SHORT-FORMAT PAPERS

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Structure of Bis(tetra-*n*-butylammonium) 1,2,3;1,2,4;1,3,4;2,3,4-Tetra-μ_3-sulfido-tetrakis[(benzenethiolato)iron]

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Abstract. $[N(n\text{-}C_4H_9)_4]_2[Fe_4(C_6H_5S)_4S_4]$, $M_r = 1273{\cdot}2$, monoclinic, $P2_1/n$, $a = 11{\cdot}929\,(2)$, $b = 23{\cdot}63\,(1)$, $c = 23{\cdot}78\,(2)$ Å, $\beta = 91{\cdot}77\,(4)°$, $V = 6700\,(6)$ Å^3, $D_m(\text{KI/H}_2\text{O}) = 1{\cdot}260$, $D_x = 1{\cdot}262$ g cm^{-3}, $Z = 4$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 11{\cdot}22$ cm^{-1}, $F(000) = 2696$, $T = 293$ K, final $R = 0{\cdot}077$ and wR (on $|F_o|^2$) $= 0{\cdot}092$ for 4223 observed reflections. The structure comprises ordered cations and anions and is similar to that of $[N(CH_3)_4]_2[Fe_4(C_6H_5S)_4S_4]$ [Que, Bobrik, Ibers & Holm (1974). *J. Am. Chem. Soc.* **96**, 4168–4178], the principal difference occurring in the detailed geometry of the Fe$_4$ portion of the $Fe_4S_4^*$ core, which in the title compound closely approaches C_{3v} symmetry. The measured Fe⋯Fe contacts fall into two sets of three [2·725 (2) and 2·747 (2) Å], in contrast to the mean value of 2·736 (3) Å for the Fe$_4$ unit of T_d symmetry in the $[N(CH_3)_4]^+$ analogue.

Experimental. The title compound was obtained as a by-product of the anaerobic reaction between $(NH_4)_2MoS_4$, $FeCl_2$, $FeCl_3$, Et_3N, NaSH, NaSPh (1:4:2:2:2:8) in dimethylformamide/methanol (1:2 v/v) followed by addition of excess $(n\text{-Bu})_4NI$, recrystallized as red–black needles from hot acetonitrile. Single crystal of size 0·44 × 0·20 × 0·20 mm, mean $\mu r = 0{\cdot}15$, Nicolet *R*3*m* diffractometer, cell parameters from 2θ values of 21 reflections with $15 \le 2\theta \le 25°$ (Sparks, 1976), ω–2θ scan at 2·02–8·37° min^{-1}, scan range 0·5° below $K\alpha_1$ to 0·5° above $K\alpha_2$, stationary background counts for half of scan time at each end, $2\theta_{\max} = 40°$,† $0 \le h \le 11$, $0 \le k \le 22$, $-22 \le l \le 22$, intensities of two standards monitored every 125 data measurements were within ±1%, 5764 independent reflections measured, profile fitting of raw intensities (Diamond, 1969), 4223 observed with $|F_o| > 3\sigma(|F_o|)$, empirical absorption correction based on ψ scans of 16 strong reflections (North, Phillips & Mathews, 1968; Kopfmann & Huber, 1968), transmission factors 0·666–0·695. The structure was solved by the direct method guided by negative quartets (DeTitta, Edmonds, Langs & Hauptman, 1975), weighting function $w = [\sigma^2(|F_o|) + 0{\cdot}0015\,|F_o|^2]^{-1}$, Fe and S atoms anisotropic, C and N atoms isotropic, all H atoms included in structure factor calculation with fixed isotropic temperature factors, the methylene H atoms ride on parent C atoms, methyl and phenyl groups treated as rigid groups, final R (317 variables) $= 0{\cdot}077$, wR (on $|F_o|^2$) $= 0{\cdot}092$, $S = 1{\cdot}533$, $(\Delta/\sigma)_{\max} = 0{\cdot}004$, extrema in final difference map +0·67 to −0·56 e Å^{-3}, atomic scattering factors from *International Tables for X-ray Crystallography* (1974), calculations on Data General Nova 3/12 minicomputer using *SHELXTL* (Sheldrick, 1982). The atomic parameters are listed in Table 1,* and selected bond distances and angles in Table 2, in accordance with the atom-numbering scheme shown in Fig. 1.

Related literature. Several well known ferredoxin model compounds have been studied, and recent attention has been focused on those bearing sterically hindered thiolato ligands in view of their unusual properties (Ueyama, Sugawara, Fuji, Nakamura & Yasuoka, 1985). An EPR study of a $CoFe_3S_4$ cluster in cobalt-doped $[N(n\text{-Bu})_4]_2[Fe_4S_4(SPh)_4]$ single crystals has just appeared (Gloux, Gloux & Rius, 1986).

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† The intensities fell off rapidly with increasing Bragg angle owing to poor crystallinity, with consequent high final R value.

* Lists of structure factors, anisotropic thermal parameters and hydrogen coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43406 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* (× 10^5 *for* Fe; × 10^4 *for other atoms*) *and thermal parameters* (Å^2 × 10^3)

	x	*y*	*z*	U_{eq} or U_{iso}
$[Fe_4(C_6H_5S)_4S_4]^{2-}$ anion				
Fe(1)	40133 (13)	29615 (7)	22731 (7)	59 (1)*
Fe(2)	40123 (13)	19176 (7)	27648 (7)	60 (1)*
Fe(3)	23233 (13)	22234 (7)	20153 (7)	61 (1)*
Fe(4)	24638 (13)	27171 (7)	30608 (7)	62 (1)*
S(1)	2135 (3)	1786 (1)	2876 (1)	67 (1)*
S(2)	2159 (3)	3165 (1)	2208 (1)	67 (1)*
S(3)	4363 (3)	2754 (1)	3218 (1)	67 (1)*
S(4)	4166 (3)	2122 (1)	1823 (1)	65 (1)*
S(5)	5248 (3)	3655 (1)	2088 (2)	75 (1)*
S(6)	5222 (3)	1184 (1)	2886 (2)	79 (1)*
S(7)	1038 (3)	1811 (2)	1429 (2)	82 (1)*
S(8)	1351 (3)	3205 (2)	3650 (2)	83 (1)*
C(1)	5899 (7)	4230 (4)	1184 (4)	121 (5)
C(2)	5810 (7)	4426 (4)	631 (4)	155 (7)
C(3)	4921 (7)	4250 (4)	280 (4)	142 (6)
C(4)	4119 (7)	3877 (4)	481 (4)	135 (6)
C(5)	4208 (7)	3681 (4)	1034 (4)	93 (4)
C(6)	5097 (7)	3858 (4)	1386 (4)	83 (4)
C(7)	4782 (8)	1302 (4)	4014 (6)	164 (7)
C(8)	4935 (8)	1144 (4)	4577 (6)	218 (10)
C(9)	5639 (8)	692 (4)	4721 (6)	170 (8)
C(10)	6190 (8)	398 (4)	4303 (6)	208 (10)
C(11)	6037 (8)	555 (4)	3741 (6)	184 (9)
C(12)	5333 (8)	1007 (4)	3596 (6)	77 (4)
C(13)	2234 (7)	2267 (4)	560 (4)	117 (5)
C(14)	2316 (7)	2484 (4)	17 (4)	138 (6)
C(15)	1354 (7)	2544 (4)	−327 (4)	136 (6)
C(16)	311 (7)	2386 (4)	−128 (4)	145 (7)
C(17)	230 (7)	2169 (4)	415 (4)	115 (5)
C(18)	1192 (7)	2110 (4)	759 (4)	71 (4)
C(19)	562 (7)	3012 (4)	4695 (4)	121 (6)
C(20)	507 (7)	2732 (4)	5210 (4)	130 (6)
C(21)	1235 (7)	2284 (4)	5334 (4)	143 (6)
C(22)	2019 (7)	2117 (4)	4943 (4)	164 (8)
C(23)	2074 (7)	2397 (4)	4429 (4)	110 (5)
C(24)	1345 (7)	2845 (4)	4305 (4)	81 (4)
$[N(n\text{-}C_4H_9)_4]^+$ ion (I)				
N(1)	8174 (8)	2637 (4)	2638 (4)	77 (3)
C(25)	7386 (11)	2328 (5)	2256 (5)	87 (4)
C(26)	7902 (11)	1991 (6)	1796 (6)	102 (5)
C(27)	7079 (12)	1619 (6)	1489 (6)	118 (5)
C(28)	7534 (15)	1307 (7)	1004 (7)	147 (7)
C(29)	8917 (11)	2231 (5)	2991 (5)	90 (4)
C(30)	8255 (12)	1828 (6)	3362 (6)	119 (5)
C(31)	9113 (19)	1553 (9)	3864 (9)	237 (11)
C(32)	9398 (22)	1193 (10)	3611 (10)	268 (13)
C(33)	7482 (10)	3000 (5)	3018 (5)	83 (4)
C(34)	8040 (12)	3352 (6)	3459 (6)	119 (5)
C(35)	7246 (13)	3735 (6)	3755 (6)	129 (6)
C(36)	7770 (18)	4085 (8)	4216 (9)	204 (9)
C(37)	8998 (11)	3000 (5)	2326 (5)	93 (4)
C(38)	8460 (13)	3468 (6)	1969 (6)	130 (6)
C(39)	9349 (15)	3862 (7)	1686 (7)	165 (8)
C(40)	9513 (21)	3546 (11)	1241 (9)	255 (12)
$[N(n\text{-}C_4H_9)_4]^+$ ion (II)				
N(2)	3092 (9)	4983 (4)	2984 (5)	95 (4)
C(41)	3342 (12)	4486 (5)	3383 (6)	99 (5)
C(42)	3687 (15)	4629 (8)	3969 (7)	152 (7)
C(43)	3992 (20)	4110 (10)	4333 (10)	204 (10)
C(44)	4403 (22)	4280 (10)	4867 (11)	255 (13)
C(45)	2145 (12)	5359 (6)	3211 (6)	108 (5)
C(46)	1063 (13)	5063 (6)	3305 (7)	125 (6)
C(47)	253 (15)	5450 (7)	3628 (7)	153 (7)
C(48)	620 (20)	5592 (10)	4214 (9)	239 (11)
C(49)	2759 (12)	4737 (5)	2427 (5)	97 (5)
C(50)	2574 (14)	5171 (7)	1956 (7)	136 (6)
C(51)	2326 (17)	4881 (8)	1410 (8)	181 (8)
C(52)	2490 (20)	5214 (10)	940 (11)	249 (12)
C(53)	4115 (11)	5363 (6)	2953 (6)	101 (5)
C(54)	5150 (12)	5080 (6)	2746 (7)	122 (6)
C(55)	6200 (15)	5409 (7)	2791 (8)	159 (7)
C(56)	7219 (15)	5132 (8)	2603 (8)	160 (7)

* U_{eq} calculated as one-third of the trace of the orthogonalized **U** tensor. Exponent of the isotropic temperature factor takes the form: $-8\pi^2U_{iso}\sin^2\theta/\lambda^2$.

Table 2. *Selected bond distances* (Å) *and angles* (°) *for the* $[Fe_4(C_6H_5S)_4S_4]^{2-}$ *ion*

Fe(1)···Fe(2)	2·725 (2)	Fe(2)···Fe(3)	2·745 (2)
Fe(1)···Fe(3)	2·724 (2)	Fe(2)···Fe(4)	2·749 (2)
Fe(1)···Fe(4)	2·725 (2)	Fe(3)···Fe(4)	2·747 (2)
Fe(1)–S(2)	2·265 (3)	Fe(2)–S(1)	2·285 (3)
Fe(1)–S(3)	2·313 (4)	Fe(2)–S(3)	2·284 (3)
Fe(1)–S(4)	2·271 (3)	Fe(2)–S(4)	2·305 (4)
Fe(3)–S(1)	2·310 (4)	Fe(4)–S(1)	2·276 (3)
Fe(3)–S(2)	2·281 (3)	Fe(4)–S(2)	2·306 (4)
Fe(3)–S(4)	2·273 (3)	Fe(4)–S(3)	2·287 (5)
Fe(1)–S(5)	2·258 (4)	Fe(2)–S(6)	2·269 (4)
Fe(3)–S(7)	2·260 (4)	Fe(4)–S(8)	2·273 (4)
S(5)–C(6)	1·74 (1)	S(6)--C(12)	1·74 (1)
S(7)–C(18)	1·76 (1)	S(8)–C(24)	1·77 (1)

S(2)–Fe(1)–S(3)	105·2 (1)	S(5)–Fe(1)–S(2)	118·3 (1)
S(2)–Fe(1)–S(4)	104·1 (1)	S(5)–Fe(1)–S(3)	104·3 (1)
S(3)–Fe(1)–S(4)	105·1 (1)	S(5)–Fe(1)–S(4)	118·4 (1)
S(1)–Fe(2)–S(3)	103·3 (1)	S(6)–Fe(2)–S(1)	120·2 (1)
S(1)–Fe(2)–S(4)	104·4 (1)	S(6)–Fe(2)–S(3)	119·7 (1)
S(3)–Fe(2)–S(4)	105·0 (1)	S(6)–Fe(2)–S(4)	102·4 (1)
S(1)–Fe(3)–S(2)	104·3 (1)	S(7)–Fe(3)–S(1)	105·7 (1)
S(1)–Fe(3)–S(4)	104·6 (1)	S(7)–Fe(3)–S(2)	118·9 (2)
S(2)–Fe(3)–S(4)	103·5 (1)	S(7)–Fe(3)–S(4)	118·2 (1)
S(1)–Fe(4)–S(2)	104·6 (1)	S(8)–Fe(4)–S(1)	120·6 (1)
S(1)–Fe(4)–S(3)	103·5 (1)	S(8)–Fe(4)–S(2)	103·3 (1)
S(2)–Fe(4)–S(3)	104·7 (1)	S(8)–Fe(4)–S(3)	118·3 (1)
Fe(2)–S(1)–Fe(3)	73·4 (1)	Fe(1)–S(2)–Fe(3)	73·6 (1)
Fe(2)–S(1)–Fe(4)	74·1 (1)	Fe(1)–S(2)–Fe(4)	73·2 (1)
Fe(3)–S(1)–Fe(4)	73·6 (1)	Fe(3)–S(2)–Fe(4)	73·6 (1)
Fe(1)–S(3)–Fe(2)	72·7 (1)	Fe(1)–S(4)–Fe(2)	73·1 (1)
Fe(1)–S(3)–Fe(4)	72·7 (1)	Fe(1)–S(4)–Fe(3)	73·7 (1)
Fe(2)–S(3)–Fe(4)	73·9 (1)	Fe(2)–S(4)–Fe(3)	73·7 (1)
Fe(1)–S(5)–C(6)	110·0 (3)	Fe(2)–S(6)–C(12)	109·6 (4)
Fe(3)–S(7)–C(18)	107·3 (3)	Fe(4)–S(8)–C(24)	108·4 (3)

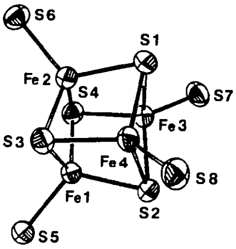

Fig. 1. Perspective view and atom labelling of the $Fe_4S_4^*S_4$ core in the $[N(n\text{-}C_4H_9)_4]_2[Fe_4(C_6H_5S)_4S_4]$ complex. The thermal ellipsoids are drawn at the 35% probability level.

References

DeTitta, G. T., Edmonds, J. W., Langs, D. A. & Hauptman, H. (1975). *Acta Cryst.* A**31**, 472–479.

Diamond, R. (1969). *Acta Cryst.* A**25**, 43–55.

Gloux, J., Gloux, P. & Rius, G. (1986). *J. Am. Chem. Soc.*, **108**, 3541–3542.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 55, 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Kopfmann, G. & Huber, R. (1968). *Acta Cryst.* A**24**, 348–351.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Que, L., Bobrik, M. A., Ibers, J. A. & Holm, R. H. (1974). *J. Am. Chem. Soc.* **96**, 4168–4178.

Sheldrick, G. M. (1982). In *Computational Crystallography*, edited by D. Sayre, pp. 506–514. Oxford Univ. Press.

Sparks, R. A. (1976). In *Crystallographic Computing Techniques*, edited by F. R. Ahmed, pp. 452–467. Copenhagen: Munksgaard.

Ueyama, N., Sugawara, T., Fuji, M., Nakamura, A. & Yasuoka, N. (1985). *Chem. Lett.* pp. 175–178, and references cited therein.