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### Bis(tetramethylammonium) tetra- $\mu_3$ -sulfido-tetrakis[(2,2-dimethylpropanethiolato-S)iron]: a heterocubane complex anion with crystallographically imposed $\bar{4}2m$ symmetry

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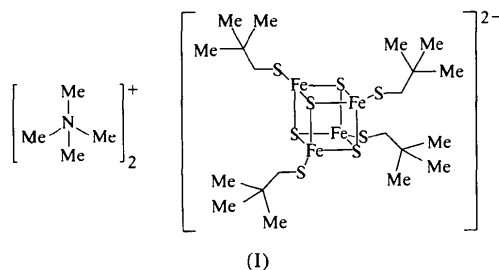
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#### Abstract

The title compound, (C<sub>4</sub>H<sub>12</sub>N)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(C<sub>5</sub>H<sub>11</sub>S)<sub>4</sub>], was prepared from iron(III) chloride by reaction with sodium 2,2-dimethylpropanethiolate, lithium sulfide and tetramethylammonium chloride in methanol. The anion has crystallographically imposed  $\bar{4}2m$  symmetry, giving rise to a compressed tetragonal arrangement of the Fe<sub>4</sub>S<sub>4</sub> core, with four short [2.246(2) Å] and eight long [2.289(2) Å] Fe—S distances.

#### Comment

Iron–sulfide–thiolate complexes of the general formula [Fe<sub>4</sub>S<sub>4</sub>(RS)<sub>4</sub>]<sup>n-</sup> (*n* = 1, 2 or 3) have been studied extensively due to their importance as model compounds for enzyme centres (Holm *et al.*, 1990) and in view of their interesting properties (Harris, 1989; Hoveyda & Holm, 1997; Noodleman *et al.*, 1995; Segal *et al.*, 1998; Zhou & Holm, 1997). The first structurally characterized example was described by Averill *et al.* (1972). Mixed iron–chalcogenide–chalcogenolate complexes of the general composition [Fe<sub>4</sub>X<sub>4</sub>(RY)<sub>4</sub>]<sup>n-</sup> (*X* = S, Se or Te; *Y* = S, Se or Te; *n* = 2 or 3) are also known (Bobrik *et al.*, 1978; Carney *et al.*, 1988; Henkel *et al.*, 1989). During our investigations of the iron–sulfide–thiolate reaction system, the title compound, [Me<sub>4</sub>N]<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(C<sub>5</sub>H<sub>11</sub>S)<sub>4</sub>], (I), was synthesized.



The structure of (I) consists of discrete [Fe<sub>4</sub>S<sub>4</sub>(C<sub>5</sub>H<sub>11</sub>S)<sub>4</sub>]<sup>2-</sup> anions and [Me<sub>4</sub>N]<sup>+</sup> counter-cations. The cations have their expected geometries, with N—C distances of 1.456(12) Å. The anion exhibits a cubane-type geometry, with a slightly compressed tetragonal [Fe<sub>4</sub>S<sub>4</sub>]<sup>2+</sup> core containing two sets of Fe—S distances: four are short [2.246(2)] and eight long [2.289(2)], giving an average of 2.275 Å. Compressed Fe<sub>4</sub>S<sub>4</sub> cubane cores have been observed in virtually all complexes containing iron in the mean oxidation state +2.5. For instance, in the chemically related anions [Fe<sub>4</sub>S<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>S)<sub>4</sub>]<sup>2-</sup> (Que *et al.*, 1974) and [Fe<sub>4</sub>S<sub>4</sub>(AdS)<sub>4</sub>]<sup>2-</sup> (AdS<sup>-</sup> = adamantanethiolate; Kambayashi *et al.*, 1992), the mean values of the Fe—S bond lengths are 2.267(5) and 2.252(16) Å, respectively, for the set of shorter ones, while the mean values of the longer ones are 2.296(4) and 2.315(10) Å, respectively. Compared with these values, the Fe—S distances observed here appear to be shortened. This shortening can most probably be traced back to a pronounced librational motion of the Fe<sub>4</sub>S<sub>8</sub> frame. A bond-length correction assuming rigid-body behaviour resulted in corrected values of 2.256 and 2.303 Å for the sets of shorter and longer bonds, respectively, and these values are in good agreement with the literature. The S—Fe—S angles occur as sets of four smaller [104.02(9)°] and eight larger [104.57(5)°] ones. The Fe—S—Fe angles are

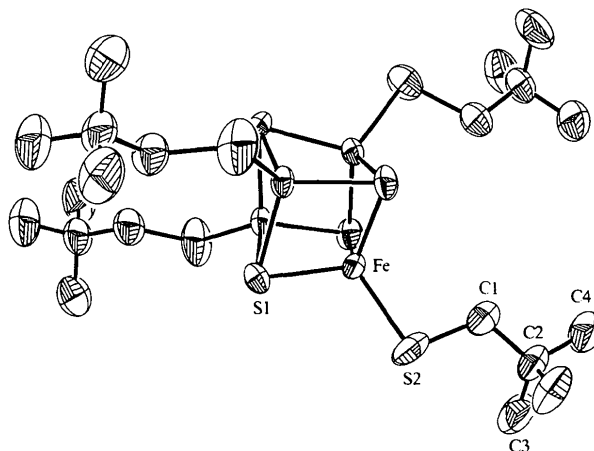


Fig. 1. The structure of the title complex anion, [Fe<sub>4</sub>S<sub>4</sub>(C<sub>5</sub>H<sub>11</sub>S)<sub>4</sub>]<sup>2-</sup>, shown with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

73.69 (8) ( $\times 8$ ) and 73.28 (6) $^\circ$  ( $\times 4$ ). The Fe $\cdots$ Fe distances are 2.745 (2) ( $\times 2$ ) and 2.706 (2) Å ( $\times 4$ ), giving an average of 2.719 Å. The mean S $\cdots$ S distance is 3.595 Å [3.609 (1) ( $\times 2$ ) and 3.588 (2) Å ( $\times 4$ )]. These values also correspond to those in [Fe<sub>4</sub>S<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>S)<sub>4</sub>]<sup>2-</sup>, where the mean Fe $\cdots$ Fe distance is 2.736 Å and the mean S $\cdots$ S distance is 3.592 Å. The Fe—S bonds to the terminal thiolate groups are 2.235 (3) Å in length.

### Experimental

All operations were performed under a nitrogen atmosphere in a glove-box. To a solution of sodium 2,2-dimethylpropane-thiolate (3.78 g, 30 mmol) in methanol (60 ml) was added iron(III) chloride (1.62 g, 10 mmol) dissolved in methanol (60 ml). The resulting brown reaction mixture was stirred for 30 min and then treated with lithium sulfide (0.45 g, 10 mmol). After stirring for a further 30 min, tetramethylammonium chloride (0.55 g, 5 mmol) was added and the resulting black slurry was filtered. Reducing the volume of the filtrate *in vacuo* to 50% and cooling to 275 K afforded the pure product as black crystals (0.94 g, 41%) after four days. One of these crystals was mounted on top of a glass capillary with grease and quickly put into the cold nitrogen stream of the cooling device of the goniometer.

### Crystal data

(C<sub>4</sub>H<sub>12</sub>N)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(C<sub>5</sub>H<sub>11</sub>S)<sub>4</sub>]  
*M<sub>r</sub>* = 912.72  
 Tetragonal  
*I*42*m*  
*a* = 11.495 (1) Å  
*c* = 19.134 (3) Å  
*V* = 2528.3 (5) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.199 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 18 reflections  
 $\theta$  = 10–20 $^\circ$   
 $\mu$  = 1.473 mm<sup>-1</sup>  
*T* = 150 K  
 Block  
 0.57 × 0.28 × 0.18 mm  
 Black

### Data collection

Siemens *P4-RA* diffractometer  
 $\omega$  scans  
 Absorption correction:  $\psi$  scan (*SHELXTL-Plus*; Sheldrick, 1990)  
*T<sub>min</sub>* = 0.550, *T<sub>max</sub>* = 0.767  
 1571 measured reflections  
 841 independent reflections

806 reflections with *F* > 4σ(*F*)  
*R<sub>int</sub>* = 0.035  
 $\theta_{\text{max}}$  = 27 $^\circ$   
*h* = 0 → 14  
*k* = 0 → 14  
*l* = 0 → 24  
 2 standard reflections every 98 reflections  
 intensity decay: none

### Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.055  
*wR*(*F*<sup>2</sup>) = 0.151  
*S* = 1.167  
 841 reflections  
 59 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0995P)^2 + 2.0754P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

( $\Delta/\sigma$ )<sub>max</sub> < 0.001  
 $\Delta\rho_{\text{max}}$  = 0.779 e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}}$  = -0.777 e Å<sup>-3</sup>  
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Fe	0.08442 (6)	0.08442	0.04928 (5)	0.0378 (4)
S1	0.1110 (1)	0.1110	-0.0659 (1)	0.0472 (5)
S2	0.1972 (2)	0.1972	0.1160 (2)	0.091 (1)
C1	0.1477 (7)	0.1477	0.2046 (6)	0.068 (3)
C2	0.2080 (7)	0.2080	0.2646 (6)	0.065 (3)
C3	0.187 (1)	0.3391 (9)	0.2624 (6)	0.095 (3)
C4	0.159 (1)	0.159	0.3327 (7)	0.090 (4)
N	1/2	0	1/2	0.079 (5)
C5	0.430 (2)	0.0775 (1)	0.4569 (8)	0.136 (6)

Table 2. Selected geometric parameters (Å,  $^\circ$ )

Fe—S2	2.235 (3)	Fe—Fe <sup>ii</sup>	2.706 (2)
Fe—S1	2.246 (2)	Fe—Fe <sup>iii</sup>	2.745 (2)
Fe—S1 <sup>i</sup>	2.289 (2)	S2—C1	1.877 (12)
S2—Fe—S1	113.79 (12)	Fe—S1—Fe <sup>i</sup>	73.28 (6)
S2—Fe—S1 <sup>i</sup>	114.37 (6)	Fe <sup>i</sup> —S1—Fe <sup>ii</sup>	73.69 (8)
S1—Fe—S1 <sup>i</sup>	104.57 (5)	C1—S2—Fe	99.5 (3)
S1 <sup>i</sup> —Fe—S1 <sup>ii</sup>	104.02 (9)		

Symmetry codes: (i)  $-y, x, -z$ ; (ii)  $y, -x, -z$ ; (iii)  $-x, -y, z$ .

An initial structural model was obtained by direct methods using *SHELXTL-Plus* (Sheldrick, 1990). The remaining atoms were obtained from difference Fourier maps, followed by least-squares refinement cycles. Refinements were performed using *SHELXL93* (Sheldrick, 1993). After anisotropic refinement of this model, H atoms were added at idealized positions. One common isotropic displacement parameter was refined for the riding H atoms.

Data collection: *P3* (Siemens, 1991*a*). Cell refinement: *P3*. Data reduction: *XDISK* (Siemens, 1991*b*). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL93*.

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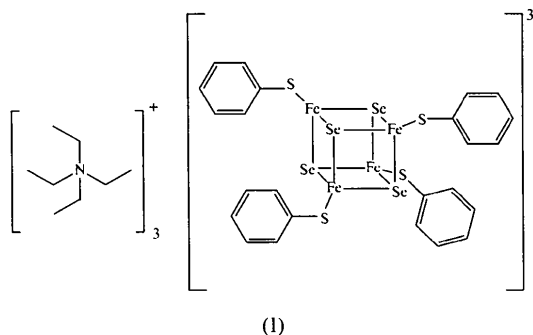
Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1305). Services for accessing these data are described at the back of the journal.

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During our investigations of iron–selenide–thiolate complexes, we were able to synthesize  $[Et_4N]_3[Fe_4Se_4(SPh)_4]$ , (I), by reaction of  $[Et_4N]_2[FeCl_4]$  with sodium thiophenolate and lithium selenide. In this mixed-



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### Tris(tetraethylammonium) tetra- $\mu_3$ -selenido-tetrakis[(thiophenolato-S)iron]

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#### Abstract

The title compound,  $[Et_4N]_3[Fe_4Se_4(SPh)_4]$ , comprises a mixed iron–selenium cubane unit, which is slightly elongated. The  $[Fe_4Se_4(SPh)_4]^{3-}$  anion contains iron in the mean oxidation state +2.25.

#### Comment

Iron–sulfide–thiolate complexes of general formula  $[Fe_4S_4(SR)_4]^{n-}$  ( $n = 1, 2,$  and  $3$ ) have been studied extensively due to their importance in many biological processes (Holm *et al.*, 1990; Krebs & Henkel, 1991; Holm, 1992; Harris, 1989). In view of their interesting electrochemical and magnetic properties, the analogous iron–chalcogenide–chalcogenolate complexes were also investigated (Bobrik *et al.*, 1978; Carney *et al.*, 1988; Henkel *et al.*, 1989). The characteristic feature of these compounds is a central cubane-like  $Fe_4E_4$  core ( $E = S, Se$  or  $Te$ ).

valence electronically delocalized compound, the mean oxidation state of iron is +2.25. The crystal structure consists of discrete  $[Fe_4Se_4(SPh)_4]^{3-}$  anions and  $[Et_4N]^+$  counter-cations in their expected geometries. There are two independent cations in the structure, one of which sits across a twofold axis. The N—C distances occur in the range 1.49 (1)–1.52 (1) Å. The anion has a crystallographically imposed twofold axis, which passes through the centroids of opposite non-planar  $Fe_2Se_2$  faces of the  $\{Fe_4Se_4\}^+$  core. The Fe atoms are coordinated by three Se and one S atom in a distorted tetrahedral manner. The central cubane unit is slightly elongated, with eight shorter and four longer Fe—Se distances. The average of the shorter ones, which occur in the range 2.396 (1)–2.425 (1) Å, is 2.408 (5) Å. The longer Fe—Se distances are 2.488 (1) (2 ×) and 2.522 (1) Å (2 ×), giving an average of 2.505 (9) Å. This value is very close to that observed in the tetramethylammonium salt determined at ambient temperature (Carney *et al.*, 1988), but is significantly larger than in the oxidized  $[Fe_4Se_4(SPh)_4]^{2-}$  complex anion (Bobrik *et al.*, 1978), where the mean Fe—Se distances are 2.385 (2) and 2.417 (5) Å. This result is expected because the mean oxidation state of iron is raised from +2.25 to +2.50. In contrast to the  $\{Fe_4E_4\}^{2+}$  cores ( $E = S, Se$  or  $Te$ ), which are compressed in all cases known so far, the stereochemistry of  $\{Fe_4E_4\}^+$  units in the crystalline state is much more complicated. In the literature, compressed as well as elongated cubanes of the latter type have been described (Ciurli *et al.*, 1990; Yu *et al.*, 1991). In our case, the  $\{Fe_4Se_4\}^+$  core is elongated. The Fe—Fe distances range from 2.675 (1) to 2.780 (2) Å, giving an average of 2.740 (19) Å. This value is virtually identical to the value observed in the tetramethylammonium salt. The mean Fe—S bond length involving the terminal thiolate groups [2.296 (2) Å] is comparable to that observed in the  $[Me_4N]^+$  salt [2.302 (8) Å], but is significantly longer than that found in the oxidized species [2.273 (7) Å].