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Crystal and Molecular Structure of Bis(tetra-*n*-butylammonium) μ -S,S'-[(Tetrakis(ethane-1,2-dithiolate)diiron(III)]

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The crystal structure of the ethanedithiolate complex $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Fe}(\text{edt})_2]_2$ (edt = ethane-1,2-dithiolate) has been determined from 1609 independent reflections collected by counter methods. The black crystals are monoclinic, space group $P2_1/c$, with $a = 10.065$ (4), $b = 16.705$ (7), $c = 16.28$ (1) Å, and $\beta = 93.30$ (2)°. The measured density was 1.21 ± 0.03 g/cm³ which agrees with the calculated density of 1.173 g/cm³ for $Z = 4$. The absorption corrected data gave a conventional R factor of 0.056 on full-matrix, least-squares refinement. The anions are tightly bound centrosymmetric dimers. Bridging ethanedithiolate sulfur atoms give rise to a planar and nearly square Fe₂S₂ ring. The Fe-Fe' distance in this ring, 3.410 (3) Å, is considered too long for direct metal-metal bonding. Each iron is five-coordinate and has four nearly equal Fe-S distances with a mean of 2.442 (10) Å. The fifth or bridging Fe-S distance is 2.503 (3) Å. The coordination about iron can be described as distorted trigonal bipyramidal. The tetra-*n*-butylammonium cation has four ordered trans chains and overall idealized symmetry D_{2d} .

Introduction

Iron-sulfur complexes are currently a subject of intense study in several laboratories²⁻⁵ prompted by their characterization in several enzyme systems.^{6,7} In view of the possibilities for polymerization, they are difficult to characterize structurally without crystallographic analysis. Recently two iron-sulfur complexes containing mercapto sulfur and or sulfide ligands only have been prepared which could conceivably afford models for iron-sulfur coordination in the enzymes ferredoxin and rubredoxin.² These are $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{C}_6\text{H}_5)_4]$ and $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Fe}(\text{edt})_2]$. This report describes the structure of the latter complex.⁸ The anion is found to be a dimer with a Fe₂S₂ bridge and five sulfur atoms about each iron. It therefore cannot be a rubredoxin model where tetrahedral coordination of only four sulfur groups has been firmly established.⁹

Experimental Section

Black crystals of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Fe}(\text{edt})_2]_2$ as large cube-shaped blocks grown from methyl cyanide were supplied by Professor R. H.

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(2) T. Herskovitz, B. A. Averill, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiher, *Proc. Nat. Acad. Sci. U. S.*, **69**, 2437 (1972).

(3) H. Buttner and R. D. Feltham, *Inorg. Chem.*, **11**, 971, (1972).

(4) D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, **9**, 2775 (1970), and references cited therein.

(5) A. L. Balch, *J. Amer. Chem. Soc.*, **91**, 6962 (1969), and references cited therein.

(6) R. Malkin and J. C. Rabinowitz, *Annu. Rev. Biochem.*, **36**, 113 (1967).

(7) T. Kimura, *Struct. Bonding (Berlin)*, **5**, 1 (1968).

(8) The preparation and other properties are being studied in the laboratory of Professor R. H. Holm and will be reported elsewhere.

(9) J. R. Herriot, L. C. Sieker, and L. H. Jensen, *J. Mol. Biol.*, **50**, 391 (1970).

Holm. They exhibit the forms {011} and {100} and cleave readily parallel to these faces. The crystal used for the final intensity measurements measured 0.20, 0.32, and 0.36 mm perpendicular to (01 $\bar{1}$), (011), and (100) respectively. Preliminary examination by precession photography (Mo K α radiation) established that the crystals are monoclinic with space group $C_{2h}^2-P2_1/c$. Mo K α radiation (λ 0.70930 Å) from a graphite monochromator was used to obtain the setting angles of 12 reflections which had been centered on a FACS-1 Picker diffractometer at 23°. The cell constants, obtained by least squares, are $a = 10.065$ (4), $b = 16.705$ (7), $c = 16.28$ (1) Å, and $\beta = 93.30$ (3)°. The measured density was 1.21 (3) g/cm³ (by flotation in aqueous zinc chloride) and the calculated density is 1.173 g/cm³ for four cations and two dimer anions in the cell. $F(000)$ is 1044 electrons, formula weight is 964.90, and $\mu(\text{Mo K}\alpha)$ is 5.9 cm⁻¹.

The mosaicity of the crystal was measured by means of the narrow-source, open-counter, ω -scan technique. Some low-order reflections showed structure, and the average width at half-height of representative strong reflections was 0.2°, which is acceptable.¹⁰ The crystal was mounted in a quartz capillary under nitrogen and had the [011] reciprocal lattice vector roughly coincident with the spindle axis. The intensities were measured using Mo K α radiation by the θ - 2θ technique at a takeoff angle of 1.7°. At this angle the intensity of a reflection was about 80% of the maximum as a function of takeoff angle. A receiving counter aperture 4.5 mm high and 6.5 mm wide was used and positioned 30 cm from the crystal. A nonsymmetric scan range from 0.95° below the K α_1 peak to 0.8° beyond the K α_2 peak was used. Scan speeds used were 1°/min (out to $2\theta = 36^\circ$) and 0.5°/min (from 36 to 39°). Stationary-counter, stationary-crystal background counts of 10 sec (out to $2\theta = 25^\circ$), 20 sec (from 25 to 33°), and 40 sec (from 33 to 39°) were made at each end of the scan. Attenuators were inserted automatically when the intensity of the reflection exceeded about 7000 counts/sec during the scan.

The unique hkl reflections out to $2\theta = 39^\circ$ were gathered. Beyond this point there were few detectable reflections. The intensities of six standard reflections were measured after every 100 reflections. The average decline of these was 3% during the experiment and a correction factor $1/(1 - (1.3 \times 10^{-5}N))$ was applied as a function of

(10) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

Table I. Positional and Thermal^a Parameters ($\times 10^4$) for $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Fe}(\text{S}_4\text{C}_4\text{H}_8)_2]$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	4116 (1) ^b	-373 (1)	776 (1)	93 (2)	35 (1)	46 (1)	3 (1)	3(1)	2 (1)
S(1)	5735 (2)	-897 (1)	29 (1)	97 (3)	34 (1)	52 (1)	4 (1)	4 (1)	0 (1)
S(2)	5574 (2)	-263 (1)	1859 (1)	131 (3)	47 (1)	49 (1)	-12 (2)	-7 (1)	-1 (1)
S(3)	2541 (3)	-15 (2)	1603 (2)	140 (4)	57 (1)	63 (1)	14 (2)	28 (2)	4 (1)
S(4)	2688 (2)	-1239 (1)	142 (2)	108 (3)	47 (1)	64 (1)	-11 (1)	-1 (1)	0 (1)
N	3952 (7)	-2378 (4)	-2318 (5)	121 (9)	40 (3)	52 (4)	4 (5)	1 (5)	-8 (3)
C(1) ^c	7188 (9)	-992 (6)	750 (7)	85 (12)	64 (5)	75 (6)	21 (6)	-29 (7)	8 (5)
C(2)	7187 (9)	-387 (6)	1419 (7)	95 (12)	62 (6)	79 (6)	-14 (7)	-17 (7)	2 (5)
C(3)	1033 (11)	-302 (8)	1033 (8)	112 (14)	104 (9)	99 (8)	7 (9)	16 (9)	13 (7)
C(4)	1126 (9)	-1096 (7)	649 (8)	86 (12)	64 (6)	105 (8)	-11 (7)	5 (8)	10 (5)
C(5)	3401 (9)	-3204 (5)	-2121 (6)	136 (13)	37 (4)	71 (6)	5 (6)	5 (7)	-10 (4)
C(6)	2821 (11)	-3275 (6)	-1280 (6)	199 (16)	50 (5)	66 (6)	-1 (8)	17 (8)	-5 (4)
C(7)	2181 (13)	-4058 (7)	-1176 (8)	240 (20)	65 (7)	91 (8)	-4 (9)	40 (10)	-2 (6)
C(8)	1670 (13)	-4180 (8)	-342 (8)	234 (21)	96 (8)	84 (8)	-8 (10)	45 (11)	9 (7)
C(9)	2878 (9)	-1724 (6)	-2246 (6)	121 (12)	47 (5)	58 (5)	16 (6)	-2 (7)	-10 (4)
C(10)	1631 (10)	-1860 (6)	-2778 (7)	142 (14)	57 (5)	77 (6)	10 (7)	-5 (8)	-6 (5)
C(11)	654 (11)	-1186 (8)	-2672 (8)	170 (17)	83 (7)	110 (9)	34 (10)	-23 (10)	-31 (6)
C(12)	-596 (14)	-1303 (10)	-3213 (9)	207 (22)	135 (11)	113 (10)	64 (13)	-14 (13)	-11 (8)
C(13)	4383 (9)	-2413 (6)	-3194 (6)	156 (13)	46 (5)	49 (5)	13 (6)	2 (7)	-10 (4)
C(14)	4996 (10)	-1645 (6)	-3485 (6)	202 (16)	51 (5)	51 (6)	0 (7)	23 (8)	-3 (4)
C(15)	5512 (14)	-1753 (7)	-4307 (8)	292 (24)	58 (6)	74 (7)	-13 (9)	6 (11)	5 (5)
C(16)	6047 (14)	-1018 (8)	-4677 (8)	291 (23)	65 (7)	101 (9)	-5 (10)	6 (12)	5 (6)
C(17)	5104 (9)	-2147 (6)	-1716 (6)	135 (13)	55 (5)	51 (5)	-4 (7)	-8 (7)	-15 (4)
C(18)	6339 (11)	-2680 (7)	-1768 (7)	172 (16)	66 (6)	75 (7)	34 (8)	-30 (9)	-9 (5)
C(19)	7482 (10)	-2388 (7)	-1206 (8)	114 (14)	80 (7)	106 (9)	9 (8)	-8 (10)	-7 (6)
C(20)	8669 (12)	-2904 (9)	-1266 (10)	154 (18)	114 (10)	156 (12)	51 (11)	16 (12)	7 (9)

^a The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^b Standard deviations of the least significant figures are given here and in subsequent tables in parentheses. ^c Atoms C(1) to C(4) are methylene carbons of the ligands; subsequent groups of four carbons are *n*-butyl groups numbered away from nitrogen (N).

N, the number of the reflections in the list. All data processing was carried out as previously described.¹¹ The value of *p* selected was 0.04. The data were corrected for absorption¹² and the transmission coefficients ranged from 0.82 to 0.89. A total of 2391 unique reflections were obtained, of which 782 had $I < 3\sigma(I)$.

Solution and Refinement of Structure. A direct-methods procedure¹³ gave a "most probable" *E* map from which sites for the Fe and all S atoms were found. The positional parameters of these atoms were refined¹⁴ by least squares, with minimization of the function $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weights *w* were taken as $4F_o^2/\sigma^2(F_o^2)$.

A subsequent difference map yielded the positions of the remaining nonhydrogen atoms. A cycle of refinement varying the scale factor, positional parameters, and individual isotropic thermal parameters led to an *R* factor, $R_1 = (\Sigma |F_o| - |F_c|) / \Sigma |F_o|$, of 0.10 and a weighted *R* factor, $R_2 = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2)^{1/2}$, of 0.12 based on reflections with $F_o^2 > 3\sigma(F_o^2)$. Subsequent cycles using anisotropic thermal parameters converged to $R_1 = 0.072$ and $R_2 = 0.088$. The resulting structure factors were used to compute difference density sections about the expected planes of the methylene hydrogen atoms in the tetra-*n*-butylammonium cation. In each case three prominent electron density regions could be assigned to methyl hydrogens. The hydrogen sites were idealized ($C-H = 1.01 \text{ \AA}$, $HCH = 109.5^\circ$) and their contributions to F_c as well as those of all the methylene hydrogens (using their calculated positions) were included in subsequent cycles of refinement as fixed contributions. After a further two refinement cycles, the weighting scheme

(11) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(12) Cahen's program AGNOST for absorption corrections includes the Coppens-Leiserowitz-Rabinovich logic for gaussian integration and Cullen's logic for the De Meulenaer and Tompa analytical formulation. The production run of the corrections used the former logic.

(13) The direct methods programs used were FAME (R. B. K. Dewar) and the MULTAN series (P. Main, M. W. Woolfson, and G. Germain). In addition to local programs, the programs used were local modifications of Zalkin's FORDAP program, Busing and Levy's ORFFE function and error program, and Johnson's ORTEP-II thermal ellipsoid plotting program. Our local least-squares program NUCLS, in its nongroup form, closely resembles the Busing-Levy ORFLS program.

(14) Scattering factors and the terms $\Delta f'$ and $\Delta f''$ for Fe and S were taken from the tabulation by D. T. Cromer and J. T. Waber in "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, in press.

Table II. Parameters for the Hydrogen Atoms

Atom ^a	10^3x	10^3y	10^3z	10^3x	10^3y	10^3z	$B, \text{ \AA}^2$
1. Methylene Groups ^c							
C(1)	719	-157	100	804	-96	42	8.0
C(2)	752	15	120	790	-55	189	8.0
C(3)	24	-31	142	79	11	57	8.0
C(4)	32	-118	21	102	-154	109	8.0
C(5)	410	-364	-219	261	-333	-257	8.0
C(6)	214	-284	-118	358	-323	-082	9.0
C(7)	284	-452	-129	138	-412	-161	10.0
C(9)	325	-117	-239	260	-169	-164	8.0
C(10)	121	-240	-263	187	-189	-338	9.0
C(11)	110	-064	-280	041	-115	-206	10.0
C(13)	356	-254	-360	505	-287	-327	8.0
C(14)	578	-148	-308	431	-119	-349	9.0
C(15)	473	-198	-472	623	-220	-431	10.0
C(17)	478	-217	-111	537	-155	-181	8.0
C(18)	665	-269	-236	612	-327	-162	9.0
C(19)	713	-238	-061	765	-179	-135	10.0
2. Methyl Groups ^d							
C(8)	234	-411	11	135	-470	-19	12.0
	96	-379	-19				
C(12)	-47	-128	-380	-106	-179	-315	12.0
	-130	-90	-315				
C(16)	542	-60	-475	674	-79	-438	12.0
	631	-109	-524				
C(20)	911	-282	-177	935	-278	-84	12.0
	850	-345	-120				

^a Carbon atom to which hydrogens are attached. ^b Isotropic temperature factor set equal to the average for the carbon type plus 1.5 \AA^2 and rounded to the nearest integer. ^c Calculated positions. ^d Observed positions idealized.

was checked by plotting $\Sigma w(|F_o| - |F_c|)^2$ averaged in ranges of $|F_o|$ vs. $|F_c|$. This function increased linearly with F_o and subsequent refinement cycles employed a multiplicative factor of $(1.37 - 0.023|F_o|)$ to $\sigma(F_o^2)$. These adjustments probably reflect an inappropriate choice of *p* used in assigning the standard deviations. The refinement converged to $R_1 = 0.056$ and $R_2 = 0.069$. The error in an observation of unit weight is 0.997. The final difference map shows no peaks of height greater than $0.64 (7) \text{ e/\AA}^3$, which is approximately 20% the height of a typical carbon peak in the initial difference map. Of the 782 reflections omitted from the

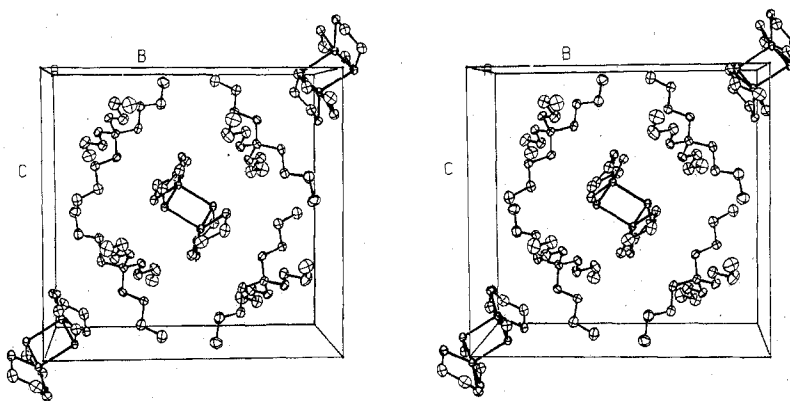


Figure 1. A stereoview of the $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Fe}(\text{edt})_2]_2$ unit cell. The view is approximately along x . Hydrogen atoms are not shown. Other atoms are drawn with 20% probability ellipsoids.

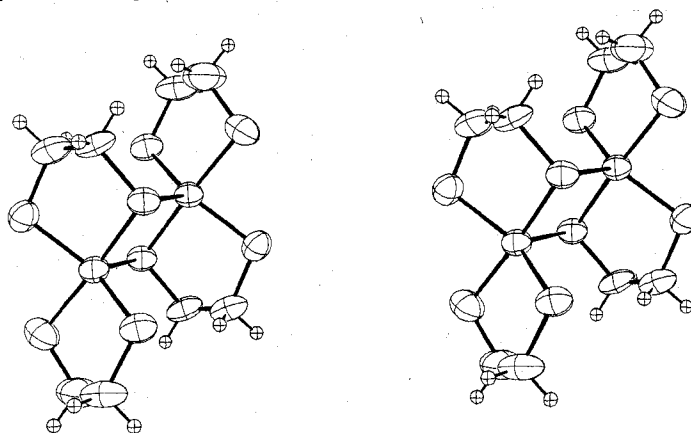


Figure 2. Stereoview of the $[\text{Fe}(\text{edt})_2]_2^{2-}$ dimer. Atoms are drawn with 50% probability ellipsoids.

refinement with $F_o^2 < 3\sigma(F_o^2)$ none has $|F_o^2 - F_c^2|/\sigma(F_o^2) > 3.5$. To see if the exclusion of these reflections (32% of the data) from the refinement was biasing the result, a cycle of refinement was done including all 2391 reflections and minimizing $\Sigma w(F_o^2 - F_c^2)^2$. The weights were taken as $1/(k^2\sigma^2(F_o^2))$ where k is the correction factor to $\sigma(F_o^2)$ mentioned above. The starting parameters for this refinement were those used for the previous cycle and not those output from it. The pattern of the parameter shifts was very similar and no divergence between the two refinements exceeding 1 standard deviation in the positional parameters occurred. The largest change was a decrease in the scale factor by 2.2 standard deviations, most probably caused by the inclusion of negative observed intensity values. The standard deviations of the parameters averaged 15% less than in the former refinement. However, as the latter refinement had not fully converged, we present the results of the converged refinement on F_o below and conclude that the exclusion of terms with $F_o^2 < 3\sigma(F_o^2)$ does not bias the values of the final parameters.

The final least-squares parameters and their standard deviations are given in Table I. The idealized positions and fixed isotropic thermal parameters of the hydrogen atoms are given in Table II. Table III contains the observed and calculated structure factors ($\times 10^3$).¹⁵ Table IV presents the rms amplitudes of vibration.

Discussion

Description of the Structure. A stereoscopic view of the unit cell of the structure is shown in Figure 1. The anions are dimeric and reside in channels parallel to x formed from the tetra- n -butylammonium cations. Excluding hydrogen atoms, there are no intermolecular close contacts less than 3.5 Å.

(15) Table III, listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-249.

Table IV. Root-Mean-Square Amplitudes of Vibration ($\text{Å} \times 10^3$)

Atom	Min	Intermed	Max
Fe	213 (2)	225 (2)	250 (2)
S(1)	213 (3)	229 (3)	265 (3)
S(2)	228 (3)	259 (3)	283 (3)
S(3)	235 (4)	277 (3)	321 (3)
S(4)	222 (3)	268 (3)	296 (3)
N	222 (10)	248 (10)	280 (10)
C(1)	165 (16)	311 (13)	338 (13)
C(2)	203 (14)	297 (13)	338 (13)
C(3)	237 (15)	347 (15)	399 (17)
C(4)	204 (14)	298 (13)	379 (14)
C(5)	218 (14)	265 (12)	315 (13)
C(6)	262 (12)	294 (14)	325 (14)
C(7)	302 (16)	308 (15)	383 (15)
C(8)	282 (16)	372 (15)	384 (16)
C(9)	222 (14)	254 (13)	306 (13)
C(10)	259 (14)	283 (13)	331 (14)
C(11)	263 (16)	303 (15)	440 (17)
C(12)	280 (17)	383 (17)	478 (19)
C(13)	224 (14)	267 (12)	300 (13)
C(14)	246 (15)	271 (15)	328 (13)
C(15)	279 (16)	318 (15)	390 (16)
C(16)	300 (16)	368 (16)	388 (16)
C(17)	217 (14)	271 (14)	309 (13)
C(18)	238 (15)	291 (13)	380 (15)
C(19)	238 (15)	331 (14)	384 (15)
C(20)	245 (17)	420 (17)	461 (17)

The $[\text{Fe}(\text{edt})_2]_2^{2-}$ Anion. Figure 2 is a stereoview of the anion and Figure 3 shows important distances as well as the labeling scheme. (There and in the text primed atoms are related to unprimed atoms by the center of symmetry.) The anion is dimeric with $\text{Fe}(\text{edt})_2$ units related by an imposed center of symmetry. The bridging atoms Fe, S(1), Fe', S(1') are necessarily coplanar and form a nearly perfect

Table V. Geometry of the $[\text{Fe}(\text{edt})_2]_2^{2-}$ Dimer

		Distances, Å	
Fe...Fe'	3.410 (3)	S(3)-C(3)	1.80 (1)
S(1)...S(1')	3.341 (4)	S(4)-C(4)	1.83 (1)
Fe-S(1)	2.265 (3)	C(1)-C(2)	1.485 (13)
Fe-S(2)	2.236 (3)	C(3)-C(4)	1.471 (16)
Fe-S(3)	2.220 (3)	S(1)...S(2)	3.175 (4)
Fe-S(4)	2.247 (3)	S(3)...S(4)	3.145 (4)
Fe-S(1')	2.503 (3)	S(2)...S(3)	3.085 (4)
S(1)-C(1)	1.83 (1)	S(1)...S(4)	3.135 (3)
S(2)-C(2)	1.82 (1)	S(1')...S(3)	3.595 (4)
		Angles, Deg	
S(1)-Fe-S(1')	88.8 (1)	Fe-S(2)-C(2)	103.9 (3)
S(1)-Fe-S(4)	88.0 (1)	Fe-S(3)-C(3)	103.1 (4)
S(1)-Fe-S(2)	89.7 (4)	Fe-S(4)-C(4)	104.6 (4)
S(3)-Fe-S(1')	98.9 (1)	S(1)-C(1)-C(2)	112.2 (7)
S(3)-Fe-S(4)	89.5 (1)	S(2)-C(2)-C(1)	113.8 (7)
S(3)-Fe-S(2)	87.6 (1)	S(3)-C(3)-C(4)	112.7 (8)
S(2)-Fe-S(1')	106.6 (1)	S(4)-C(4)-C(3)	112.7 (8)
S(2)-Fe-S(4)	142.1 (1)	Fe-S(1)-Fe'	91.2 (1)
S(1')-Fe-S(4)	111.2 (1)	Fe'-S(1)-C(1)	109.9 (3)
Fe-S(1)-C(1)	105.2 (4)		
		Torsion Angles, ° Deg	
Fe-S(2)-C(2)-C(1)	37.7 (8)	Fe-S(3)-C(3)-C(4)	43.4 (10)
S(2)-C(2)-C(1)-S(1)	-44.3 (9)	S(3)-C(3)-C(4)-S(4)	-44.9 (12)
C(2)-C(1)-S(1)-Fe	28.4 (8)	C(3)-C(4)-S(4)-Fe	23.7 (10)
C(1)-S(1)-Fe-S(2)	-4.3 (4)	C(4)-S(4)-Fe-S(3)	2.2 (4)
S(1)-Fe-S(2)-C(2)	-14.9	S(4)-Fe-S(3)-C(3)	-21.7 (4)

^a The sign of the torsion angle of the atoms I-J-K-L is positive if when looking from J to K a clockwise motion of atom I would superimpose it on atom L.

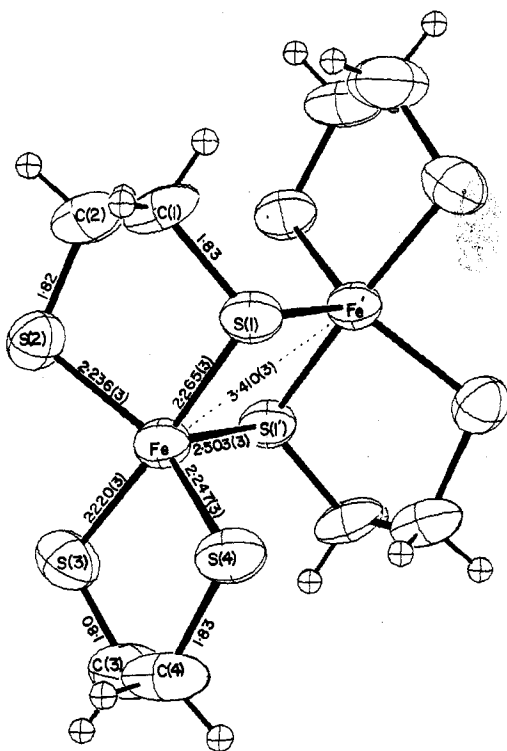


Figure 3. The $[\text{Fe}(\text{edt})_2]_2^{2-}$ dimer showing important distances and the labeling scheme.

square with vertex angles less than 2° from 90° (Table V). The Fe_2S_2 four-membered ring is now a well-established feature of iron-sulfur complexes. The $[\text{Fe}(\text{edt})_2]_2^{2-}$ complex has the largest $\text{Fe}\cdots\text{Fe}'$ distance and internal angles closest to 90° of those so far studied. Nonplanar Fe_2S_2 rings are known in $[\text{Fe}(\text{CO})_3\text{SCH}_3]_2$ ¹⁶ as are cases of planar rings where there are additional bridges such as ethyl thio-xanthate between the iron atoms in $[\text{Fe}(\text{SC}_2\text{H}_5)_2]_2^{2-}$.

(16) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 328 (1963).

$(\text{S}_2\text{CSC}_2\text{H}_5)_2]_2^{2-}$.⁴ These have short Fe-Fe distances and acute ($\sim 73^\circ$) Fe-S-Fe' angles. The Fe-Fe distance in $[\text{Fe}(\text{edt})_2]_2^{2-}$ is beyond the range of values (2.37-3.05 Å)¹⁷ for which iron-iron bonding has been postulated. For the planar Fe_2S_2 rings in the complexes $[\text{Fe}(\text{NO})_2(\text{SC}_2\text{H}_5)_2]_2$,¹⁸ $[\text{Fe}(\text{mnt})_2]_2^{2-}$,¹⁹ and $[\text{Fe}(\text{S}_2\text{C}_2(\text{CF}_3))_2]_2^{2-}$ Table VI shows that based on this criterion, Fe-Fe bonding would only be likely in the first and last complexes. It is not clear what factors dictate the planarity of the Fe_2S_2 ring. It can be seen from the $[\text{Fe}(\text{CO})_3\text{SCH}_3]_2$ structure¹⁶ that the special requirements of Fe-Fe bonding can cause nonplanarity. Repulsive electrostatic and 1,3 non-bonding interactions within the ring will favor planarity but impose a constraint on the valence-bond angles to add up to 360° . Delocalization of electrons in the ring through π orbitals would also favor planarity, but it is not possible to decide from the structural data the importance of such a contribution.

The coordination polyhedron about the iron atoms is best described as a trigonal bipyramid. Thus the iron lies only 0.045 (2) Å from the S(1'), S(2), S(4) plane and the angles formed by the apical S(1) and S(3) atoms at Fe with the equatorial atoms S(1'), S(2), S(4) are all within 3° of 90° with the exception of the S(1')-Fe-S(3) angle which is 98.9° . The angle S(2)-Fe-S(4) is $142.0(1)^\circ$ and represents the largest departure from an ideal trigonal bipyramid, where it would be 120° . As is the case with the $[\text{Cu}_2\text{Cl}_8]^{2-}$ dimer,²⁰ where the geometry is also close to trigonal bipyramidal, this angle is opposite the longest metal-ligand bond. This bond, Fe-S(1'), has a distance of 2.503 (3) Å and is significantly longer than the other four Fe-S distances which range from

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(18) J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Crystallogr., Sect. B*, **25**, 1262 (1969).

(19) W. C. Hamilton and I. Bernal, *Inorg. Chem.*, **6**, 2003 (1967). mnt = 1,2-dicyano-1,2-ethylenedithiol.

(20) D. J. Hodgson, P. K. Hale, and W. E. Hatfield, *Inorg. Chem.*, **10**, 1061 (1971).

Table VI. Geometry of Planar Fe₂S₂ Rings

Complex ^a	Distances, Å			Angles, deg		Ref
	Fe—S	Fe···Fe'	S···S'	Fe—S—Fe'	S—Fe—S'	
[Fe(edt) ₂] ₂ ²⁻	2.265 (3) ^b 2.503 (3)	3.410 (3)	3.341 (4)	91.2 (1)	88.8 (1)	This work
[Fe(mnt) ₂] ₂ ²⁻	2.280 (7) ^b 2.460 (7)	3.08		81.0 (3)	99.0 (3)	20
[Fe(NO) ₂ (SC ₂ H ₅) ₂] ₂	2.26 (2)	2.720 (3)	3.633 (4)	73.7 (1)	106.6 (1)	18
[Fe(S ₂ C ₂ (CF ₃) ₂) ₂ ²⁻	2.190 (3) ^b 2.311 (3)	2.767 (4)		75.6 (1)	105.0 (1)	c

^a mnt = 1,2-dicyano-1,2-ethylenedithiol; edt = ethanedithiol dianion. ^b Average of four distances. ^c Private communication from R. Eisenberg for the structure of [Fe₂(μ-SCH₃)₂(CO)₆][Fe₂(S₂C₂(CF₃)₂)₂].

Table VII. Bond Distances and Angles in the Tetra-n-butylammonium Cation^a

Distance, Å		Angle, deg	
N--C(5)	1.528 (11)	C(5)-N-C(13)	106.8 (7)
N--C(9)	1.546 (11)	C(9)-N-C(17)	106.4 (6)
N--C(13)	1.516 (11)	C(5)-N-C(17)	111.4 (7)
N--C(17)	1.524 (11)	C(5)-N-C(9)	111.0 (7)
N--C(av)	1.529 (6)	C(9)-N-C(13)	109.7 (7)
C(5)--C(6)	1.523 (13)	C(13)-N-C(17)	111.6 (7)
C(6)--C(7)	1.472 (15)	N-C(5)-C(6)	114.9 (8)
C(7)--C(8)	1.495 (16)	N-C(9)-C(10)	114.5 (7)
C(9)--C(10)	1.500 (12)	N-C(13)-C(14)	113.9 (8)
C(10)--C(11)	1.512 (14)	N-C(17)-C(18)	114.0 (7)
C(11)--C(12)	1.507 (16)	N-C _α -C _β (av)	114.3 (7)
C(13)--C(14)	1.512 (13)	C(5)-C(6)-C(7)	111.4 (9)
C(14)--C(15)	1.474 (14)	C(9)-C(10)-C(11)	110.5 (9)
C(15)--C(16)	1.485 (16)	C(13)-C(14)-C(15)	110.5 (9)
C(17)--C(18)	1.535 (13)	C(17)-C(18)-C(19)	111.8 (9)
C(18)--C(19)	1.510 (14)	C _α -C _β -C _γ (av)	110.8 (4)
C(19)--C(20)	1.481 (16)	C(6)-C(7)-C(8)	113.7 (1.1)
C--C(av)	1.500 (6)	C(10)-C(11)-C(12)	111.3 (1.0)
C(7)--C(8) ^b	1.510 (17)	C(14)-C(15)-C(16)	115.0 (1.1)
C(11)--C(12) ^b	1.529 (18)	C(18)-C(19)-C(20)	111.2 (1.1)
C(15)--C(16) ^b	1.494 (18)	C _β -C _γ -C _δ (av)	113.5 (1.0)
C(19)--C(20) ^b	1.528 (17)		

^a Standard deviation in averages estimated from internal agreement. ^b Corrected for thermal motion.

2.220 (3) to 2.265 (3) Å (mean 2.242 (10) Å). This distribution of bond lengths is very similar to that found in the [Fe(mnt)₂]₂²⁻ complex.¹⁹ Here the nonbridging Fe-S distances average 2.23 Å and the bridge bond is 2.46 (1) Å. This complex differs from the one reported here in having a nearly perfect square-pyramidal coordination about iron. This difference in coordination geometry can be ascribed to the extensive delocalization of electrons in square-planar [M(mnt)₂]₂²⁻ complexes.²¹ The [Fe(edt)₂]₂²⁻ ion cannot have such a stabilizing arrangement. It is interesting that, although the bond angles at the iron differ widely between the two complexes, the Fe-S distances are nearly the same. The geometries of the two independent Fe-S-CH₂-CH₂-S five-membered rings of [Fe(edt)₂]₂²⁻ are virtually identical (Table V). The rings have opposite absolute configurations; in terms of Figure 3 and the IUPAC suggested rules²² the FeS(3)S(4)C(3)C(4) ring is λ and the FeS(1)S(2)C(1)C(2) ring δ. The torsion angles C(4)-S(1)-Fe-S(2) (-4.3 (4)°) of one ring and C(4)-S(4)-Fe-S(3) (2.2 (4)°) of the other are both near 0° and show that the rings have an unsymmetric envelope conformation. The atoms C(2) and C(3) are the "envelope flap tips" in each ring. Bridging at the S(1) atom does not lead to any important differences between the ring conformations.

The Tetra-n-butylammonium Cation. Each n-butyl arm has the zigzag trans conformation and the overall idealized symmetry is D_{2d}. Figure 4 shows that the experimentally

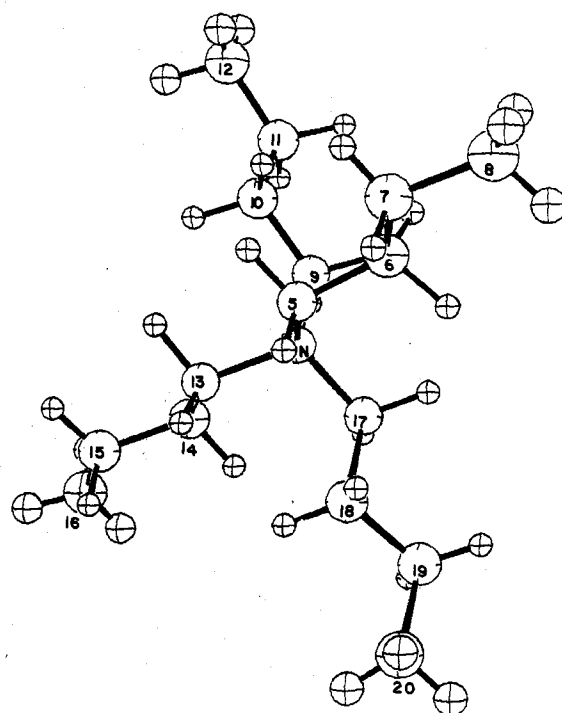


Figure 4. The [(n-C₄H₉)₄N] cation showing the orientations of the methyl groups and the carbon atom numbering scheme.

Table VIII. Conformation of the Tetra-n-butylammonium Ion

Atoms	Torsion angle, ^a deg
N-C(5)-C(6)-C(7)	173.7 (9)
C(5)-C(6)-C(7)-C(8)	176.3 (10)
N-C(9)-C(10)-C(11)	-179.4 (9)
C(9)-C(10)-C(11)-C(12)	178.9 (11)
N-C(13)-C(14)-C(15)	174.1 (9)
C(13)-C(14)-C(15)-C(16)	175.7 (10)
N-C(17)-C(18)-C(19)	175.7 (9)
C(17)-C(18)-C(19)-C(20)	179.7 (12)
C(5)-N-C(9)-C(10)	-56.7 (11)
C(5)-N-C(13)-C(14)	-178.3 (8)
C(5)-N-C(17)-C(18)	65.3 (11)
C(9)-N-C(5)-C(6)	-56.3 (10)
C(9)-N-C(13)-C(14)	61.3 (10)
C(9)-N-C(17)-C(18)	-173.6 (9)
C(13)-N-C(5)-C(6)	-175.9 (8)
C(13)-N-C(9)-C(10)	61.1 (10)
C(13)-N-C(17)-C(18)	-54.0 (11)
C(17)-N-C(5)-C(6)	62.1 (10)
C(17)-N-C(9)-C(10)	-178.1 (8)
C(17)-N-C(13)-C(14)	-56.3 (10)

^a See footnote a of Table V.

placed methyl hydrogen atoms are staggered with respect to groups on the γ-carbon atoms. Table VII gives the individual bond distances and angles. The torsion angles about the bonds are all close to 180° or in the case of branching at the nitrogen, 60° (Table VIII). Corrections for thermal motion

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 (22) *Inorg. Chem.*, 9, 1 (1970).

Table IX. Geometry of Tetra-*n*-butylammonium Ions^a

No.	Structure type ^b	N-C	C-C	N-C _α -C _β	C _α -C _β -C _γ	C _β -C _γ -C _δ	C(<i>i</i>)-N-C(<i>i'</i>) ^c	C(<i>i</i>)-N-C(<i>j</i>) ^c	Ref
1	4t (<i>D</i> _{2d})	1.529 (6)	1.500 (6)	114.3 (3)	110.8 (4)	113.5 (10)	106.6 (5)	110.9 (4)	This work
2	3t, 1g (<i>D</i> _{2d})	1.52 (1)	1.515 (10)	115.2 (4)	110.5 (8)	113.3 (5)	106.3 (5)	111.1 (8)	24
3	4t (<i>D</i> _{2d})	1.52 (1)	1.523 (8)	115.0 (10)	107.5 (11)	110.7 (6)	105.9 (9)	111.3 (5)	23
4	4t (<i>S</i> ₄)	1.54 (2)	1.54 (1)	113 (1)	106 (1)	108 (2)	110.5 (10)	109 (1)	26 ^d
5	2t, 2d (<i>D</i> _{2d})	1.54 (2)	1.52 (2)	112.5 (10)	110 (3)		104 (2)	112.5 (10)	25 ^d
6	4t (<i>D</i> _{2d})	1.56 (2)	1.56 (2)	111 (1)	105 (1)	108 (2)			20 ^d
7	3t, 1d (<i>S</i> ₄)	1.55 (3)	1.56 (2)	110 (2)	105 (2)	112 (3)	116.5 (10)	107 (1)	27 ^d

^a Standard errors in parentheses refer to the mean and were obtained from internal agreement. ^b The numbers of trans (t), gauche (g), or trans-gauche disordered (d) arms are given. Values for disordered arms were not included in the averages. The approximate point group is given in parentheses. ^c C(*i*) and C(*i'*) are carbon atoms attached to N and related by the unique twofold axis in the appropriate point group *D*_{2d} or *S*₄. ^d The contributions of hydrogen atoms to *F*_c were not included in these structures.

to the CH₂-CH₃ bond distances were made assuming the methyl group to ride on the methylene carbon. The corrected values are given at the bottom of Table VII. The largest correction was +0.047 Å to the shortest distance (C(19)-C(20), 1.481 Å) and the mean correction was 0.023 Å.

The same conformation (trans arms, *D*_{2d} point group) has been found previously^{20,23} or with some trans-gauche disorder of the arms,^{24,25} usually at the C_β-C_γ bond. Another conformation has been found^{26,27} in which the arms have the trans arrangement but are arranged about nitrogen with close to *S*₄ molecular symmetry. To regenerate the *D*_{2d} arrangement, an appropriate pair of arms must be rotated about their N-C_α bonds by 120° in the same sense. The relative energies of the two conformers must be similar as they both have the same number of 180 and 60° torsion angles about the nitrogen center. The two conformers fill space in very different ways: the *D*_{2d} molecule is relatively flat with its arms in square array in contrast to the tetrahedral array of the *S*₄ molecule. This confers on tetra-*n*-butylammonium a versatility to crystallize as the conformer best matching the packing requirements of the cation.

The geometries of tetra-*n*-butylammonium ions are compared in Table IX. The hydrogen atom contributions to the structure factors were not included in structures 4-7. In the first three structures where hydrogen atom contributions were included, the N-C and C-C bond distances are up to 0.06 Å shorter and the N-C-C and C-C-C bond angles several degrees larger than in the last four structures. In spite of this expected result, each determination shows the same trend in the relative magnitudes of the N-C_α-C_β, C_α-C_β-C_γ, and C_β-C_γ-C_δ angles. The C-N-C angles have been divided into two sets in Table IX. In each conformer the C(*i*)-N-C(*i'*) angles are bisected by the *S*₄ operation of both the point groups *S*₄ and *D*_{2d}. The six angles have been averaged together in former studies giving results close to 109.5°. The first three structures show a significant difference between the two angle classes of 4.5-5.4°. The two C(*i*)-N-C(*i'*) angles are here less than the others, whereas the *S*₄ conformation (structures 4 and 7) shows a reversed trend. The above angular trends must arise from the differing nonbonded force fields in each region of the molecule and it is clearly inappropriate to average the results having regard only to the chemical nature of the atoms.

Registry No. [(C₄H₉)₄N]₂[Fe(edt)₂]₂, 36841-25-5.

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