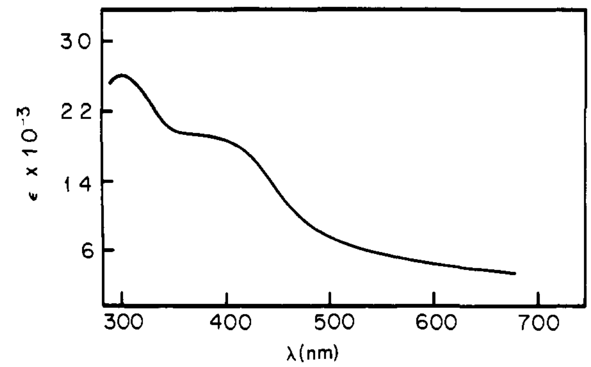


Figure 1. Electronic spectrum of $[Fe_4S_4(SCH_2CH_2COO^-)_4]^{6-}$ in 0.1 M aqueous β-mercaptopropionate, pH 9.20.

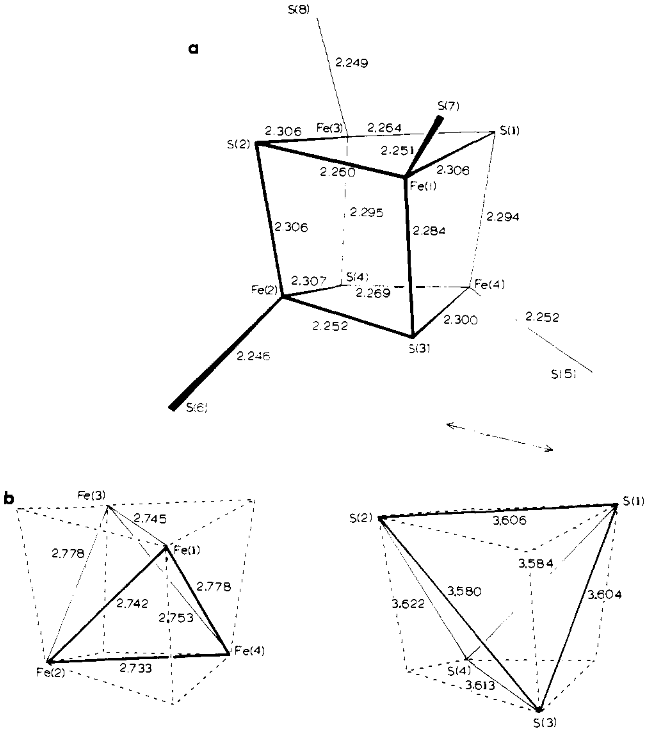


Figure 2. (a) Distances in Å in the $(Fe_4S_4{}^*)S_4$ cluster. The double-headed arrow in the lower right hand corner indicates the direction in which the box sides are contracted by 0.04 Å. (b) Distances in Å in the iron and the sulfur tetrahedra. These diagrams are drawn in the same orientation as Figure 2a.

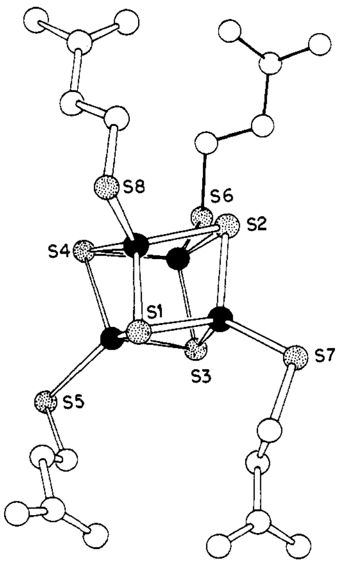


Figure 3. General view of the molecule. Iron atoms are black and sulfur atoms are speckled. The disorder in the side chain attached to S(5) has been averaged. The direction in which the box sides are contracted is indicated by a double-headed arrow.

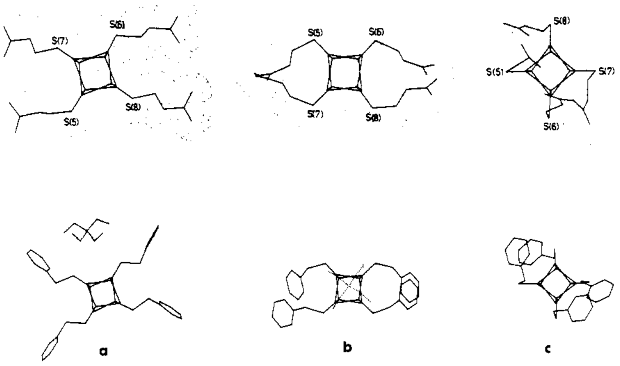


Figure 4. Comparison of side chain conformations in the structure studied here with those in $(Et_4N)_2[Fe_4S_4(SCH_2Ph)_4]$ (ref 7, 8). Note that in c the view is down the direction in which the box sides are contracted. van der Waals radii are indicated by stippling in the upper diagrams. In a and b the tetraethylammonium cations are also drawn in. These diagrams may be compared with Figures 6 and 7, respectively. The analogy is striking.

direction is ascribed to the Jahn-Teller effect.[24,25] The deviation of the cluster from $\bar{4}3m(T_d{}^3)$ symmetry is illustrated in Figure 2b where it is shown that the iron and the sulfur tetrahedra are not symmetrical.

The side chains of the cluster extend in the *b* direction (also the direction of contraction of the box). This enables the carboxyl group oxygen atoms to coordinate around the sodium ion channel. A comparison of side chain conformations with those for another model compound[7,8] is shown in Figure 4. These diagrams show that in both compounds the side chains extend in the direction of contraction of the box. One of the side chains, the one involving S(5), is disordered. This conclusion was reached from the facts that the atomic positions for C(1S5) and C(2S5) would not refine well and that two peaks were found in Fourier and difference Fourier maps near each of the positions that these atoms would be expected to occupy. In effect the rather flexible side chain is constrained at both ends: at the cluster at S(5), and at the sodium coordination polyhedron (O(1S5), and O(2S5)). However, no chemical significance could be attached to the disorder of C(1S5) and C(2S5). It seems that there is enough space for some variation to occur in the orientation of this side chain. The atom C(3S5) is probably also slightly disordered so that the C(2S5)–C(3S5)–O angles may lie near the normal value (117.6° for the other three carboxyl groups). Values for the disordered atoms lie in the range 103–133° (Table 2, microfilm edition).

2. Packing Around the Sodium Ions. A column of sodium ions and oxygen atoms extends through the entire crystal in the direction of the *c* axis. The atoms which pack around these sodium ions are listed in Table III and illustrated diagrammatically in Figure 5. Each sodium ion is surrounded by five oxygen atoms at 2.20–2.57 Å except for Na(5) which is surrounded by six oxygen atoms at 2.27–2.67 Å. In general the shorter distances are those from the sodium ion to two different carboxyl groups at similar *y* values. The average Na···O distance is 2.36 Å for five-coordinated sodium and 2.46 Å for six-coordinated sodium. Each sodium ion, except for Na(4), is surrounded by three sodium ions at less than 3.7 Å. There are only two other sodium ions near Na(4). O···Na···O angles are listed in the microfilm edition (Table 3).

Table I. Fractional Coordinates and Averaged Anisotropic Thermal Parameters (with estimated standard deviations in parentheses)[a]

	x	*y*	*z*	B_{av}
Fe(1)	0.324 56 (5)	0.148 47 (3)	0.946 73 (8)	2.61 (5)
Fe(2)	0.225 30 (5)	0.091 91 (3)	0.955 41 (8)	2.70 (5)
Fe(3)	0.316 47(5)	0.081 84 (3)	0.793 49 (7)	2.54 (5)
Fe(4)	0.229 14 (5)	0.147 37 (3)	0.775 04 (8)	2.72 (5)
S(1)	0.336 42 (8)	0.151 34 (5)	0.752 00 (14)	2.95 (8)
S(2)	0.331 83 (8)	0.077 90 (5)	0.989 55 (13)	2.88 (8)
S(3)	0.219 62 (9)	0.163 93 (5)	0.964 97 (15)	3.21 (8)
S(4)	0.208 47 (10)	0.076 02 (6)	0.763 91 (18)	3.05 (8)
S(5)	0.168 27 (8)	0.187 74 (5)	0.654 00 (14)	4.39 (10)
S(6)	0.154 34 (9)	0.062 45 (6)	1.069 43 (16)	3.67 (9)
S(7)	0.390 89 (9)	0.190 25 (6)	1.053 90 (16)	3.87 (10)
S(8)	0.374 59 (9)	0.036 46 (6)	0.691 65 (17)	4.23 (10)
Na(1)	0.280 05 (14)	0.392 47 (8)	0.674 00 (22)	3.96 (16)
Na(2)	0.205 03 (12)	0.347 42 (8)	0.899 64 (22)	3.68 (15)
Na(3)	0.252 93 (15)	0.382 92 (8)	0.153 66 (23)	4.08 (16)
Na(4)	0.28055 (14)	0.344 23 (9)	0.40043 (22)	4.49 (16)
Na(5)	0.346 52 (12)	0.353 28 (9)	0.908 39 (22)	3.67 (15)
C(1S5A)	0.193 7 (9)	0.246 0 (6)	0.703 3 (16)	4.4 (4)[b]
C(1S5B)	0.209 4 (10)	0.238 1 (7)	0.615 2 (18)	5.2 (5)[b]
C(2S5A)	0.236 1 (9)	0.259 2 (6)	0.708 4 (15)	4.6 (4)[b]
C(2S5B)	0.255 5 (9)	0.254 3 (6)	0.644 2 (17)	4.2 (5)[b]
C(3S5)	0.270 5 (4)	0.302 9 (2)	0.672 7 (7)	3.6 (4)
O(1S5)	0.277 1 (3)	0.322 5 (2)	0.764 9 (4)	4.0 (3)
O(2S5)	0.283 3 (3)	0.318 1 (2)	0.579 9 (5)	5.8 (4)
C(1S6)	0.157 3 (4)	0.006 1 (2)	1.041 4 (8)	5.8 (5)
C(2S6)	0.212 5 (4)	−0.017 6 (2)	1.091 7 (8)	5.2 (5)
C(3S6)	0.213 8 (4)	−0.065 2 (3)	1.067 8 (7)	4.5 (4)
O(1S6)	0.241 9 (3)	−0.087 9 (2)	1.140 4 (5)	5.5 (3)
O(2S6)	0.186 3 (3)	−0.079 5 (2)	0.978 4 (5)	6.2 (4)
C(1S7)	0.356 5 (4)	0.244 1 (2)	1.043 0 (7)	4.3 (4)
C(2S7)	0.308 8 (4)	0.252 8 (2)	1.128 7 (6)	4.4 (4)
C(3S7)	0.283 1 (3)	0.298 5 (2)	1.132 6 (6)	3.7 (4)
O(1S7)	0.281 3 (2)	0.319 9 (2)	1.041 4 (4)	4.0 (3)
O(2S7)	0.264 2 (3)	0.310 7 (2)	1.226 0 (4)	5.7 (3)
C(1S8)	0.334 6 (5)	−0.015 6 (2)	0.699 1 (7)	6.2 (5)
C(2S8)	0.302 1 (4)	−0.028 5 (3)	0.597 9 (9)	6.3 (5)
C(3S8)	0.276 2 (4)	−0.074 3 (2)	0.590 6 (6)	4.6 (4)
O(1S8)	0.282 9 (3)	−0.097 8 (2)	0.676 5 (4)	5.4 (3)
O(2S8)	0.249 7 (3)	−0.085 7 (2)	0.499 2 (4)	6.3 (3)
N(TB)	0.275 2 (3)	0.119 9 (2)	0.367 7 (4)	3.1 (3)
C(1T)	0.234 2 (3)	0.147 0 (2)	0.284 4 (6)	3.6 (4)
C(2T)	0.197 6 (4)	0.183 7 (3)	0.336 0 (7)	5.3 (5)
C(3T)	0.150 5 (4)	0.202 8 (3)	0.254 6 (8)	5.6 (5)
C(4T)	0.113 6 (5)	0.238 8 (4)	0.305 0 (9)	9.2 (7)
C(5T)	0.317 1 (3)	0.148 3 (2)	0.444 2 (5)	3.3 (4)
C(6T)	0.363 9 (4)	0.175 6 (3)	0.382 4 (6)	4.7 (5)
C(7T)	0.388 5 (4)	0.211 6 (3)	0.455 3 (8)	6.2 (5)
C(8T)	0.439 7 (6)	0.237 0 (4)	0.404 0 (10)	9.5 (8)
C(9T)	0.313 5 (4)	0.090 0 (2)	0.295 8 (5)	3.7 (4)
C(10T)	0.359 8 (4)	0.061 8 (3)	0.362 9 (6)	4.8 (4)
C(11T)	0.383 5 (4)	0.025 7 (3)	0.291 0 (7)	5.3 (5)
C(12T)	0.435 6 (5)	0.000 4 (3)	0.350 9 (9)	8.5 (6)
C(13T)	0.232 8 (4)	0.094 1 (2)	0.446 6 (6)	3.9 (4)
C(14T)	0.192 2 (5)	0.060 2 (3)	0.388 9 (7)	6.4 (5)
C(15T)	0.145 2 (4)	0.041 3 (3)	0.458 3 (8)	6.6 (6)
C(16T)	0.105 1 (5)	0.006 3 (3)	0.408 2 (9)	9.0 (7)
O(1P1)	0.155 1 (3)	0.379 0 (2)	0.049 0 (5)	6.7 (3)
C(1P1)	0.103 2 (4)	0.392 8 (3)	0.082 3 (7)	5.2 (5)
N(2P1)	0.078 5 (3)	0.430 1 (2)	0.057 6 (6)	5.9 (4)
C(3P1)	0.017 3 (4)	0.439 0 (3)	0.106 2 (8)	6.2 (6)
C(4P1)	0.005 0 (5)	0.399 7 (4)	0.172 0 (9)	8.6 (7)
C(5P1)	0.056 9 (5)	0.367 7 (3)	0.155 3 (9)	7.9 (6)
C(6P1)	0.109 1 (5)	0.461 6 (3)	−0.012 8 (10)	8.4 (7)
O(1P2)	0.444 8 (2)	0.325 8 (2)	0.918 5 (5)	5.7 (3)
C(1P2)	0.484 7 (4)	0.298 3 (3)	0.904 2 (8)	5.8 (5)
N(2P2)	0.484 3 (4)	0.268 6 (3)	0.834 2 (8)	8.1 (5)
C(3P2)	0.536 8 (6)	0.238 2 (3)	0.835 6 (11)	8.9 (7)
C(4P2)	0.578 2 (6)	0.257 3 (4)	0.935 9 (14)	13.0 (11)
C(5P2)	0.547 8 (5)	0.293 5 (4)	0.979 8 (10)	8.7 (7)
C(6P2)	0.430 5 (6)	0.260 0 (4)	0.749 4 (9)	9.1 (7)
O(1P3)	0.383 7 (2)	0.401 4 (2)	0.752 1 (5)	6.1 (3)
C(1P3)	0.435 2 (4)	0.396 6 (3)	0.707 8 (8)	5.7 (5)
N(2P3)	0.491 1 (3)	0.405 7 (2)	0.742 9 (8)	8.4 (5)
C(3P3)	0.541 9 (5)	0.393 8 (4)	0.674 4 (12)	10.6 (9)

Table I (*continued*)

	x	y	z	B_{av}
C(4P3)	0.505 2 (7)	0.374 3 (6)	0.571 6 (13)	13.9 (13)
C(5P3)	0.439 7 (6)	0.375 3 (4)	0.586 8 (10)	9.4 (8)
C(6P3)	0.502 3 (7)	0.426 6 (4)	0.857 3 (9)	10.6 (9)
O(1P4)	0.365 0 (5)	0.374 4 (3)	0.315 4 (10)	12.8 (7)
C(1P4)	0.409 6 (8)	0.392 5 (6)	0.271 5 (12)	12.1 (10)
N(2P4)	0.426 3 (9)	0.426 6 (4)	0.252 5 (12)	13.9 (10)
C(3P4)	0.475 8 (9)	0.440 6 (7)	0.182 8 (17)	11.9 (14)
C(4P4)	0.507 7 (9)	0.389 3 (6)	0.181 0 (17)	12.6 (14)
C(5P4)	0.461 1 (9)	0.356 3 (7)	0.218 8 (17)	11.6 (13)
C(6P4)	0.385 0 (9)	0.462 8 (5)	0.286 8 (13)	15.6 (10)
O(1P5)	0.127 1 (3)	0.350 2 (2)	0.765 8 (6)	9.1 (5)
C(1P5)	0.090 4 (4)	0.360 4 (3)	0.687 1 (9)	5.8 (5)
N(2P5)	0.033 4 (3)	0.377 2 (2)	0.699 9 (6)	5.2 (4)
C(3P5)	−0.000 9 (4)	0.384 0 (3)	0.593 5 (8)	6.9 (6)
C(4P5)	0.101 2 (5)	0.354 4 (4)	0.560 3 (9)	8.6 (8)
C(5P5)	0.045 4 (6)	0.374 7 (4)	0.503 5 (9)	9.5 (8)
C(6P5)	0.005 4 (5)	0.386 0 (3)	0.808 5 (8)	7.0 (6)

Hydrogen atoms (calculated positions)

	x	y	z		x	y	z
H(S61)	0.115	−0.012	1.058	H(P45a)	0.442	0.340	10.153
H(S61a)	0.160	−0.001	0.959	H(P56)	0.037	0.379	0.872
H(S62)	0.253	−0.007	1.072	H(P56a)	−0.007	0.417	0.812
H(S62a)	0.218	−0.018	1.173	H(P56b)	−0.033	0.368	0.816
H(S71)	0.385	0.263	1.050	H(P53)	−0.016	0.414	0.588
H(S71a)	0.332	0.247	0.964	H(P53a)	−0.038	0.364	0.586
H(S72)	0.274	0.236	1.118	H(P54)	0.058	0.402	0.466
H(S72a)	0.327	0.246	1.215	H(P54a)	0.026	0.355	0.445
H(S81)	0.366	−0.042	0.721	H(P55)	0.141	0.369	0.539
H(S81a)	0.304	−0.020	0.764	H(P55a)	0.103	0.323	0.541
H(S82)	0.261	−0.010	0.573	H(T1)	0.260	0.161	0.225
H(S82a)	0.322	−0.027	0.535	H(T1A)	0.205	0.127	0.243
H(P16)	0.150	0.450	−0.038	H(T2)	0.180	0.177	0.406
H(P16a)	0.081	0.468	−0.081	H(T2A)	0.227	0.207	0.356
H(P16b)	0.117	0.488	0.032	H(T3)	0.167	0.213	0.187
H(P13)	−0.016	0.443	0.044	H(T3A)	0.130	0.179	0.234
H(P13a)	0.020	0.465	0.158	H(T4)	0.087	0.249	0.258
H(P14)	−0.037	0.387	0.145	H(T4A)	0.093	0.227	0.380
H(P14a)	0.003	0.407	0.255	H(T4B)	0.147	0.261	0.343
H(P15)	0.040	0.342	0.113	H(T5)	0.290	0.168	0.491
H(P15a)	0.078	0.359	0.230	H(T5A)	0.341	0.131	0.495
H(P26)	0.397	0.283	0.756	H(T6)	0.398	0.157	0.361
H(P26a)	0.447	0.260	0.670	H(T6A)	0.345	0.184	0.322
H(P26b)	0.412	0.231	0.765	H(T7)	0.351	0.230	0.470
H(P23)	0.559	0.239	0.762	H(T7A)	0.399	0.201	0.528
H(P23a)	0.522	0.209	0.853	H(T8)	0.458	0.256	0.451
H(P24)	0.620	0.266	0.908	H(T8A)	0.473	0.217	0.387
H(P24a)	0.584	0.235	0.998	H(T8B)	0.423	0.247	0.337
H(P25)	0.575	0.320	0.972	H(T9)	0.282	0.072	0.244
H(P25a)	0.538	0.289	1.062	H(T9A)	0.340	0.106	0.245
H(P36)	0.461	0.432	0.892	H(T10)	0.399	0.079	0.389
H(P36a)	0.528	0.407	0.909	H(T10A)	0.342	0.052	0.426
H(P36b)	0.526	0.454	0.848	H(T11)	0.343	0.006	0.277
H(P33)	0.570	0.372	0.714	H(T11A)	0.396	0.036	0.207
H(P33a)	0.567	0.419	0.652	H(T12)	0.453	−0.022	0.299
H(P34)	0.519	0.344	0.562	H(T12A)	0.478	0.018	0.362
H(P34a)	0.515	0.391	0.501	H(T12B)	0.426	−0.011	0.418
H(P35)	0.422	0.346	0.587	H(T13)	0.261	0.080	0.499
H(P35a)	0.418	0.393	0.527	H(T13A)	0.201	0.115	0.480
H(P46)	0.405	0.491	0.266	H(T14)	0.169	0.066	0.305
H(P46a)	0.342	0.460	0.246	H(T14A)	0.217	0.041	0.365
H(P46b)	0.380	0.462	0.371	H(T15)	0.163	0.033	0.527
H(P43)	0.505	0.462	0.222	H(T15A)	0.110	0.067	0.476
H(P43a)	0.460	0.450	0.105	H(T16)	0.072	−0.004	0.461
H(P44)	0.546	0.388	0.234	H(T16A)	0.075	0.017	0.329
H(P44a)	0.520	0.382	0.102	H(T16B)	0.127	−0.013	0.386
H(P45)	0.480	0.337	0.280				

[a] Positional parameters are listed as fractions of cell edges. Anisotropic temperature factors are expressed as $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$. Values of $B_{av} = (B_{11} + B_{22} + B_{33})/3$ are listed. Values of B_{ij} are listed in the microfilm edition. Isotropic temperature factors are expressed as $\exp(-B \sin^2 \theta/\lambda^2)$ with B values given in Å^2. Estimated standard deviations are listed in parentheses with respect to the last digits given for any parameter. [b] Isotropic refinement because of disorder.

Table II. Average Dimensions of the Box and Comparison with Other Compounds (Å and deg)

Bond or angle	No. of bonds or angles	I[a]	II[b]	III[c]	IV[d]	V[e]
Fe S*	8	2.300 (3)	2.310 (3)	2.296 (4)	2.25 (6)	2.32 (8)
Fe S*	4	2.261 (3)	2.239 (4)	2.267 (5)		
Fe S	4	2.250 (3)	2.251 (3)	2.263 (3)	2.21 (3)	2.22 (3)
Fe Fe	2	2.778 (3)	2.776 (2)	2.730 (2)	2.73 (4)	2.81 (5)
Fe Fe	4	2.743 (3)	2.732 (3)	2.739 (4)		
S*S*	2	3.613 (3)	3.645 (3)	3.650 (4)		
S*S*	4	3.596 (3)	3.586 (4)	3.592 (6)		
Fe Fe Fe	4	60.8 (2)	61.11 (5)	59.79 (6)	60.0 (14)	60.0 (16)
Fe Fe Fe	8	59.6 (2)	59.45 (5)	60.11 (7)		
S*S*S*	4	60.3 (2)	61.11 (4)	61.08 (8)		
S*S*S*	8	59.8 (2)	59.46 (4)	59.47 (8)		
S*Fe S*	12	103.9 (2)	104.09 (6)	104.3 (1)	103.3 (32)	103.6 (28)
Fe S*Fe	12	74.1 (2)	73.81 (5)	73.50 (9)	74.7 (16)	74.5 (18)
S*Fe S	12	109.9–119.3 (2)	110.2–117.3 (2)	100.2–135.7 (1)	114.9 (48)	114.1 (57)

[a] I = $[(C_4H_9)_4N{\cdot}Na_5][Fe_4S_4(SCH_2CH_2COO)_4]_6$, this work. [b] II = $(Et_4N)_2[Fe_4S_4(SCH_2Ph)_4]$, ref 7 and 8 (Herskovitz et al.; Averill et al.). [c] III = $(Me_4N)_2[Fe_4S_4(SPh)_4]$, ref 9 (Que et al.). [d] IV = $HiPIP_{oxidized}$, ref 23 (Freer et al.). [e] V = $HiPIP_{reduced}$, ref 23 (Freer et al.).

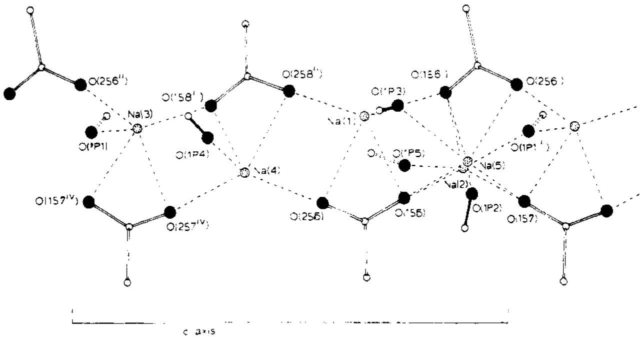


Figure 5. Packing around the sodium ions. Sodium ions are speckled and oxygen atoms are black. The superscripts are: i = $\frac{1}{2} - x$, $\frac{1}{2} + y$, $2 - z$; ii = $\frac{1}{2} - x$, $\frac{1}{2} + y$, $1 - z$; iii = $x, y, 1 + z$; iv = $x, y, z - 1$. The c axial length is indicated.

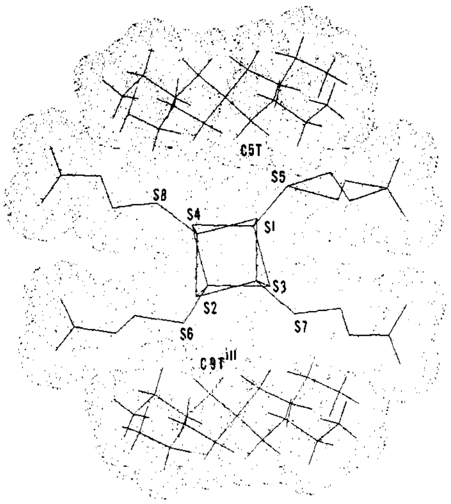


Figure 6. Packing of tetrabutylammonium cations around a cluster. van der Waals radii are indicated by stippling. Hydrogen atoms on the cluster anion are omitted for clarity.

There is no evidence of hydrogen bond formation by any of the carboxyl groups, leading to the presumption that all four carboxyl groups are ionized and that the charge on the box itself is doubly negative. All short O···O contacts are between oxygen atoms that are both coordinated to the same sodium ion. This is not a condition under which hydrogen bond formation occurs.[26] The cation count of six (five sodium and one tetrabutylammonium cation), together with the four ionized carboxyl groups indicates that the charge on the box itself is doubly negative. This corresponds to the charge on reduced HiPIP and oxidized ferredoxin,[10] and is the same as that in the other model compounds.[7-9]

3. Tetrabutylammonium Cation. The tetrabutylammonium cation is fully extended as shown in Figure 6. There is no evidence of disorder, and all hydrogen atoms were located readily for this ion. Dimensions are similar (including variations in the C-N-C bond angles) to those listed in another recent determination of such a cation[27] (microfilm edition, Table 4). Sulfur atoms of the Fe_4S_4* cluster pack against methylene groups of the tetrabutylammonium cation although the C-H···S interactions are not linear (microfilm edition, Table 5). The faces of the cluster that the tetrabutylammonium cation packs against are not the symmetrical faces of the cluster. The cation packs between clusters in the direction of the c axis (the direction of the sodium ion channel).

4. *N*-Methylpyrrolidones of Crystallization. Distances, angles, and deviations from planarity in the five *N*-methylpyrrolidone molecules of crystallization are given in the microfilm edition (Table 6) and are compared with those of another pyrrolidone derivative.[28] There is considerable disorder in these molecules, and as a result the distances are only approximate. These molecules of crystallization help complete the coordination around each of the five sodium ions.

5. Packing in the Unit Cell. Bacterial ferredoxins have two clusters which, in *P. aerogenes*, are approximately 12 Å apart.[5,29] The unit cell dimension in the c direction in the compound studied here is a similar distance, 11.70 Å, and this is the closest distance between clusters. This unit cell dimension is also found in the two other model compounds studied.[7-9] Tetrabutylammonium cations pack between these clusters of compound I as shown in Figures 6 and 7. The shortest contacts of sulfur atoms are to atoms in the tetrabutylammonium cations (Figure 6). The *N*-methylpyrrolidones of crystallization pack in lines parallel to the b axis as shown in Figure 7. General short packing distances are listed in the microfilm edition (Table 7).

6. Implications. The half-wave potential, a measure of the ability of the compound to give away an electron, has been determined polarographically to be −0.58 V (vs. SHE)[11] for I in aqueous solution, a value similar to the reduction potential

Table III. Surroundings of Sodium Ions and of Oxygen Atoms

(a) Surroundings of Sodium Ions
esd values 0.006 Å for Na···O, 0.004 Å for Na···Na, 0.011 Å for Na(3)···O(1P1)

Na(1)	O(1S5)	2.430
	O(2S5)	2.568
	O(1S6^{i})	2.323
	O(2S8^{ii})	2.203
	O(1P3)	2.346
Na(2)	O(1S5)	2.371
	O(1S6^{i})	2.365
	O(1S7)	2.416
	O(1P1^{iii})	2.302
	O(1P5)	2.221
Na(3)	O(2S6^{ii})	2.363
	O(1S7^{iv})	2.452
	O(2S7^{iv})	2.414
	O(1S8^{ii})	2.240
	O(1P1)	2.355
Na(4)	O(2S5)	2.251
	O(2S7^{iv})	2.306
	O(1S8^{ii})	2.399
	O(2S8^{ii})	2.575
	O(1P4)	2.283
Na(5)	O(1S5)	2.380
	O(1S6^{i})	2.659
	O(2S6^{i})	2.590
	O(1S7)	2.365
	O(1P2)	2.241
	O(1P3)	2.518
Mean Na–O		
5-coordinate		2.359
6-coordinate		2.459
Na(1)	Na(2)	3.439
Na(1)	Na(4)	3.538
Na(1)	Na(5)	3.261
Na(2)	Na(3^{iii})	3.288
Na(2)	Na(5)	2.986
Na(3)	Na(4)	3.159
Na(3)	Na(5^{iv})	3.675

^{i} $\frac{1}{2} - x, \frac{1}{2} + y, 2 - z$. ^{ii} $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$. ^{iii} $x, y, 1 + z$. ^{iv} $x, y, z - 1$.

(b) Surroundings of Oxygen Atoms (no superscripts—see above)
(Atoms shared by a carboxyl group are marked with an asterisk.)

O(1S5)	O(1S6)	O(1S7)	O(1S8)
Na(1)*	Na(1)	Na(2)	Na(3)
Na(2)	Na(2)	Na(3)*	Na(4)*
Na(5)	Na(5)*	Na(5)	
O(2S5)	O(2S6)	O(2S7)	O(2S8)
Na(1)*	Na(3)	Na(3)*	Na(1)
Na(4)	Na(5)*	Na(4)	Na(4)*

of a natural ferredoxin, −0.53 to −0.58 V (determined by EPR-monitored potentiometric titration).[30] Values of half-wave potentials for the model compounds with phenyl or benzyl groups lie in the range −1.3 to −0.7 V (in DMF vs. SCE).[31] It is readily apparent that half-wave potentials may be altered by changing the groups attached to the box. Thus a stronger (or weaker) reducing agent may be made by changing the ligands, so that electrons are now more (or less) readily donated to a molecule to be reduced as the cluster compound is oxidized. It has been suggested[11] that the box in ferredoxins may accept (on reduction) an electron at a low negative potential, then undergo ligand exchange and, as a result, be able (on oxidation) to give up an electron at the more negative potential. In this way an electron pump action occurs.

Recent x-ray evidence on *P. aerogenes* ferredoxin,[5] which contains two of these boxes, reveals that nature may have set up the enzyme in such a manner as to provide for facile ligand exchange. Thus one box is bound to the enzyme via cysteinyl residues 8, 11, 14, and 45 while the other box is bound via cysteinyl residues 35, 38, 41, and 18. The coordination of each box by three residues from one end of the polypeptide chain and one residue from the opposite end may set up a situation that can be caused to be strained so that one ligand on each box can be readily substituted.

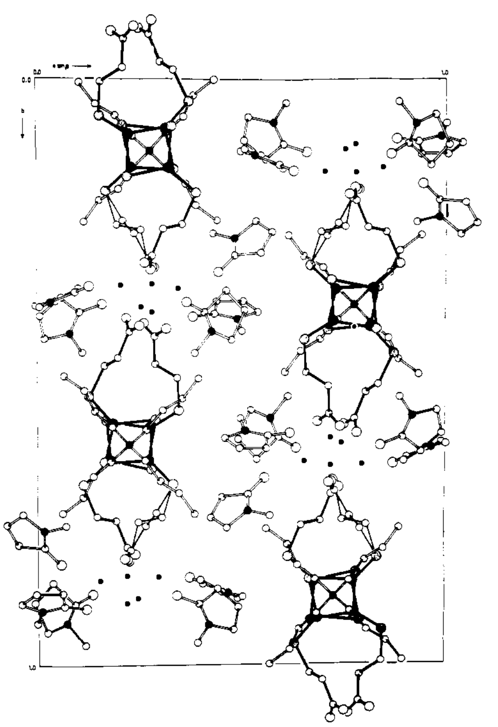


Figure 7. View down *c*. One unit cell is shown. Bonds in the cluster ion are marked in black. The disorder in the side chains attached to S(5) is indicated by thinner lines. Sodium ions are indicated by small black circles; sulfur atoms are stippled. Nitrogen and iron atoms are black circles and oxygen atoms are indicated by larger circles than are carbon atoms.

It was previously observed that the hydrolysis product of I, which is evidenced as a peak at −0.75 V (vs. SHE) in the differential pulse polarogram, can have a half-life on the order of days.[11] This decomposition product may be the species present in the systems studied by Schrauzer et al.,[32] since tetranuclear Fe-S clusters exhibit only fleeting stability under the described reaction conditions.[11,33]

The synthesis presented here provides a facile route to a water soluble, tetranuclear, iron-sulfur complex which this study shows to be a ferredoxin active site structural analogue.[33] The reduction potential of the β-mercaptopropionic acid (p*K* 10.27)[34] complex was found to be on the verge of the physiological range. If the previously observed trends[31] of $E^{1/2}$ vs. mercaptan p*K* are followed by this system in water, the $E^{1/2}$ values of complexes of less basic mercaptocarboxylates might fall even closer while still maintaining the desirable characteristic of water solubility.

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Supplementary Material Available: The following tables are also provided: Table 1, anisotropic temperature factors; Table 2, dimensions of the cluster, (a) detailed dimensions of the box, (b) dimensions of the side chains, (c) deviations from planes in the cluster (Å), (d) angles between planes in the cluster (deg); Table 3, oxygen-sodium-oxygen angles; Table 4, distances and angles in the tetrabutylammonium cation; Table 5, shortest contacts around sulfur atoms; Table 6, dimensions of *N*-methylpyrrolidone molecules, (a) distances and angles, (b) deviations from planes in Å; Table 7, some general distances in the structure (13 pages). Ordering information is given on any current masthead page.

References and Notes

(1) The Institute for Cancer Research.
(2) The University of California.
(3) The asterisk after a sulfur atom, S, is used for atoms in the cube of a cluster, in order to differentiate them from external sulfur atoms. Abbreviations: DMF = dimethylformamide; HIPIP = high potential iron protein; SHE = standard hydrogen electrode; SCE = standard calomel electrode.
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(14) The spectrum of the freshly dissolved sample has the general characteristics of previously reported analogues[31] with maxima near 300 and 400 nm but with significantly broader peaks in aqueous solution with added mercaptide than observed for the other analogues in different solvents. As the slow hydrolysis progresses, the absorbance increases at all wavelengths.
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Nucleophilic Substitution Reactions of Pentafluorosulfur and Tetrafluoro(trifluoromethyl)sulfur Halides

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Abstract: Pentafluorosulfur halides [SF_5X (X = Cl, Br)] form R_2NSF_4X ($R = CH_3$) at −78 °C with $R_2NSi(CH_3)_3$, while CF_3SF_4Cl undergoes defluorination and reduction to $CF_3SCl(NR_2)_2$ ($R = CH_3$, C_2H_5) at 25 or −78 °C. The latter compounds are hydrolyzed slowly to $CF_3S(O)NR_2$ and are oxidized easily to $CF_3S(O)Cl(NR_2)_2$ with *m*-chloroperbenzoic acid. Stepwise defluorination reactions of SF_5X (X = Cl, Br) and CF_3SF_4Cl with the reactive nucleophile $LiN{=}C(CF_3)_2$ result in the formation of the stable compounds, $SF_3X[{=}NCF(CF_3)_2]$, $SFX[{=}NCF(CF_3)_2]_2$, $CF_3SF_2Cl[{=}NCF(CF_3)_2]$, and $CF_3SCl[{=}NCF(CF_3)_2]_2$. With CH_3NH_2, $CF_3SF_2Cl[{=}NCF(CF_3)_2]$ forms the sulfur dimide, $CF_3S({=}NCH_3)_2[N{=}C(CF_3)_2]$.

The failure of sulfur hexafluoride to react with nucleophilic reagents has been recognized as due to kinetic rather than thermodynamic factors. Thus the free energy of hydrolysis is favorable ($\Delta G^\circ > -48$ kcal mol^{-1}) although the compound is unaffected by boiling aqueous sodium hydroxide. Inertness is also displayed toward other nucleophiles such as the cyanide ion. This behavior contrasts sharply with the high reactivity toward nucleophiles which is shown by sulfur tetrafluoride in which the mean S–F bond energy (78 kcal mol^{-1}) is slightly higher than that in the hexafluoride. Fluorine exchange has also been observed in the tetrafluoride but not in the hexafluoride. The inertness of the sulfur (VI) compound is attributed to the fact that the highly symmetrical octahedral structure is coordinatively saturated and lacks a point of attack for nucleophiles unless conditions are provided which bring about extreme electronic rearrangement.

In contrast to the hexafluoride, pentafluorosulfur chloride and pentafluorosulfur bromide undergo hydrolysis with aqueous alkali and the bromide is also attacked by water. Other pentaflurosulfur derivatives of the type SF_5X ($X = CF_3$, SF_5, OSF_5, etc.) are not attacked by alkali, however, and the suggestion has been made that the primary attack by nucleophiles in the case of SF_5Cl and SF_5Br is on the positive halogen.[1]

Molecules such as SF_5CF_3, SF_5SF_5, and SF_5OSF_5 do not possess a well-defined positive center at which such attack can