January, 1991] © 1991 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 64, 11—15 (1991)

Crystal Structures of Polymorphic $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)$

Mamoru Shimoi,* Asako Satoh, and Hiroshi Ogino*
Department of Chemistry, Faculty of Science, Tohoku University,
Aoba-ku, Sendai 980
(Received June 30, 1990)

$[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)$ crystals showed polymorphism depending on the recrystallization conditions. Recrystallization from acetonitrile–H_2O solution gave monoclinic crystals: $C2/c$ with lattice constants $a=18.555(2)$, $b=7.650(1)$, $c=17.850(3)$ Å, $\beta=96.81(2)°$, and $Z=4$. Recrystallization from *N,N*-dimethylacetamide–ether solution gave tetragonal crystals: $I\bar{4}$ with lattice constants $a=12.917(2)$, $c=7.637(1)$ Å, and $Z=2$. Molecular structures of both crystal systems are almost the same as each other, if the structure for the latter was analyzed assuming that enantiomeric cations are disordered.

Cubane type metal clusters $[M_4L_4X_4]$ are known for many kinds of metals, terminal ligands L, and bridging ligands X.[1)] Among them $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{n+}$ as well as $[Fe_4(\eta^5\text{-}C_5H_5)_4Se_4]^{n+}$ have been studied in relation to the structures of clusters and their oxidation states.[1—6)] Molecular orbital calculation showed that $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^+$ has a lower symmetry, D_2, than the D_{2d} symmetries of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ and $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{2+}$ due to a first-order Jahn–Teller effect.[5)] In fact, Dahl et al. reported that the Fe_4 core of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ Br has D_2 symmetry.[4)]

In the course of our study for isolation of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{n+}$ species,[7)] we found polymorphism of the hexafluorophosphate of the monocation: monoclinic and tetragonal. As will be shown below, the space group of the tetragonal crystal was determined to be $I\bar{4}$. This space group would impose D_{2d} symmetry on the cation, which contradicts the molecular orbital calculation. To elucidate the origin of this discrepancy, we undertook the X-ray crystal structure analyses for both forms.

Experimental

Materials. $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ (PF_6) was prepared as described in a preceding report.[7)]

Crystal Structure Determination of Monoclinic $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ (PF_6). An acetonitrile solution of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ (PF_6) was layered on water in a test tube and allowed to stand for 5 days. The slow diffusion of water into acetonitrile gave black crystals with parallelepiped shape. A crystal with the dimensions 0.1×0.1×0.3 mm was used for the collection of intensity data. The data with $3<2\theta/°<60$ were collected with Mo $K\alpha$ radiation monochromated by graphite, applying ω–2θ scan mode with the use of a Rigaku AFC-6A automated four-circle diffractometer. The unit cell dimensions were determined by the least-squares method with 71 reflection data $(25<2\theta/°<30)$. The crystal data are listed in Table 1. The probable space group is either Cc or $C2/c$ according to the systematic absence. The successful

Table 1. Crystal Data of Monoclinic and Tetragonal $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)$

Formula	$C_{20}H_{20}F_6Fe_4PS_4$	$C_{20}H_{20}F_6Fe_4PS_4$
Formula weight	756.99	756.99
Crystal system	Monoclinic	Tetragonal
Space group	$C2/c$	$I\bar{4}$
Systematic absence	$h\ k\ l$: $h+k=2n+1$ $h\ 0\ l$: $l=2n+1$	$h\ k\ l$: $h+k+l=2n+1$
a/Å	18.555 (2)	12.917 (2)
b/Å	7.650 (1)	
c/Å	17.850 (3)	7.637 (1)
β/°	96.81 (2)	
Z	4	2
V/Å^3	2515.9 (7)	1274.2 (3)
D_m/g cm^{-3}	2.00	1.98
D_c/g cm^{-3}	2.00	1.97
μ(Mo $K\alpha$)/cm^{-1}	27.5	27.1
Crystal size/mm	0.1×0.1×0.3	0.1×0.2×0.3
Scan mode	2θ–ω	2θ–ω
$2\theta_{max}$/°	60	60
Reflcns measd	$\pm h, k, l$	h, k, l
No. of reflcns measd	4758	2150
No. of reflcns used ($\lvert F_o\rvert>3\sigma(F_o)$)	2309	590
$R^{a)}$	0.053	0.052
$R_w^{b)}$	0.067	0.052

a) $R=\Sigma\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$. b) $R_w=[\Sigma w(\lvert F_o\rvert-\lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$; $w=[\sigma^2(\lvert F_o\rvert)+aF_o^2]^{-1}$, where $a=0.0015$ for monoclinic $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)$. Unit weighting scheme was applied for tetragonal $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)$.

refinement justified the choice of the latter centrosymmetric space group. The conventional heavy atom method was used: A Patterson function gave the positions of two iron atoms, two sulfur atoms, and a phosphorus atom. Other non-hydrogen atoms were located by successive block-diagonal least-squares and Fourier syntheses. Anisotropic temperature factors were applied to non-hydrogen atoms. The hydrogen atoms were located from a difference Fourier synthesis and refined with isotropic temperature factors. Convergence was reached at R=0.053 and R_w=0.067. A final difference Fourier synthesis was virtually featureless.

Crystal Structure Determination of Tetragonal $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ (PF_6). Black columnar tetragonal crystals were obtained by slow diffusion of diethyl ether into a *N,N*-dimethylacetamide solution of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ (PF_6). A crystal with the dimensions 0.1×0.2×0.3 mm was used for the collection of the intensity data. Crystal data is also included in Table 1. Of the possible space groups, $I4$, $I\bar{4}$, and $I4/m$ according to the systematic absence, $I\bar{4}$ was chosen because a four-fold axis cannot be imposed on the cubane cluster. The structure was solved by the heavy atom method: the positions of each one of the iron and sulfur atoms were obtained from a Patterson function, and the positions of carbon, phosphorus, and fluorine atoms were deduced from successive least-squares and Fourier syntheses. However, unrestricted refinement gave quite large thermal parameters. Therefore the crystal was considered to be disordered. Each atom except for the phosphorus atom on a special position was divided into two halves applying 50% occupancy factors for each atom, for the reason mentioned in the discussion. Anisotropic temperature factors were applied for iron, sulfur, and phosphorus atoms and isotropic ones for carbon and fluorine atoms. The final R value was 0.052.

All the calculations were carried out on an NEC ACOS-2000 computer at the computer center of Tohoku University, using Universal Crystallographic Computation Program System UNICS III.[8] The atomic scattering factors were taken from Ref. 9 for non-hydrogen atoms and from Ref. 10 for hydrogen atoms.

Table 2. Final Atomic Parameters for Monoclinic $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)$
(Coordinates are multiplied by 10^4.)

Atom	x	y	z	$B_{eq}/Å^2$
Fe(1)	168.6 (4)	2296.4 (10)	1610.6 (4)	2.8
Fe(2)	890.3 (4)	−24.9 (9)	2517.4 (4)	2.6
S(1)	−66.6 (7)	−496 (2)	1683.6 (8)	2.8
S(2)	768.1 (7)	2773 (2)	2732.7 (8)	3.1
C(11)	−315 (4)	3831 (10)	712 (4)	4.6
C(12)	263 (4)	4742 (8)	1105 (4)	4.4
C(13)	893 (4)	3766 (10)	1040 (4)	4.6
C(14)	701 (4)	2290 (10)	612 (4)	5.2
C(15)	−54 (4)	2358 (10)	408 (4)	5.3
C(21)	1558 (3)	−1705 (10)	1947 (4)	4.5
C(22)	1431 (3)	−2392 (8)	2654 (5)	4.7
C(23)	1722 (3)	−1236 (10)	3219 (4)	4.9
C(24)	2027 (3)	151 (10)	2864 (5)	5.3
C(25)	1930 (3)	−124 (10)	2093 (4)	4.8
P(1)	2500	2500	5000	4.8
F(1)	2060 (3)	3820 (9)	5450 (3)	8.5
F(2)	2845 (3)	1666 (9)	5770 (3)	8.0
F(3)	1839 (3)	1206 (9)	4970 (4)	9.5

Results and Discussion

Description of the Crystal Structure of Monoclinic $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ (PF_6). The positional and equivalent isotropic temperature factors are listed in Table 2. The bond lengths and angles are listed in Table 3.[11] The structure of the cubane cation is shown in Fig. 1. A crystallographic C_2 axis passes through the centers of the Fe(1)–Fe(1′) and Fe(2)–Fe(2′) bonds. Thus the Fe(1)–Fe(2) bond is equivalent to the Fe(1′)–Fe(2′) bond and the Fe(1)–Fe(2′) bond is equivalent to the Fe(1′)–Fe(2) bond. Furthermore, the interatomic distances of Fe(1)–Fe(1′) and Fe(2)–Fe(2′) are almost the same (3.308 (4) and 3.297 (2) Å). Therefore, the Fe_4 core has approximate D_2 symmetry: opposite bonds of the tetrahedron are equivalent. This feature is compatible with the structure predicted by a molecular orbital calculation.[5] Due to a first-order Jahn–Teller effect, $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^+$ should have D_2 symmetry which is lower than the D_{2d} symmetry of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ and $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{2+}$.[5] Nineteen cluster

Table 3. Selected Bond Lengths (l) and Bond Angles (ϕ) for Monoclinic $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)$

Bond length	(l/Å)	Bond length	(l/Å)
Fe(1)–Fe(1′)	3.308 (4)	Fe(1)–Fe(2′)	3.188 (2)
Fe(2)–Fe(2′)	3.297 (2)	Fe(1)–Fe(2)	2.656 (2)
Fe(1)–S(1)	2.187 (2)	Fe(2)–S(1)	2.207 (2)
Fe(2)–S(2)	2.191 (2)	Fe(2′)–S(1)	2.240 (3)
Fe(1)–S(2)	2.203 (3)	Fe(1)–S(2′)	2.239 (3)
Bond angle	**(ϕ/°)**	**Bond angle**	**(ϕ/°)**
S(1)–Fe(1)–S(2)	100.97 (11)	S(1)–Fe(2)–S(1′)	81.26 (9)
S(1)–Fe(2)–S(2)	100.73 (8)	S(2)–Fe(2)–S(1′)	87.30 (9)
Fe(1)–S(1)–Fe(2)	74.36 (6)	Fe(1)–S(1)–Fe(2′)	92.11 (8)
Fe(1)–S(2)–Fe(2)	74.36 (9)	Fe(2)–S(1)–Fe(2′)	95.71 (13)
S(1)–Fe(1)–S(2′)	87.43 (8)	Fe(1)–S(2)–Fe(1′)	96.28 (8)
S(2)–Fe(1)–S(2′)	80.60 (12)	Fe(2)–S(2)–Fe(1′)	92.04 (8)
Fe(1′)–Fe(1)–Fe(2)	63.52 (6)	Fe(2′)–Fe(1)–Fe(2)	68.00 (4)
Fe(1′)–Fe(1)–Fe(2′)	48.22 (5)	Fe(1)–Fe(2′)–Fe(2)	48.31 (3)
Fe(1′)–Fe(2′)–Fe(2)	63.69 (3)	Fe(1′)–Fe(2′)–Fe(1)	68.26 (4)

Table 4. Comparison of Bond Lengths (l) and Bond Angles[a] (ϕ) between $[\mathrm{Fe_4}(\eta^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}]\mathrm{Br}$ and Monoclinic and Tetragonal $[\mathrm{Fe_4}(\eta^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}](\mathrm{PF_6})$

Bond length[d]	$[\mathrm{Fe_4}(\eta^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}]\mathrm{Br}$[b] l/Å	Monoclinic $[\mathrm{Fe_4}(\eta^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}](\mathrm{PF_6})$[c] l/Å	Tetragonal $[\mathrm{Fe_4}(\eta^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}](\mathrm{PF_6})$[c] l/Å
Fe(1)-Fe(1′)	3.319 (3)	3.303 (3)[a]	3.302 (6)[a]
Fe(1)-Fe(2′)	3.188 (3)	3.188 (2)	3.213 (4)
Fe(1)-Fe(2)	2.652 (5)[a]	2.656 (2)	2.631 (4)
Fe(1)-S(1)	2.186 (5)	2.187 (2)	2.178 (6)
Fe(2)-S(1)	2.210 (5)	2.207 (2)	2.147 (6)
Fe(1)-S(2)	2.214 (5)	2.203 (3)	2.238 (6)
Fe(2)-S(2)	2.183 (5)	2.191 (2)	2.211 (6)
Fe(1)-S(2′)	2.245 (5)	2.239 (3)	2.278 (6)
Fe(2′)-S(1)	2.246 (5)	2.240 (3)	2.227 (7)
Bond angle	ϕ/°	ϕ/°	ϕ/°
S(1)-Fe(1)-S(2)	100.9 (2)	100.85 (10)	101.12 (22)
Fe(1)-S(1)-Fe(2)	74.2 (2)	74.36 (8)	73.74 (19)
S(1)-Fe(1)-S(2′)	87.5 (2)	87.37 (9)	86.75 (22)
S(2)-Fe(1)-S(2′)	80.5 (2)	80.93 (11)	81.04 (23)
Fe(1)-S(1)-Fe(2′)	92.1 (2)	92.08 (8)	92.53 (21)
Fe(2)-S(1)-Fe(2′)	96.3 (2)	96.00 (11)	95.98 (24)

a) Average value. b) Ref. 4. c) This work. d) The atomic numbering schemes for the bromide and the tetragonal hexafluorophosphate are made to coincide with monoclinic $[\mathrm{Fe_4}(\eta^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}](\mathrm{PF_6})$.

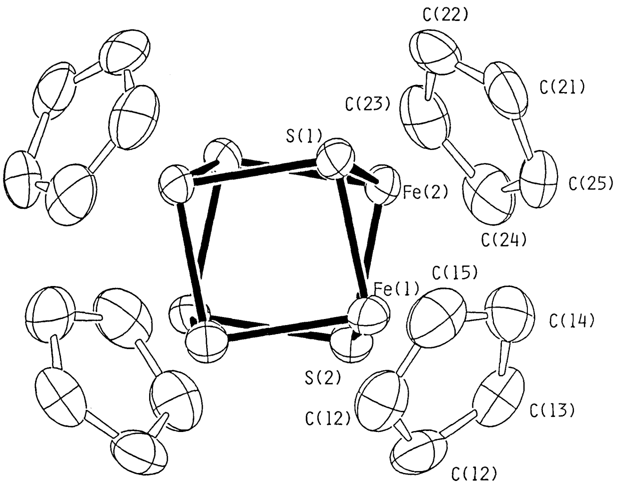

Fig. 1. ORTEP diagram of $[\mathrm{Fe_4}(\eta^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}]^+$ ion in the monoclinic hexafluorophosphate. Hydrogen atoms are omitted for clarity.

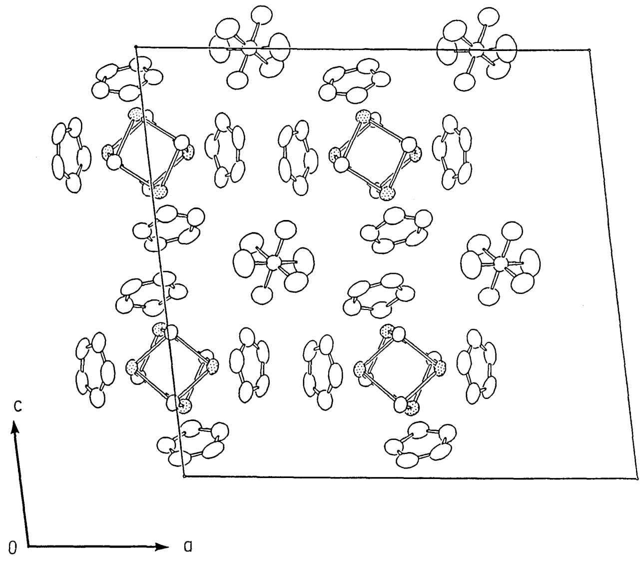

Fig. 2. Packing diagram of monoclinic $[\mathrm{Fe_4}(\eta^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}](\mathrm{PF_6})$.

electrons in $[\mathrm{Fe_4}(\eta^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}]^+$ result in a total Fe–Fe bond order of 2.5 for $\mathrm{Fe_4}$ core. The two shortest Fe–Fe bonds (Fe(1)–Fe(2) and Fe(1′)–Fe(2′) are 2.656 (2) Å) correspond to those with bond order 1; the next shortest Fe–Fe bonds (Fe(1)–Fe(2′) and Fe(1′)–Fe(2) are 3.188 (2) Å) correspond to those with bond order 0.25, and the longest bonds (Fe(1)–Fe(1′) and Fe(2)– Fe(2′)), to those with bond order 0.

The structure is quite similar to that already reported for the monocation complex, $[\mathrm{Fe_4}(\eta^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}]\mathrm{Br}$.[4] A comparison of the bond lengths and angles including the tetragonal hexafluorophosphate is shown in Table 4. The only difference between the bromide and the monoclinic hexafluorophosphate is that a crystallographic C_2 axis passes through the shortest Fe–Fe bonds for the former, but passes through the longest ones for the latter.

Figure 2 shows the packing diagram of a unit cell. A cation is surrounded by four anions tetrahedrally and four cations form a square surrounding an anion. This packing mode is similar to those for PdO, PtO, and PtS.[12]

Description of Crystal Structure of Tetragonal $[\mathrm{Fe_4}(\eta^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}](\mathrm{PF_6})$. Atomic parameters are shown in Table 5. The bond lengths and angles are listed in Table 4.[11] Figure 3 shows the ORTEP diagram of the

Table 5. Final Atomic Parameters for Tetragonal $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)$ (Coordinates for Fe, S, and P atoms are multiplied by 10^4 and those for C and F atoms are 10^3.)

Atom	x	y	z	$B_{eq}/Å^2$
Fe(1A)	948 (2)	870 (2)	1151 (3)	4.0
Fe(1B)	1157 (3)	524 (2)	1181 (4)	5.4
S(1A)	974 (5)	487 (4)	−1626 (6)	5.3
S(1B)	859 (4)	761 (4)	−1642 (5)	4.9
P(1)	0	5000	2500	18.5
Atom	**x**	**y**	**z**	**B_{iso}**
C(11A)	239 (2)	89 (2)	258 (3)	6.9 (6)
C(11B)	175 (3)	194 (3)	238 (5)	11.4 (11)
C(12A)	152 (2)	134 (2)	360 (3)	6.0 (5)
C(12B)	181 (1)	93 (1)	356 (3)	4.7 (4)
C(13A)	114 (2)	210 (2)	302 (3)	5.7 (5)
C(13B)	245 (2)	31 (2)	279 (4)	8.1 (7)
C(14A)	167 (2)	236 (2)	131 (3)	6.2 (5)
C(14B)	277 (3)	74 (3)	126 (5)	11.5 (10)
C(15A)	259 (1)	135 (1)	92 (3)	4.9 (4)
C(15B)	225 (1)	181 (1)	112 (3)	5.2 (4)
F(1A)	−33 (2)	385 (2)	312 (4)	17.2 (10)
F(1B)	−31 (4)	401 (3)	179 (6)	26.0 (17)
F(2A)	−46 (4)	468 (4)	48 (8)	18.0 (20)
F(2B)	−59 (4)	463 (5)	442 (9)	21.4 (24)

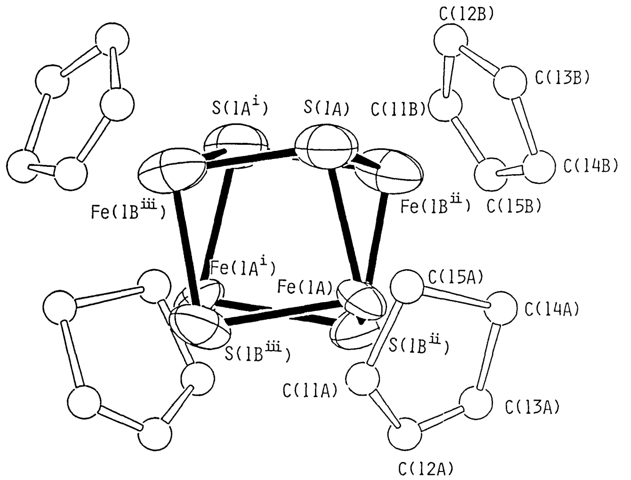

Fig. 3. ORTEP diagram of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^+$ ion in the tetragonal hexafluorophosphate. The atomic numbering scheme corresponds to that in Table 4 as follows: Fe(1A)=Fe(2), Fe(1A^{i})=Fe(1′), Fe(1B^{ii})=Fe(2), Fe(1B^{iii})=Fe(2′), S(1A)=S(1), S(1A^{i})=S(1′), S(1B^{ii})=S(2), S(1B^{iii})=S(2), (Key to the symmetry operation; i, $-x$, $-y$, z; ii, y, $-x$, $-z$; iii, $-y$, x, $-z$).

cation. The conventional analysis applying the space group $I\bar{4}$ gave the cation D_{2d} symmetry which is incompatible with the molecular orbital calculation. Furthermore it gave quite large thermal parameters for the iron, sulfur, and carbon atoms. Therefore we adopted a disordered model by dividing these atoms into two halves, respectively. Thus this model gave a pair of enantiomeric cation structures which has approximate D_2 symmetry, compatible with the molecular orbital calculation. Thermal parameters and reliability factors thus obtained are reasonable. Bond lengths and angles are similar to the monoclinic hexafluorophosphate and the bromide (Table 4). The PF_6 anion showed also a disordered pattern around $\bar{4}$ (S_4) axis.

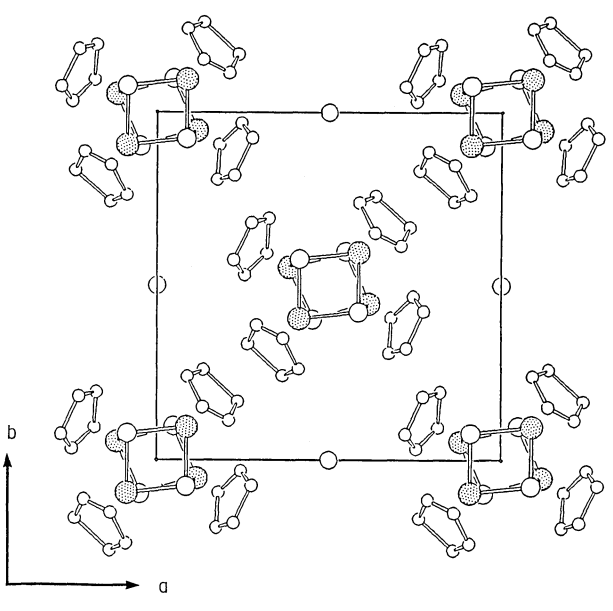

Fig. 4. Packing diagram of tetragonal $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)$. Only one orientation of the disordered pairs of cations is depicted and fluorine atoms are omitted for clarity.

Figure 4 shows the packing diagram, only one orientation of disordered molecules being shown for clarity. A cation is surrounded by four anions tetrahedrally and an anion vice versa, in a deformed zinc blende type packing.[12]

The apparent D_{2d} symmetry for tetragonal $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ (PF_6) is derived from the disordered packing of enantiomers with D_2 symmetry. The lower density for the tetragonal crystal reflects the disordered packing.

References

1) S. Harris, *Polyhedron,* **8**, 2843 (1989) and references therein.

2) R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *Inorg. Chem.,* **5**, 892 (1966).

3) C. H. Wei, G. R. Wilkes, P. M. Treichel, and L. F. Dahl, *Inorg. Chem.,* **5**, 900 (1966).

4) Trinh-Toan, W. P. Fehlhammer, and L. F. Dahl, *J. Am. Chem. Soc.,* **99**, 402 (1977).

5) Trinh-Toan, B. K. Teo, J. A. Ferguson, T. J. Meyer, and L. F. Dahl, *J. Am. Chem. Soc.,* **99**, 408 (1977).

6) H. Ogino, H. Tobita, K. Yanagisawa, M. Shimoi, and C. Kabuto, *J. Am. Chem. Soc.,* **109**, 5841 (1987).

7) H. Ogino, A. Satoh, and M. Shimoi, *Bull. Chem. Soc. Jpn.,* **63**, 2314 (1990).

8) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyuusho Hokoku,* **55**, 69 (1979).

9) "International Tables for X-Ray Crystallography," Kynoch, Birmingham, England (1974), Vol. IV, Tables 2.2A and 2.3.1.

10) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

11) Some additional bond lengths and angles, the positional and thermal parameters of hydrogen atoms, the final anisotropic thermal parameters, and F_o—F_c tables are deposited as Document No. 9091 at the Office of the Editor of Bull. Chem. Soc. Jpn.

12) R. C. Evans, "An Introduction to Crystal Chemistry," 2nd ed, Cambridge University Press, Cambridge (1964).