

- (14) Confirmation that the crystals employed in the x-ray study were isomer A was afforded by examination of the ^{11}B NMR spectra of a solution of those crystals following data collection.
- (15) W. M. Maxwell, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 3490 (1976).
- (16) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976), and references therein.
- (17) (a) D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963); (b) L. Zakharkin, V. Kalinin, and L. S. Podvisotskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2310 (1967); (c) L. Zakharkin and V. Kalinin, *ibid.*, 194 (1969); (d) V. Stanko, Yu. V. Gol'tyapin, and V. Brattsev, *Zh. Obshch. Khim.*, **39**, 1175 (1969); (e) L. I. Zakharkin, V. N. Kalinin, B. A. Kvasov, and A. P. Synakin, *ibid.*, **41**, 1726 (1971).
- (18) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **13**, 1411 (1974).
- (19) F. Y. Lo, C. E. Strouse, K. P. Callahan, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **97**, 428 (1975).
- (20) E. I. Tolpin and W. N. Lipscomb, *Inorg. Chem.*, **12**, 2257 (1973).
- (21) (a) R. N. Grimes, *Ann. N.Y. Acad. Sci.*, **239**, 180 (1974); (b) R. N. Grimes, D. C. Beer, L. G. Sneddon, V. R. Miller, and R. Weiss, *Inorg. Chem.*, **13**, 1138 (1974).
- (22) H. Vahrenkamp, V. A. Uchtman, and L. F. Dahl, *J. Am. Chem. Soc.*, **90**, 3272 (1968).
- (23) A. Hock and O. S. Mills, "Advances in the Chemistry of Coordination Compounds", Macmillan, New York, N.Y., 1961, p 640.
- (24) (a) W. E. Carroll, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 2263 (1975); (b) M. Green, J. L. Spencer, F. G. A. Stone, and A. J. Welch, *ibid.*, 179 (1975); (c) A. J. Welch, *ibid.*, 1473 (1975); (d) A. J. Welch, *ibid.*, 2270 (1975); (e) M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *ibid.*, 2274 (1975); (f) M. Green, J. L. Spencer, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 794 (1974); (g) C. G. Salentine, C. E. Strouse, and M. F. Hawthorne, *Inorg. Chem.*, **15**, 1832 (1976); (h) distorted closo geometry has been postulated for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{C}_2\text{B}_3\text{H}_7$ (see ref 21b).
- (25) W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, N.Y., 1963.

Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Inorganic Derivatives of Iron-Sulfide-Thiolate Dimers and Tetramers. Structures of Tetrachloro- μ -disulfido-diferrate(III) and Tetrakis(chloro- μ_3 -sulfido-iron) Dianions

M. A. BOBRIK, KEITH O. HODGSON, and R. H. HOLM*

Received January 18, 1977

AIC700345

Reaction of benzoyl chloride with the complexes $[\text{Fe}_2\text{S}_2(\text{SR})_4]^{2-}$ and $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ affords $[\text{Fe}_2\text{S}_2\text{Cl}_4]^{2-}$ and $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$, respectively, which are members of a complete set of new dimeric and tetrameric inorganic dianions with terminal chloride, bromide, and iodide ligands. The structures of the tetraethylammonium salts of the chloride dimer and tetramer have been determined. Both compounds crystallize in space group $P2_1/c$ (C_{2h}^2) of the monoclinic system with dimensions $a = 8.842$ (2) Å, $b = 10.186$ (2) Å, $c = 15.985$ (3) Å, and $\beta = 109.28$ (2)° for the dimer salt ($Z = 2$) and $a = 13.600$ (7) Å, $b = 12.895$ (9) Å, $c = 18.707$ (5) Å, and $\beta = 110.29$ (3)° for the tetramer salt ($Z = 4$). Anion structures are nearly identical with those previously determined for their thiolate precursors. $[\text{Fe}_2\text{S}_2\text{Cl}_4]^{2-}$ has crystallographically imposed centrosymmetry and is formed by S...S edge sharing of two tetrahedra. The Fe...Fe and mean Fe-S and Fe-Cl distances are 2.716, 2.201, and 2.252 Å, respectively; bond angles at Fe vary from 103.8 to 112.7°. $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ exhibits cubane-type stereochemistry but is distorted from T_d to effective D_{2d} symmetry. The bonded Fe-S distances occur as sets of four (2.260 (3) Å) and eight (2.295 (3) Å), giving an average of 2.283 Å; the average Fe-Cl distance is 2.216 (2) Å. The Fe_4 unit is nearly tetrahedral with an average Fe...Fe distance of 2.766 (5) Å. These structures are compared with those of thiolate dimer and tetramer dianions, revealing that Fe_2S_2 and Fe_4S_4 core structures are nearly invariant to the nature of the terminal ligands. Dimer-tetramer structural comparisons in both the chloride and thiolate series show larger core distances and smaller terminal ligand distances in the tetramers; these differences are believed to arise mainly from electronic properties rather than from steric effects of terminal ligands.

Introduction

Our past and continuing investigations of iron-sulfur complexes of the general types $[\text{Fe}(\text{SR})_4]^{2-}$, $[\text{Fe}_2\text{S}_2(\text{SR})_4]^{2-}$, and $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ have emphasized their utility as synthetic analogues of the active sites of iron-sulfur proteins in equivalent oxidation levels.¹⁻⁵ Much of this work has recently been reviewed.^{1,2} In examinations of the reactivity properties of binuclear and tetranuclear dianions, certain results have proven and other observations have implied the existence of a substantial body of reaction chemistry involving substitution of terminal thiolate ligands with retention of planar Fe_2S_2 and cubane-type Fe_4S_4 core structures. The species $[\text{Fe}_2\text{S}_2(\text{SR})_4]^{2-}$ and $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ react cleanly with excess thiol $\text{R}'\text{SH}$ affording the correspondingly substituted complexes $[\text{Fe}_2\text{S}_2(\text{SR}')_4]^{2-}$ and $[\text{Fe}_4\text{S}_4(\text{SR}')_4]^{2-}$, respectively. Such reactions form the basis of the core extrusion method for identification of active sites in iron-sulfur proteins.⁸ A study of the tetrameric anion $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{CH}_2\text{CO}_2)_4]^{6-}$ in aqueous solution has shown the existence of solvolytic reactions and led to the preliminary kinetic order $\text{Cl}^- \sim \text{Br}^- < \text{OH}^- < \text{CN}^-$ for displacement of coordinated thiolate by other nucleophiles.⁹ Product species were not isolated. A final observation of pertinence is that reaction of $[\text{Fe}_4\text{S}_4(\text{SET})_4]^{2-}$ with benzoyl

chloride affords the thioester PhCOSEt ;¹⁰ the fate of the Fe_4S_4 portion of the reactant was not ascertained. This reaction displays the nucleophilic reactivity of coordinated thiolate, a property obligatory to the proposed mechanism of thiolate substitution by $\text{R}'\text{SH}$.¹¹ Analogy with this reaction suggested that the other reaction product from benzoyl chloride should be $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$. This point has been confirmed by product isolation.¹² In addition it has been shown that the dimeric complexes $[\text{Fe}_2\text{S}_2(\text{SR})_4]^{2-}$ undergo equally facile reactions with benzoyl halides. These reactions, together with halide substitution reactions, have led to isolation of a series of new, fundamental, and strictly inorganic anions of the types $[\text{Fe}_4\text{S}_4\text{X}_4]^{2-}$ and $[\text{Fe}_2\text{S}_2\text{X}_4]^{2-}$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$). The synthesis and properties of these complexes will be described elsewhere.¹² Here we detail the structures of the tetraethylammonium salts of $[\text{Fe}_2\text{S}_2\text{Cl}_4]^{2-}$ and $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ and compare these with the structures of their binuclear and tetranuclear thiolate precursors.

Experimental Section

Crystal Data for $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2\text{Cl}_4]$ and $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4\text{Cl}_4]$. Crystals of both compounds were obtained under anaerobic conditions. $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2\text{Cl}_4]$ was dissolved in a minimal volume of acetonitrile at room temperature and the solution was very slowly cooled to -15

Table I. Summary of Crystal Data, Intensity Collection, and Structure Solution and Refinement

	(Et ₄ N) ₂ [Fe ₄ S ₄ Cl ₄]	(Et ₄ N) ₂ [Fe ₂ S ₂ Cl ₄]
Formula	Fe ₄ S ₄ Cl ₄ N ₂ C ₁₆ H ₄₀	Fe ₂ S ₂ Cl ₄ N ₂ C ₁₆ H ₄₀
a, Å	13.600 (7)	8.842 (2)
b, Å	12.895 (9)	10.186 (2)
c, Å	18.707 (5)	15.985 (3)
β, deg	110.29 (3)	109.28 (2)
V, Å ³	3077	1359
Z	4	2
d _{calcd} (d _{obsd}), g/cm ³	1.63 (1.60) ^a	1.41 (1.40) ^b
Space group	P2 ₁ /c (C _{2h} ⁵)	P2 ₁ /c (C _{2h} ⁵)
Crystal dimensions, mm	0.50 × 0.35 × 0.25 ^c	0.30 × 0.25 × 0.20 ^d
Radiation ^e	Mo (λ(Kα) 0.710 69 Å)	
Absorption coeff, μ, cm ⁻¹	25.04 ^f	16.32 ^g
Takeoff angle, deg	3.0	3.0
Scan speed	1–29.3° min ⁻¹ (θ–2θ scan)	
Scan range, deg	0.6 below Kα ₁ to 0.6 above Kα ₂	
Background counts	Background/scan time = 0.25	
2θ limit, deg	45.0	55.0
Phasing technique	Direct methods	Heavy atom
Unique data	2425	1872
(F _o ² > 3σ(F _o ²))		
No. of variables	271	118
Error in observation weight, e	1.20	1.45
R, %	3.7	3.6
R _w , %	4.7	5.1

^a Determined by flotation in iodomethane/2-propanol. ^b Determined by flotation in 1,3-diodopropane/THF. ^c Prism. ^d Rhomb. ^e Monochromatized from mosaic graphite. ^f Absorption correction applied. ^g Absorption correction not applied.

^hC. (Et₄N)₂[Fe₄S₄Cl₄] was obtained by recrystallization from acetonitrile/2-propanol. The black air-sensitive crystals of both compounds were transferred under dinitrogen to thin-walled 0.3-mm glass capillaries which were then sealed. Diffraction studies of both crystals were carried out on a Syntex P2₁ four-circle diffractometer. The machine parameters are summarized in Table I. Fifteen machine-centered reflections whose 2θ values ranged from 4 to 20° were used in the least-squares refinement of the orientation matrix and lattice parameters for the two crystals. Axial photographs indicated that both crystals had 2/m diffraction symmetry and thus confirmed that they belong to the monoclinic system. The space group was established by inspection of intensities from the full data collections. ω scans of five low-angle reflections for each crystal (2θ < 7.5°) gave full widths at half-maximum of less than 0.3° in all cases

indicating mosaicity suitable for data collection.

Data Collection and Reduction. The parameters utilized in data collection are given in Table I. Throughout data collection standards were collected (110, 201, and 231 for the Fe₂S₂ compound and 011 and 112 for the Fe₄S₄ compound). In neither case was any significant variation in the intensities observed. The data sets were processed using the program ENXDR.¹³ The parameter *p*, introduced to avoid overweighting the strong reflections, was set to 0.05. Intensities and σ's were calculated according to the expressions

$$I = N_T - 2(N_{B1} + N_{B2})$$

$$\sigma(F_o)^2 = [N_T + J^2(N_{B1} + N_{B2}) + (pI)^2]^{1/2}/Lp$$

$$\sigma(F_o) = \sigma(F_o)^2/2F_o$$

where *N_T*, *N_{B1}*, and *N_{B2}* are the total peak and two background counts, *J* is the ratio of peak scan time to background scan times, and *Lp* is the Lorentz-polarization factor. The crystal of the Fe₄S₄ complex was very asymmetric and, because the absorption coefficient was fairly large (Table I), an absorption correction was applied using a Gaussian numerical integration program. The applied corrections to *F*² ranged from 1.47 to 1.92 with an average correction of 1.64. Because of the small size and regular shape of the crystal used for the Fe₂S₂ structure and the lower absorption coefficient, no correction was applied. In each case, the final data set was obtained by averaging data measured more than once and rejecting symmetry-extinct reflections.

Structure Solution and Refinement. The two structures were solved by conventional methods. The direct-methods program,¹³ MULTAN, based on 373 normalized structure factors, was used to produce 32 phase sets for the Fe₄S₄ compound. That set with an absolute figure of merit of 1.034 yielded trial positions for the four Fe, four S, and four Cl atoms. A Patterson function was used to locate the Fe atom in the Fe₂S₂ compound. Subsequent difference Fourier methods were used to locate the remaining atoms in each structure. The structures were refined by full-matrix least squares in which the function minimized was $\sum w(|F_o| - |F_c|)^2$ where *F_o* and *F_c* are the observed and calculated structure factors and *w* is the weighting factor given by $1/\sigma(F_o)^2$. Atomic scattering factors for neutral Fe, S, Cl, N, C, and H were taken from tabulated values.¹⁴ Corrections for anomalous dispersion effects for the nonhydrogen atoms including both Δ*f*' and Δ*f*" were included in the calculations. The final least-squares cycles included calculated fixed contributions from the H atoms, with their temperature factors set to 1 Å² greater than the value of the atom to which they are bonded. The unweighted and weighted agreement factors are given by $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$, respectively. The error in an observation of unit weight is given by $[w(|F_o| - |F_c|)^2 / (NO - NV)]^{1/2}$, where NO is the number of observations (reflections) and NV is the number of variables refined. The final *R* factors are given in Table I. For the Fe₄S₄ and Fe₂S₂ compounds the largest parameter shift in the final least-squares cycle was 0.38 and 0.14 times its esd, respectively. The highest peak

Table II. Positional and Thermal Parameters for (Et₄N)₂[Fe₂S₂Cl₄] and (Et₄N)₂[Fe₄S₄Cl₄] (Anions Only)

Atom	x	y	z	β ₁₁ ^a	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃
[Fe ₂ S ₂ Cl ₄] ²⁻									
Fe	0.107 98 (5) ^b	0.086 55 (5)	0.051 10 (3)	0.012 66 (6)	0.007 43 (4)	0.004 53 (2)	0.001 32 (9)	0.003 60 (5)	-0.000 17 (5)
Cl(1)	0.243 96 (12)	0.240 59 (10)	0.004 95 (7)	0.021 2 (1)	0.009 15 (9)	0.008 13 (5)	-0.002 9 (2)	0.012 3 (1)	-0.000 3 (1)
Cl(2)	0.187 25 (12)	0.107 82 (12)	0.199 85 (6)	0.019 0 (1)	0.017 48 (14)	0.004 68 (4)	0.001 5 (2)	0.004 2 (1)	-0.001 1 (1)
S	-0.152 48 (10)	0.111 31 (9)	-0.009 01 (6)	0.013 2 (1)	0.007 69 (8)	0.005 73 (4)	0.004 7 (2)	0.004 2 (1)	0.000 29 (9)
[Fe ₄ S ₄ Cl ₄] ²⁻									
Fe(1)	0.799 95 (8)	0.253 69 (7)	0.481 10 (5)	0.006 02 (7)	0.004 75 (5)	0.003 48 (3)	0.000 6 (1)	0.003 28 (7)	0.000 09 (7)
Fe(2)	0.737 10 (7)	0.448 86 (7)	0.419 38 (5)	0.005 87 (7)	0.004 81 (5)	0.002 99 (3)	0.000 0 (1)	0.003 08 (6)	0.000 18 (7)
Fe(3)	0.746 00 (8)	0.402 57 (7)	0.565 82 (5)	0.006 86 (7)	0.005 60 (6)	0.003 06 (3)	0.000 2 (1)	0.003 90 (7)	-0.000 25 (7)
Fe(4)	0.592 21 (7)	0.314 76 (7)	0.442 24 (5)	0.005 64 (7)	0.005 66 (6)	0.003 88 (3)	-0.000 9 (1)	0.003 37 (7)	0.000 31 (8)
Cl(1)	0.905 9 (2)	0.119 3 (1)	0.494 8 (1)	0.008 2 (2)	0.005 7 (1)	0.006 23 (7)	0.002 5 (2)	0.005 6 (2)	0.000 6 (2)
Cl(2)	0.743 8 (1)	0.573 3 (1)	0.339 6 (1)	0.009 6 (1)	0.006 2 (1)	0.003 86 (5)	-0.001 1 (2)	0.004 9 (1)	0.001 5 (1)
Cl(3)	0.799 0 (2)	0.457 1 (2)	0.685 9 (1)	0.010 8 (2)	0.008 7 (1)	0.003 39 (5)	0.000 3 (2)	0.005 1 (1)	-0.001 8 (1)
Cl(4)	0.427 0 (2)	0.265 9 (2)	0.386 0 (1)	0.006 1 (2)	0.010 1 (2)	0.006 01 (8)	-0.003 3 (2)	0.003 4 (2)	0.000 7 (2)
S(1)	0.615 8 (1)	0.486 0 (1)	0.475 5 (1)	0.006 7 (1)	0.005 4 (1)	0.004 27 (5)	0.002 1 (2)	0.004 7 (1)	0.000 5 (1)
S(2)	0.691 7 (1)	0.233 4 (1)	0.550 8 (1)	0.008 1 (1)	0.005 7 (1)	0.004 14 (5)	-0.000 5 (2)	0.005 2 (1)	0.001 9 (1)
S(3)	0.687 3 (1)	0.290 5 (1)	0.362 5 (1)	0.006 9 (1)	0.005 5 (1)	0.003 18 (5)	-0.000 8 (2)	0.002 6 (1)	-0.001 3 (1)
S(4)	0.882 0 (1)	0.409 8 (1)	0.519 5 (1)	0.005 8 (1)	0.005 8 (1)	0.003 20 (5)	-0.000 7 (2)	0.003 0 (1)	-0.000 2 (1)

^a The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^b Estimated standard deviations are given in parentheses in this and succeeding tables.

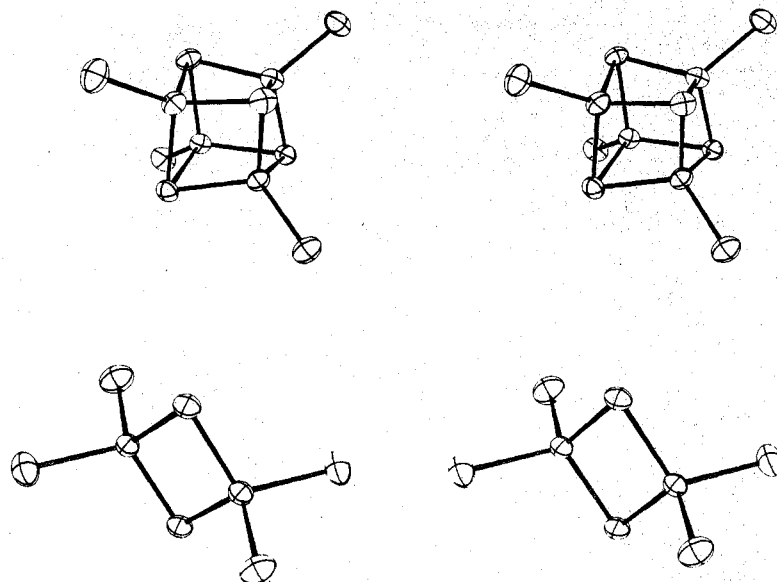


Figure 1. Stereoviews of $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ (top) and $[\text{Fe}_2\text{S}_2\text{Cl}_4]^{2-}$ (bottom). In each view the 30% probability ellipsoids of thermal vibration are shown.

Table III. Bond Distances (Å) and Angles (deg) for $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2\text{Cl}_4]$

Distances			
Fe...Fe' ^a	2.716 (1)	N-C(3)	1.511 (4)
Fe-S	2.199 (1)	N-C(4)	1.513 (4)
Fe-S'	2.202 (1)	C(1)-C(5)	1.505 (4)
Fe-Cl(1)	2.245 (1)	C(2)-C(6)	1.514 (4)
Fe-Cl(2)	2.258 (1)	C(3)-C(7)	1.551 (5)
N-C(1)	1.525 (4)	C(4)-C(8)	1.448 (5)
N-C(2)	1.555 (3)		

Angles			
S-Fe-S'	103.79 (3)	C(1)-N-C(4)	111.9 (2)
S-Fe-Cl(1)	111.92 (4)	C(2)-N-C(3)	112.4 (2)
S-Fe-Cl(2)	111.52 (4)	C(2)-N-C(4)	107.8 (2)
S'-Fe-Cl(1)	111.79 (4)	C(3)-N-C(4)	108.9 (2)
S'-Fe-Cl(2)	112.65 (4)	N-C(1)-C(5)	114.1 (2)
Cl(1)-Fe-Cl(2)	105.37 (4)	N-C(2)-C(6)	113.3 (2)
Fe-S-Fe'	76.21 (3)	N-C(3)-C(7)	114.1 (3)
C(1)-N-C(2)	106.9 (2)	N-C(4)-C(8)	115.7 (3)
C(1)-N-C(3)	109.1 (2)		

^a Primed atoms are related to the corresponding unprimed atoms by the center of symmetry within the anion.

in the final difference Fourier map of either compound was ca. 0.12 of the height of a C atom peak.

Listed in Table II are thermal and positional parameters of $[\text{Fe}_2\text{S}_2\text{Cl}_4]^{2-}$ and $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$. Bond distances and angles are given in Tables III and IV, and best weighted least-squares planes of the anions are set out in Tables V and VI. Root-mean-square amplitudes of thermal vibration are presented in Table VII, and comparisons of average bond distances and angles are contained in Table VIII. Given in Table IX are positional and thermal parameters of the cations of both compounds, and calculated hydrogen atom positions are available in Table X.¹⁵ Table XI lists values of $10|F_o|$ and $10|F_c|$ for both compounds.¹⁵ General temperature factor expressions are tabulated in Table XII.¹⁵

Results and Discussion

The structures of $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2\text{Cl}_4]$ and $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4\text{Cl}_4]$ consist of discrete cations and anions. Both compounds crystallize in the monoclinic space group $P2_1/c$ (C_{2h}^5). Crystal data are summarized in Table I. Metrical data for the tetraethylammonium ions are contained in Tables III and IV; other crystallographic cation information is tabulated elsewhere.¹⁵ The cations exhibit tetrahedral geometry and unexceptional distances and ethyl group conformations. There was no evidence of cation disorder in either structure. Further

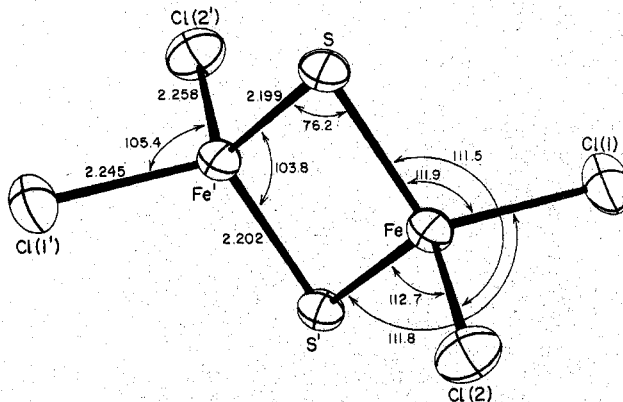


Figure 2. Structure of the centrosymmetric $[\text{Fe}_2\text{S}_2\text{Cl}_4]^{2-}$ anion, including the atom-labeling scheme, selected bond distances and angles, and 30% probability ellipsoids of thermal vibration.

discussion deals with anion structures only. Stereoviews of both anions are shown in Figure 1.

$(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2\text{Cl}_4]$. The atom-labeling scheme and values of bond distances and angles for $[\text{Fe}_2\text{S}_2\text{Cl}_4]^{2-}$ are given in Figure 2. Individual bond angles and distances are listed in Table III and best weighted least-squares planes are specified in Table V. In this structure the closest approach between anion and cation¹⁵ atoms is $\text{Cl}(2)\cdots\text{H}(1)$ (2.87 Å); all anion-anion distances exceed 4.0 Å. There are two cations and one anion per two asymmetric units, and thus the anion possesses crystallographically imposed centrosymmetry. As for the two dianions⁶ bis[*o*-xylyl- α,α' -dithiolato- μ -sulfido-ferrate(III)], $[\text{Fe}_2\text{S}_2(\text{S}_2\text{-}o\text{-xy})]^{2-}$ (1), and bis[*p*-tolyl- μ -

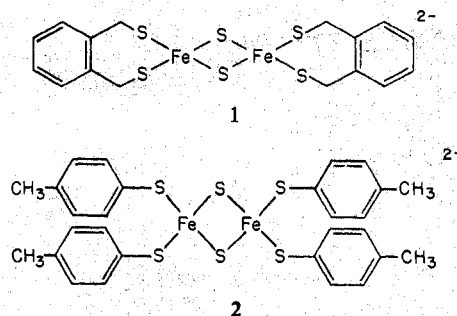


Table IV. Bond Distances (Å) and Angles (deg) for $(Et_4N)_2[Fe_4S_4Cl_4]$

Fe-Cl		Fe...S		S-Fe-S		Fe-Fe-Fe	
Fe(1)-Cl(1)	2.211 (2)	Fe(1)-S(1)	3.882 (2)	S(2)-Fe(1)-S(3)	103.4 (1)	Fe(2)-Fe(1)-Fe(4)	59.70 (3)
Fe(2)-Cl(2)	2.215 (2)	Fe(2)-S(2)	3.898 (2)	S(2)-Fe(1)-S(4)	105.1 (1)	Fe(1)-Fe(2)-Fe(3)	59.41 (3)
Fe(3)-Cl(3)	2.222 (2)	Fe(3)-S(3)	3.884 (2)	S(3)-Fe(1)-S(4)	102.3 (1)	Fe(2)-Fe(3)-Fe(4)	59.98 (3)
Fe(4)-Cl(4)	2.216 (2)	Fe(4)-S(4)	3.895 (2)	S(1)-Fe(2)-S(3)	104.8 (1)	Fe(1)-Fe(4)-Fe(3)	59.42 (3)
Mean	2.216 (2) ^a	Mean	3.890 (4)	S(1)-Fe(2)-S(4)	103.1 (1)	Mean	59.63
Fe-S		Fe...Fe		S(3)-Fe(2)-S(4)		Fe(2)-Fe(1)-Fe(3)	
Fe(1)-S(3)	2.266 (2)	Fe(1)-Fe(3)	2.746 (1)	S(1)-Fe(3)-S(2)	103.1 (1)	Fe(3)-Fe(1)-Fe(4)	
Fe(2)-S(4)	2.254 (2)	Fe(2)-Fe(4)	2.764 (1)	S(1)-Fe(3)-S(4)	102.9 (1)	Fe(1)-Fe(2)-Fe(4)	
Fe(3)-S(1)	2.252 (2)	Mean	2.755	S(2)-Fe(3)-S(4)	105.1 (1)	Fe(3)-Fe(2)-Fe(4)	
Fe(4)-S(2)	2.269 (2)	Fe(1)-Fe(2)	2.777 (1)	S(1)-Fe(4)-S(2)	102.7 (1)	Fe(1)-Fe(3)-Fe(2)	
Mean	2.260 (3)	Fe(1)-Fe(4)	2.776 (1)	S(1)-Fe(4)-S(3)	104.4 (1)	Fe(1)-Fe(3)-Fe(4)	
Fe(1)-S(2)	2.295 (2)	Fe(2)-Fe(3)	2.765 (1)	S(2)-Fe(4)-S(3)	102.8 (1)	Fe(1)-Fe(4)-Fe(2)	
Fe(1)-S(4)	2.293 (2)	Fe(3)-Fe(4)	2.765 (1)	Mean	103.5	Fe(2)-Fe(4)-Fe(3)	
Fe(2)-S(1)	2.291 (2)	Mean	2.771 (3)	S-Fe-Cl		Mean	
Fe(2)-S(3)	2.294 (2)	Mean (of 6)	2.766 (5)	S(2)-Fe(1)-Cl(1)	111.4 (1)	Mean (of 12)	
Fe(3)-S(2)	2.289 (2)			S(3)-Fe(1)-Cl(1)	118.0 (1)	S-S-S	
Fe(3)-S(4)	2.300 (2)			S(4)-Fe(1)-Cl(1)	115.2 (1)	S(2)-S(1)-S(4)	
Fe(4)-S(1)	2.286 (2)	N-C		S(1)-Fe(2)-Cl(2)	111.2 (1)	S(1)-S(2)-S(3)	
Fe(4)-S(3)	2.309 (2)	N(1)-C(11)		S(3)-Fe(2)-Cl(2)	114.0 (1)	S(2)-S(3)-S(4)	
Mean	2.295 (3)	N(1)-C(12)		S(4)-Fe(2)-Cl(2)	119.6 (1)	S(1)-S(4)-S(3)	
S...S		N(1)-C(13)		S(1)-Fe(3)-Cl(3)	120.2 (1)	Mean	
S(1)-S(3)	3.632 (2)	N(1)-C(14)		S(2)-Fe(3)-Cl(3)	113.8 (1)	S(2)-S(1)-S(3)	
S(2)-S(4)	3.642 (2)	N(2)-C(21)		S(4)-Fe(3)-Cl(3)	110.3 (1)	S(3)-S(1)-S(4)	
Mean	3.637	N(2)-C(22)		S(1)-Fe(4)-Cl(4)	115.3 (1)	S(1)-S(2)-S(4)	
S(1)-S(2)	3.557 (2)	N(2)-C(23)		S(2)-Fe(4)-Cl(4)	119.0 (1)	S(3)-S(2)-S(4)	
S(1)-S(4)	3.560 (3)	N(2)-C(24)		S(3)-Fe(4)-Cl(4)	110.9 (1)	S(1)-S(3)-S(2)	
S(2)-S(3)	3.579 (2)	Mean		Mean	114.9	S(1)-S(3)-S(4)	
S(2)-S(4)	3.550 (2)			C-N-C		S(1)-S(4)-S(2)	
Mean	3.562 (6)			C(11)-N(1)-C(12)		S(2)-S(4)-S(3)	
Fe-S-Fe		C-C		C(11)-N(1)-C(13)		Mean	
Fe(2)-S(1)-Fe(3)	74.96 (6)	C(11)-C(15)		C(11)-N(1)-C(14)		C-C-N	
Fe(2)-S(1)-Fe(4)	74.28 (6)	C(12)-C(16)		C(12)-N(1)-C(13)		C(15)-C(11)-N(1)	
Fe(3)-S(1)-Fe(4)	75.07 (6)	C(13)-C(17)		C(12)-N(1)-C(14)		C(16)-C(12)-N(1)	
Fe(1)-S(2)-Fe(3)	73.61 (6)	C(14)-C(18)		C(13)-N(1)-C(14)		C(17)-C(13)-N(1)	
Fe(1)-S(2)-Fe(4)	74.91 (6)	C(21)-C(25)		C(21)-N(2)-C(22)		C(18)-C(14)-N(1)	
Fe(3)-S(2)-Fe(4)	74.70 (5)	C(22)-C(26)		C(21)-N(2)-C(23)		C(25)-C(21)-N(2)	
Fe(1)-S(3)-Fe(2)	75.04 (5)	C(23)-C(27)		C(21)-N(2)-C(24)		C(26)-C(22)-N(2)	
Fe(1)-S(3)-Fe(4)	74.69 (6)	C(24)-C(28)		C(22)-N(2)-C(23)		C(27)-C(23)-N(2)	
Fe(2)-S(3)-Fe(4)	73.80 (5)	Mean		C(22)-N(2)-C(24)		C(28)-C(24)-N(2)	
Fe(1)-S(4)-Fe(2)	75.29 (6)			C(23)-N(2)-C(24)		Mean	
Fe(1)-S(4)-Fe(3)	73.45 (6)			Mean		115.2 (7)	
Fe(2)-S(4)-Fe(3)	74.75 (6)					115.4	
Mean	74.55						

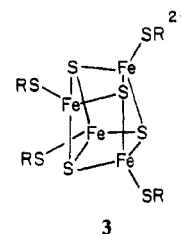
^a If given, the value in parentheses is the standard deviation as estimated from the variance among the averaged values. The estimated standard deviation of the mean is not given for any angular quantity, as the variations exceed those expected from a sample taken from the same population.

sulfido-ferrate(III)], $[Fe_2S_2(S-p\text{-tol})_4]^{2-}$ (**2**), the dimeric structure occurs by means of S...S edge sharing of two distorted tetrahedra. The Fe-S-Fe angle of $[Fe_2S_2Cl_4]^{2-}$ is expanded from the idealized value of 70.5° for the interior bridge angle of two perfect tetrahedra sharing a common edge.¹⁶ The dihedral angle between the Fe_2S_2 and Fe_2Cl_4 planes is 89.5° and the independent Fe-S distances are the same within experimental error. Departure of stereochemistry at the Fe sites from idealized T_d symmetry is evident from bond angle values, which vary from 103.8 (S-Fe-S') to 112.7° (S'-Fe-Cl(2)). The Cl(1)-Fe-Cl(2) angle is 105.4°. The small difference (0.013 Å) in the two Fe-Cl distances degrades the Fe site symmetry to rhombic and reduces the overall anion symmetry from D_{2h} to C_{2h} . Weak van der Waals interactions among the two chlorine atoms and nearby hydrogen atoms of the cations may be responsible for the marginally unequal Fe-Cl distances and the value of the Cl-Fe-Cl angle, which is less than terminal ligand S-Fe-S angles in $[Fe_2S_2(S_2\text{-oxyl})_2]^{2-}$ (106.4°⁶) and $[Fe_2S_2(S-p\text{-tol})_4]^{2-}$ (111.2°).⁶ Adjacent to each chlorine atom are two such H atoms, which are located at distances slightly less than the sum of van der Waals radii (3.0 Å¹⁷).

$(Et_4N)_2[Fe_4S_4Cl_4]$. The atom-labeling scheme and Fe-S and Fe-Cl distances for $[Fe_4S_4Cl_4]^{2-}$ are set out in Figure 3. Bond

angles and important internuclear distances are available in Table IV and best weighted least-squares planes are given in Table VI. The closest approach between anion and cation¹⁵ atoms is H(31)...Cl(3) (2.84 Å) and that between anion atoms is S(1)...S(1) (3.59 Å).

It is evident from Figures 1 and 3 that $[Fe_4S_4Cl_4]^{2-}$ exhibits the overall cubane-type stereochemistry found for the dianions $[Fe_4S_4(SR)_4]^{2-}$ (**3**, R = CH_2Ph ,¹⁸ Ph^7) and for a host of other



tetranuclear species as well.¹⁹ As with the Fe_4S_4 cores of the complexes **3**, the core of $[Fe_4S_4Cl_4]^{2-}$ departs from idealized cubic (T_d) symmetry toward the point group $D_{2d}\bar{4}2m$ where the (noncrystallographically imposed) 4 axis passes through the top and bottom faces of the polyhedron in Figure 3. In view of previous detailed discussions of the structures of type

Table V. Best Weighted Least-Squares Planes^a for $[\text{Fe}_2\text{S}_2\text{Cl}_4]^{2-}$

Plane no.	$Ax + By + Cz - D = 0$				Atoms	Dev from plane, A
	A	B	C	D		
1	0.4234	0.3872	-0.8190	0.0000	Fe, Fe' S, S'	0.000 (0) -0.000 (1)
2	-0.7499	0.6558	-0.0874	0.0000	Cl(1) Fe Cl(1), Cl(2) S	1.791 (1) -0.003 (0) 0.004 (1) 1.732 (1)

Dihedral Angle between Planes 1 and 2: 89.5°

^a Orthogonalized coordinates.Table VI. Best Weighted Least-Squares Planes^a for $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$

Plane no.	$Ax + By + Cz - D = 0$															
	A	B	C	D												
1	-0.4630	-0.4132	-0.7842	-11.5527												
2	-0.1655	0.9073	-0.3865	-0.1870												
3	0.2993	0.2075	-0.9313	-4.8465												
4	-0.9285	0.2803	-0.2437	-6.9631												
5	0.7723	0.6171	-0.1510	6.7213												
6	0.4745	-0.6900	-0.5466	-4.5642												
7	0.8716	-0.0506	-0.4876	2.5550												
8	-0.4387	0.3483	-0.8284	-9.3112												
9	-0.2131	-0.9374	-0.2756	-6.9788												
10	-0.2057	-0.9371	-0.2821	-9.0667												
11	-0.4422	0.3540	-0.8241	-7.1934												
12	0.8695	-0.0512	-0.4913	0.4192												

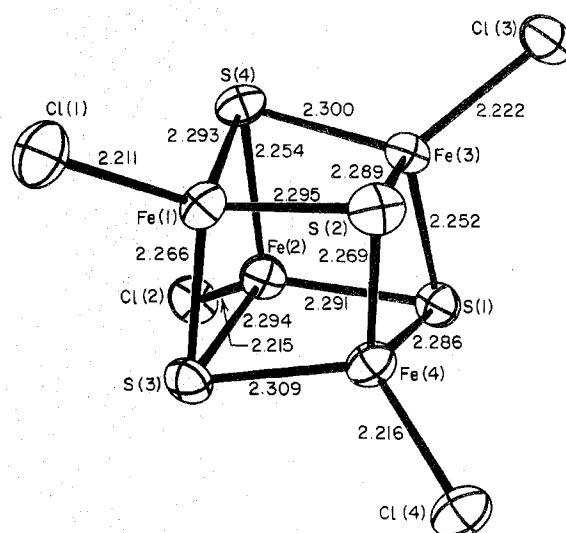
Deviations (A) from plane no.

Atom	1	2	3	4	5 ^b	6 ^c	7	8	9	10	11	12
Fe(1)	-0.010 (1)		-0.014 (1)	0.011 (1)	0.014 (1)	0.013 (1)	-0.075 (1)	0.055 (1)	-0.067 (1)	0.065 (1)	-0.051 (1)	0.067 (1)
Fe(2)	0.009 (1)			-0.012 (1)	-0.017 (1)	-0.018 (1)	-0.070 (1)	0.055 (1)	-0.069 (1)	0.070 (1)	-0.057 (1)	0.069 (1)
Fe(3)		-0.012 (1)	0.014 (1)									
Fe(4)		0.012 (1)	-0.039 (2)									
S(1)	-0.028 (2)			0.036 (2)	-0.028 (2)	-0.027 (2)		-0.205 (2)	0.251 (2)	-0.248 (2)	0.197 (2)	-0.239 (2)
S(2)	0.030 (2)			-0.032 (2)	0.032 (2)	0.028 (2)	0.251 (2)	-0.182 (2)	0.224 (2)	-0.230 (2)	0.184 (2)	-0.249 (2)
S(3)		-0.031 (2)	0.036 (2)									
S(4)		0.031 (2)										

^a Orthogonalized coordinates. ^b Cl(1), -0.048 (2); Cl(3), 0.053 (2). ^c Cl(2), -0.040 (2); Cl(4), 0.064 (2).

Table VII. Root-Mean-Square Amplitudes of Thermal Vibration (Å)

$(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4\text{Cl}_4]$				$(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2\text{Cl}_4]$			
Atom	Min	Inter-med	Max	Atom	Min	Inter-med	Max
Fe(1)	0.198	0.223	0.233	Fe	0.195	0.211	0.239
Fe(2)	0.201	0.214	0.220	S	0.181	0.231	0.265
Fe(3)	0.207	0.219	0.239	Cl(1)	0.215	0.256	0.311
Fe(4)	0.205	0.225	0.248	Cl(2)	0.230	0.267	0.306
S(1)	0.199	0.235	0.261	N	0.188	0.208	0.244
S(2)	0.197	0.251	0.269	C(1)	0.204	0.232	0.242
S(3)	0.200	0.235	0.246	C(2)	0.183	0.232	0.261
S(4)	0.213	0.223	0.227	C(3)	0.199	0.225	0.306
Cl(1)	0.208	0.264	0.312	C(4)	0.196	0.238	0.300
Cl(2)	0.207	0.256	0.282	C(5)	0.226	0.245	0.295
Cl(3)	0.212	0.279	0.299	C(6)	0.210	0.279	0.288
Cl(4)	0.212	0.291	0.322	C(7)	0.208	0.267	0.418
N(1)	0.166	0.215	0.240	C(8)	0.219	0.271	0.338
C(11)	0.201	0.220	0.260				
C(12)	0.126	0.262	0.275				
C(13)	0.202	0.218	0.269				
C(14)	0.188	0.252	0.257				
C(15)	0.207	0.273	0.308				
C(16)	0.190	0.310	0.384				
C(17)	0.228	0.281	0.313				
C(18)	0.217	0.262	0.326				
N(2)	0.186	0.205	0.225				
C(21)	0.239	0.245	0.271				
C(22)	0.198	0.289	0.294				
C(23)	0.204	0.248	0.338				
C(24)	0.207	0.255	0.294				
C(25)	0.237	0.258	0.381				
C(26)	0.245	0.307	0.330				
C(27)	0.227	0.296	0.337				
C(28)	0.253	0.260	0.473				

Figure 3. Structure of the cubane-type anion $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$, including the atom-labeling scheme, selected bond distances, and 30% probability ellipsoids of thermal vibration.

the Fe_4 portion of the core is essentially tetrahedral.

Structural Comparisons with Thiolate Complexes. Comparison of mean values of selected structural parameters of $[\text{Fe}_2\text{S}_2\text{Cl}_4]^{2-}$ with **1** and **2** and of $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ with two type **3** complexes are given in Table VIII. In reactions with benzoyl chloride these thiolate complexes serve as precursors to the corresponding chloride dimer or tetramer, which are formed in nearly quantitative yield.¹² The single most important observation is that mean dimensions of $\text{Fe}_2\text{S}_2^{2+}$ and $\text{Fe}_4\text{S}_4^{2+}$ cores are nearly independent of the nature of the terminal ligands. This finding reinforces the earlier point,⁶ made on the basis of structures **1**–**3** only, that cores are integral substructural units which in the indicated oxidation levels may be transferred intact from one ligand environment to another,^{6,7,21} including those in proteins,⁸ with no important structural changes.² The two equal Fe–S core distances in $[\text{Fe}_2\text{S}_2(\text{S}-p\text{-tol})_4]^{2-}$ and $[\text{Fe}_2\text{S}_2\text{Cl}_4]^{2-}$ suggest that two such unequal distances, as found in $[\text{Fe}_2\text{S}_2(\text{S}_2\text{-}o\text{-}xy)_2]^{2-}$ (2.185, 2.232 Å), are not likely to be of frequent occurrence. The consistent D_{2d} core symmetry of $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]^{2-}$,¹⁸ $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$,⁷ and $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$, which can be recognized by the same 2 + 4 division of S··S distances in each case, leaves little doubt that this type of distortion from cubic

3 complexes,^{7,18,20} present considerations are restricted to a brief enumeration of the more important structural features: (i) each face of the Fe_4S_4 core is a rhomb (mean S–Fe–S and Fe–S–Fe angles 103.5 and 74.55°, respectively) which is distinctly nonplanar (Table VI, planes 7–12); (ii) none of the planes 1–6 passing through the core is perfect within experimental error; (iii) core distances and angles under D_{2d} symmetry divide into the sets Fe–Fe, S··S (2 + 4), Fe–S (4 + 8) and Fe–Fe–Fe, S–S–S, S–Fe–S, Fe–S–Fe (4 + 8), with differences in all parameters but the last two types of angles resolvable; (iv) the S_4 portion of the core deviates markedly from tetrahedral symmetry, the two S··S distances (mean 3.637 Å) perpendicular to the $\bar{4}$ axis being longer than the four distances (mean 3.562 Å) in the faces parallel to this axis; (v)

Table VIII. Comparison of Average Bond Distances (Å) and Angles (deg) for $[\text{Fe}_2\text{S}_2^*(\text{SR})_4]^{2-}$ – $[\text{Fe}_2\text{S}_2^*\text{Cl}_4]^{2-}$ and $[\text{Fe}_4\text{S}_4^*(\text{SR})_4]^{2-}$ – $[\text{Fe}_4\text{S}_4^*\text{Cl}_4]^{2-}$

Distance or angle	$[\text{Fe}_2\text{S}_2^*(\text{S}_2\text{-}o\text{-}xy)_2]^{2- a}$	$[\text{Fe}_2\text{S}_2^*(\text{S}-p\text{-tol})_4]^{2- a}$	$[\text{Fe}_2\text{S}_2^*\text{Cl}_4]^{2- b}$
Fe··Fe ^c	2.698	2.691	2.716
Fe–S*	2.209	2.201	2.201
Fe–X ^d	2.305	2.312	2.252
S··S	3.498	3.483	3.463
S*–Fe–S*	104.7	104.6	103.8
Fe–S*–Fe ^e	75.3	75.4	76.2
X(1)–Fe–X(2) ^d	106.4	111.2	105.4
Distance or angle	$[\text{Fe}_4\text{S}_4^*(\text{SCH}_2\text{Ph})_4]^{2- e}$	$[\text{Fe}_4\text{S}_4^*(\text{SPh})_4]^{2- f}$	$[\text{Fe}_4\text{S}_4^*\text{Cl}_4]^{2- b}$
Fe··Fe ⁱ	2.776 (2), ^g 2.732 (4)	2.730 (2), 2.739 (4)	2.755 (2), 2.766 (4)
Fe–S* ^h	2.239 (4), 2.310 (8)	2.267 (4), 2.296 (8)	2.260 (4), 2.295 (8)
Fe–X ^d	2.251	2.263	2.216
X–Fe–S* ^d	115.1	114.4	114.9
Fe–S*–Fe	73.8	73.5	74.6
S*–Fe–S*	104.1	104.3	103.5
Fe–Fe–Fe ^j	61.11 (4), 59.46 (8)	59.79 (4), 60.11 (8)	59.63 (4), 60.19 (8)

^a Et_4N^+ salt; data from ref 6. ^b Et_4N^+ salt; this work. ^c Atoms related by symmetry center labeled with primes. ^d Terminal ligand denoted by X. ^e Et_4N^+ salt; data from ref 18. ^f Me_4N^+ salt; data from ref 7. ^g Figures in parentheses are the numbers of values averaged where two distances or angles are given. ^{h–j} Mean of all values: (h) 2.286 (CH₂Ph, Ph), 2.283 (Cl); (i) 2.747 (CH₂Ph), 2.736 (Ph), 2.762 (Cl); (j) 60.01 (CH₂Ph), 59.99 (Ph), 60.00 (Cl).

symmetry is an inherent electronic property of the $\text{Fe}_4\text{S}_4^{2+}$ core. Results of SCF- $X\alpha$ -SW calculations indicate that, at least for the dianions 3, distortions from idealized T_d symmetry may arise from the Jahn-Teller effect.²² The qualitative symmetry-factored MO model described by Gall et al.²³ also admits the possibility of ground-state Jahn-Teller distortions. Of the two structures of type 3 complexes $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ is more nearly similar to $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ inasmuch as both have near-tetrahedral Fe_4 arrangements.

An obvious corollary to the structural similarities of Table VIII is a similarity of properties which are not strongly dependent on the identity of the terminal ligands. While this matter will be explored elsewhere,¹² it is of interest to point out here that both electronic spectra and redox potentials show a large ligand dependence, including variations in halide, whereas magnetic susceptibilities obtained from 4.2 to 330 K are much less ligand dependent. Both dimers and tetramers possess Fe...Fe distances sufficiently short to afford stabilizing interactions and one pathway for spin coupling between or among Fe sites. $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ and $[\text{Fe}_2\text{S}_2\text{Cl}_4]^{2-}$ act as intramolecular antiferromagnetically coupled species, similar to the behavior of their thiolate precursors.^{3,24,25} Thus for $[\text{Fe}_2\text{S}_2(\text{S}_2\text{-}o\text{-xyl})_2]^{2-}$ and $[\text{Fe}_2\text{S}_2\text{Cl}_4]^{2-}$ $-J$ is 148^3 and 158^{12} cm^{-1} , respectively.

Dimer-Tetramer Comparisons. In making metrical dimer-tetramer comparisons for thiolate and chloride complexes two features are emphasized. First, formal Fe oxidation states differ, being +3 in dimers and +2.5 in electronically delocalized tetramers.²⁶ Recent determinations of distances in the Fe(II) complexes $[\text{FeCl}_4]^{2-}$ (2.292 (2) \AA^{27}), $[\text{Fe}(\text{S}_2\text{-}o\text{-xyl})_2]^{2-}$ (2.356 (13) \AA^4), and $[\text{Fe}(\text{SPh})_4]^{2-}$ (2.355 \AA^{28}) and in the Fe(III) complexes $[\text{FeCl}_4]^-$ (2.185 (2),²⁹ 2.182 (1) \AA^{30}) and $[\text{Fe}(\text{S}_2\text{-}o\text{-xyl})_2]^-$ (2.267 (3) \AA^4), where oxidation states are well defined, leads to the prediction that directly bonded distances in tetramers should exceed corresponding distances in dimers. This order holds for core Fe-S distances but is reversed for terminal Fe-X distances (X = Cl, SR; Table VIII), a matter for which we have no satisfactory explanation. The second feature emphasized is the planar structures of dimer Fe_2S_2 cores as compared with the nonplanar structures of rhomboid Fe_2S_2 faces of Fe_4S_4 cores. Because of D_{2d} symmetry, faces approximately parallel and perpendicular to the tetramer 4 axis are not exactly equidimensional. Nonetheless there exists a clear dimensional similarity between dimer cores and tetramer faces. Corresponding distances and angles for $[\text{Fe}_2\text{S}_2\text{Cl}_4]^{2-}$ and $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ (Tables III and IV) do not differ by more than 0.11 \AA and 2.8° , respectively. Comparable differences exist in the thiolate series, for which it was observed⁶ that the electrochemical reaction sequence^{6,31} $[\text{Fe}_2\text{S}_2(\text{SR})_4]^{2-} \rightarrow [\text{Fe}_2\text{S}_2(\text{SR})_4]^{3-} \rightarrow [\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ is presumably facilitated by the dimer core-tetramer face structural similarity. The corresponding overall conversion $[\text{Fe}_2\text{S}_2\text{Cl}_4]^{2-} \rightarrow [\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ occurs upon electrochemical reduction and will be described elsewhere.¹²

In passing from a dimer to a tetramer in both the thiolate and chloride series core dimensions (Fe-S, Fe...Fe, S...S distances) generally increase while terminal Fe-X distances decrease. It has been recently observed that these same trends hold in structural comparison of the pair $\text{Ag}_2\text{Br}_2(\text{PPh}_3)_4/\text{Ag}_4\text{Br}_4(\text{PPh}_3)_4$,³² in which both species contain Ag(I). The latter, as its chloride¹⁹ and one modification of its iodide³³ analogue, has cubane-type stereochemistry with nonbonding Ag...Ag distances. It was contended on reasonable grounds,³² more recently amplified,¹⁹ that the observed structural trends were not due to electronic factors but to inter- and intramolecular steric effects brought about by the bulky triphenylphosphine ligands. The argument was extended to $[\text{Fe}_2\text{S}_2(\text{SR})_4]^{2-}/[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ pairs, implying that the di-

mensional differences were caused by steric interactions of terminal ligands in the complexes thus far studied and that the Fe atoms in both species are in "probably very similar" oxidation states.³² The present work clearly demonstrates that for $[\text{Fe}_2\text{S}_2\text{Cl}_4]^{2-}$ and $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$, in which steric influences are minimized by the presence of the smallest terminal ligand yet introduced synthetically,¹² the same pattern of structural variation is observed. The similarities in geometric behavior of the silver and iron cluster complexes are apparently fortuitous; the core expansion and terminal bond contraction evident in going from dimeric to tetrameric iron dianions arise predominantly from electronic effects. Last, while not desiring to initiate unproductive discussion of the metal oxidation state in delocalized tetramer dianions or the similarity of oxidation states in dimer and tetramer dianions, we do observe that at near-parity of terminal ligands, the ⁵⁷Fe isomer shifts (mm/s relative to Fe metal, 4.2 or 77 K) increase in the order $[\text{Fe}(\text{S}_2\text{-}o\text{-xyl})_2]^- (+0.13^4) < [\text{Fe}_2\text{S}_2(\text{S}_2\text{-}o\text{-xyl})_2]^{2-} (+0.17^3) < [\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]^{2-} (+0.34^{34}) < [\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]^{3-} (+0.48^5) < [\text{Fe}(\text{S}_2\text{-}o\text{-xyl})_2]^{2-} (+0.61^4)$. The similar series $[\text{Fe}_2\text{S}_2(\text{SPh})_4]^{2-} < [\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-} < [\text{Fe}_4\text{S}_4(\text{SPh})_4]^{3-} < [\text{Fe}(\text{SPh})_4]^{2-}$ holds for benzenethiolate complexes.^{3,5,34,35} Thus at least total s-electron density at the nucleus is different in dimer and tetramer dianions and isomer shifts change monotonically with formal oxidation state in a manner fully consistent with the results for various Fe-S phases containing integral and fractional metal oxidation states.³⁶

Acknowledgment. This research was supported by National Institutes of Health Grant GM-22352. K.O.H. is an Alfred P. Sloan Foundation Fellow. We thank T. K. Eccles for technical assistance.

Registry No. $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2\text{Cl}_4]$, 62682-81-9; $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4\text{Cl}_4]$, 62758-02-5.

Supplementary Material Available: Tables IX-XII, showing positional and thermal parameters of the cations in $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2\text{Cl}_4]$ and $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4\text{Cl}_4]$, calculated hydrogen atom positions for both compounds, listings of $10|F_o|$ and $10|F_c|$ for both compounds, and general temperature factors (U_{ij} 's) for both compounds (27 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) R. H. Holm, *Endeavour*, **34**, 38 (1975).
- (2) R. H. Holm and J. A. Ibers in "Iron-Sulfur Proteins", Vol. III, W. Lovenberg, Ed., Academic Press, New York, N.Y., 1977; Chapter 7.
- (3) W. O. Gillum, R. B. Frankel, S. Foner, and R. H. Holm, *Inorg. Chem.*, **15**, 1095 (1976).
- (4) R. W. Lane, J. A. Ibers, R. B. Frankel, G. C. Papaefthymiou, and R. H. Holm, *J. Am. Chem. Soc.*, **99**, 84 (1977).
- (5) R. W. Lane, A. G. Wedd, W. O. Gillum, E. J. Laskowski, R. H. Holm, R. B. Frankel, and G. C. Papaefthymiou, *J. Am. Chem. Soc.*, **99**, 2350 (1977).
- (6) J. J. Mayerle, S. E. Denmark, B. V. DePamphilis, J. A. Ibers, and R. H. Holm, *J. Am. Chem. Soc.*, **97**, 1032 (1975).
- (7) L. Que, Jr., M. A. Bobrik, J. A. Ibers, and R. H. Holm, *J. Am. Chem. Soc.*, **96**, 4168 (1974).
- (8) L. Que, Jr., R. H. Holm, and L. E. Mortenson, *J. Am. Chem. Soc.*, **97**, 463 (1975); W. O. Gillum, L. E. Mortenson, J.-S. Chen, and R. H. Holm, *ibid.*, **99**, 584 (1977); C. L. Hill, D. J. Steenkamp, R. H. Holm, and T. P. Singer, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 547 (1976).
- (9) R. C. Job and T. C. Bruice, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 2478 (1975).
- (10) E. E. van Tamelen, private communication and results presented at the 1st International Symposium on Nitrogen Fixation, Washington State University, Pullman, Wash., June 1974.
- (11) G. R. Dukes and R. H. Holm, *J. Am. Chem. Soc.*, **97**, 528 (1975).
- (12) G. B. Wong, M. A. Bobrik, and R. H. Holm, results to be submitted for publication.
- (13) In addition to the local data reduction program ENXDR, the programs used included full-matrix least squares and Fourier programs; ABSCOR, a numerical method absorption correction program which applies a Gaussian grid to the crystal; a modified version of ORFFE (Busing and Levy's function and error program); the direct-methods program, MULTAN, of Main, Germain, and Woolfson; and Johnson's ORTEP. All calculations were carried out on a PDP 11/45 computer.
- (14) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
- (15) Supplementary material.
- (16) R. H. Summerville and R. Hoffman, *J. Am. Chem. Soc.*, **98**, 7240 (1976).

- (17) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 260.
- (18) B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 3523 (1973).
- (19) B.-K. Teo and J. C. Calabrese, *Inorg. Chem.*, **15**, 2467 (1976). This article contains an extensive list of references to structural determinations of cubanelike cluster compounds of the general type $M_4X_4L_{4n}$.
- (20) C. J. Fritchie, Jr., *Acta Crystallogr., Sect. B*, **31**, 802 (1975).
- (21) L. Que, Jr., J. R. Anglin, M. A. Bobrik, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **96**, 6042 (1974).
- (22) C. Y. Yang, K. H. Johnson, R. H. Holm, and J. G. Norman, Jr., *J. Am. Chem. Soc.*, **97**, 6596 (1975).
- (23) R. S. Gall, C. T.-W. Chu, and L. F. Dahl, *J. Am. Chem. Soc.*, **96**, 4019 (1974).
- (24) T. Herskovitz, B. A. Averill, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiher, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 2437 (1972).
- (25) E. J. Laskowski, W. O. Gillum, R. H. Holm, R. B. Frankel, and G. C. Papaefthymiou, results to be submitted for publication.
- (26) R. H. Holm, B. A. Averill, T. Herskovitz, R. B. Frankel, H. B. Gray, O. Siiman, and F. J. Grunthaler, *J. Am. Chem. Soc.*, **96**, 2644 (1974).
- (27) J. W. Lauher and J. A. Ibers, *Inorg. Chem.*, **14**, 348 (1975).
- (28) D. Coucouvanis, D. Swenson, N. C. Baenziger, D. G. Holah, A. Kostikas, A. Simopoulos, and V. Petrouleas, *J. Am. Chem. Soc.*, **98**, 5721 (1976).
- (29) T. J. Kistenmacher and G. D. Stucky, *Inorg. Chem.*, **7**, 2150 (1968).
- (30) F. A. Cotton and C. A. Murillo, *Inorg. Chem.*, **14**, 2467 (1975).
- (31) J. Cambray, R. W. Lane, A. G. Wedd, R. W. Johnson, and R. H. Holm, *Inorg. Chem.*, in press.
- (32) B.-K. Teo and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, **185** (1976).
- (33) B.-K. Teo and J. C. Calabrese, *Inorg. Chem.*, **15**, 2474 (1976).
- (34) R. B. Frankel, B. A. Averill, and R. H. Holm, *J. Phys. (Paris)*, **35**, C6-107 (1974).
- (35) A. Kostikas, V. Petrouleas, A. Simopoulos, D. Coucouvanis, and D. G. Holah, *Chem. Phys. Lett.*, **38**, 582 (1976).
- (36) W. M. Reiff, I. E. Grey, A. Fan, Z. Eliezer, and H. Steinfink, *J. Solid State Chem.*, **13**, 32 (1975).

Contribution from the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and the Department of Chemistry, University of California, Berkeley, California 94720

Crystal Structure of Tetrakis[bis(*N,N'*-dimethylethylenediamido)uranium(IV)], a Tetrameric Globular Complex¹

JOHN G. REYNOLDS, ALLAN ZALKIN,* DAVID H. TEMPLETON,* and NORMAN M. EDELSTEIN*

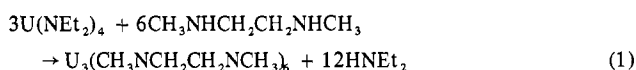
Received January 21, 1977

AIC700471

The tetrameric compound $U_4(CH_3NCH_2CH_2NCH_3)_8$ is a minor product of the reaction of tetrakis(diethylamido)uranium(IV) with dimethylethylenediamine in pentane. The crystals are orthorhombic, space group *Fddd*, with $a = 12.02$ (2) Å, $b = 22.73$ (4) Å, and $c = 34.32$ (6) Å; $d_{\text{calcd}} = 2.32$ g/cm³ for $Z = 8$. X-ray diffraction intensity data were collected by an automated diffractometer using graphite-monochromated Mo $K\alpha$ radiation. For 399 reflections with $F^2 > 2\sigma$, $R_1 = 0.078$ and $R_2 = 0.060$. Four bis[*N,N'*-dimethylethylenediamido]uranium(IV) units are connected by bridging nitrogen atoms to form a closed tetrameric complex in which the four uranium atoms are 3.6 Å apart at the corners of a twisted square. Each uranium atom is bonded to six nitrogen atoms in a highly distorted trigonal prism. Attached to each uranium atom are two nitrogen atoms from a nonbridging dimethylethylenediamido ligand and four from two bridging ligands.

Introduction

We recently reported the synthesis, crystal structure, and magnetic and optical properties of a novel trimeric amide complex of uranium, $U_3(CH_3NCH_2CH_2NCH_3)_6$.² This compound was synthesized by the aminolysis reaction



The three uranium atoms in this compound form a linear chain and the center U atom is linked to each of the terminal U atoms by a triple nitrogen bridge. Each of the dimethylethylenediamido ligands has one N atom which acts as a bridge (four-coordinate) while the second N atom is bonded to a terminal U atom and two carbon atoms (three-coordinate) and is coplanar with these atoms. The uranium-uranium distance is 3.54 Å but even at this short distance the magnetic data show no evidence of metal-metal interaction down to 4.2 K. As a minor product of the above reaction we isolated some red-brown crystals which have now been shown to consist of tetrameric molecules. We report in this paper the characterization of this tetramer by determination of its crystal structure.

Experimental Section

N,N'-Dimethylethylenediamine was added to a solution of $U(NEt_2)_4$ in pentane at 77 K as previously described.² The reaction mixture was warmed to room temperature and after 24 h the precipitate which formed was filtered and vacuum-dried. Two types of crystals were grown from the filtrate, the major product (~95%) being the previously described trimer $U_3(CH_3NCH_2CH_2NCH_3)_6$ and the minor product being orthorhombic red-brown crystals, $U_4(CH_3NCH_2CH_2NCH_3)_8$. Crystals were obtained for x-ray diffraction by removing them from the walls of the flask with a tungsten needle in an ar-

gon-atmosphere box. The separation of the two types of crystals was achieved by noting their different shapes and colors. The crystals were placed in quartz capillaries which were then sealed with vacuum grease. The capillaries were fire-sealed immediately upon removal from the box. Only the yellow trimer crystals were found upon recrystallization from pentane of the initial precipitate.

We examined several crystals with a Picker FACS-I automated diffractometer equipped with a graphite monochromator and molybdenum tube. We obtained cell dimensions by a least-squares procedure from the angular positions of seven manually centered reflections for which the 2θ values were between 15 and 20°. With one of the crystals we collected intensity data to $2\theta = 30^\circ$, yielding 257 independent reflections with $I > \sigma$. From these data the uranium positions were determined, in good agreement with the final results described below, but we failed to find a satisfactory structure for the light atoms. In retrospect one can recognize a poorly resolved image of the final structure in the electron density maps, but other spurious features are also present. Later another crystal (which is described in Table I) permitted measurement of some reflections as high as $2\theta = 40^\circ$. The space group and cell dimensions are also given in Table I with some other details of the experiment. The highly reactive nature of the crystals precluded a direct measurement of the density. ω scans of several low-angle reflections showed widths of half-peak height of about 0.20°. A total of 2102 scans were measured and later averaged to give a set of 1122 unique data of which only 421 had $F^2 > 2\sigma$. Three standard reflections were measured after each 200th scan to monitor for crystal decay, instrumental stability, and crystal alignment. No significant change occurred for 004 and 080. An abrupt increase for 400 suggested a change of alignment after 372 reflections in the range $h = -11$ to -6 had been measured, and on this basis these intensities were adjusted upward by about 5%, an amount less than the individual statistical errors.

Absorption corrections were calculated using an analytical algorithm.³ The crystal shape was described by seven surface planes. Azimuthal scans of integrated intensities were performed for nine reflections in as diverse a region of reciprocal space as the instrument