and S–C–N planes of 14–35°[24–28] in contrast to the coplanarity of these same planes in the present structure. This difference could be due to the hydrogen bonding or the closed d^{10} subshell of Cu(I) or to a combination of the two effects.

It is interesting to note that this is the first Cu(I) complex with thiourea or substituted thioureas that does not form a chain, polymer, or dimer structure but rather exists as a molecular entity. Moreover, this particular structure does not contain any of the delocalized three-center bonds as the others exhibit but only "normal" electron-pair bonds. We have also prepared the analogous $Ag(dmt)_3Cl$ complex. At first glance Weissenberg and oscillation photographs of $Ag(dmt)_3Cl$ appear to be isomorphous with $Cu(dmt)_3Cl$. A closer examination of the oscillation photographs of $Ag(dmt)_3Cl$ reveals approximately 10–20 weak reflections which make the *c* axis 6 times larger than the copper cell. Effectively, this places the molecular units in general positions removing all symmetry constraints. However, the two structures must be nearly isostructural since all but 10–20 reflections appear identical. Nevertheless, oscillation photographs of $Cu(dmt)_3Cl$ for 48-hr duration revealed no extraneous reflections.

Acknowledgment.—This research was supported by the National Institutes of Health, Grant GM-13985. R. L. G. is grateful for PRF and NDEA research fellowship support.

---

[24] A. Lopez-Castro and M. R. Truter, *J. Chem. Soc.*, 1309 (1963).

[25] (a) J. E. O'Connor and E. L. Amma, *Chem. Commun.*, 892 (1968); (b) J. E. O'Connor and E. L. Amma, *Inorg. Chem.*, **8**, 2367 (1969).

[26] D. A. Berta, W. A. Spofford, III, P. Boldrini, and E. L. Amma, *ibid.*, **9**, 136 (1970).

[27] M. S. Weininger, J. E. O'Connor, and E. L. Amma, *ibid.*, **8**, 424 (1969).

[28] R. L. Girling and E. L. Amma, to be submitted for publication.

CONTRIBUTION FROM THE MATERIALS SCIENCE LABORATORIES, DEPARTMENT OF CHEMICAL ENGINEERING,
THE UNIVERSITY OF TEXAS AT AUSTIN, AUSTIN, TEXAS 78712

The Crystal Structure of $Ba_7Fe_6S_{14}$, a Trinuclear Iron Complex[1]

BY I. E. GREY, H. HONG, AND H. STEINFINK*

Received June 3, 1970

The phase $Ba_7Fe_6S_{14}$ has been synthesized and is monoclinic, *C2/c*, $a = 25.490$ (2) Å, $b = 8.244$ (1) Å, $c = 14.949$ (2) Å, $\beta = 118.852$ (6)°, $Z = 4$ (temperature 25°). The structure consists of a trinuclear iron cluster in which a central FeS_4 tetrahedron shares two edges with other tetrahedra. The clusters link by corner sharing into infinite zigzag chains parallel to the *b* axis. The three iron atoms in a cluster form a straight line and are approximately 2.8 Å apart. The average Fe–S bond distance around each cation is 2.30 (3) Å, with no significant differences among them. The Ba–S distances of 3.3 Å are close to the sum of the ionic radii. Two barium ions are in eightfold, one is in sevenfold, and one is in sixfold coordination.

Introduction

In the course of an investigation of the system BaS–M–S (M = Mn,[2] Fe, Co, Ni[3]) we studied reactions of the type BaS + Fe + *x*S (*x* = 1–1.5). Mixtures corresponding to the compositions $BaFeS_2$, $Ba_4Fe_4S_9$, $Ba_5Fe_5S_{12}$, and $Ba_2Fe_2S_5$ were prepared and allowed to react under vacuum at temperatures ranging from 800 to 1100°. A compound having the composition $Ba_5Fe_5S_{12}$ had previously been reported.[4]

Each reaction product was highly crystalline, the crystals being in the form of large black shiny slabs, and all products gave nearly identical powder X-ray data. Each reaction mixture yielded predominantly the same compound and this was further verified by selecting single crystals from each of the products. Weissenberg and precession photographs were identical in every case, indicating a compound with monoclinic symmetry and unit cell parameters $a \simeq 25.4$ Å, $b \simeq 8.2$ Å, $c \simeq 14.9$ Å, and $\beta = 118°$. Using the resulting molecular volume and the measured density of the $Ba_5Fe_5S_{12}$ sample, an unreasonable number of molecules per unit cell was calculated ($Z = 5.5$). A single crystal was then selected for crystal structure analysis in order to elucidate its stoichiometry and structural parameters.

Experimental Section

Weissenberg and precession photographs of single crystals selected from the various reaction mixtures showed diffraction symmetry 2/*m* and the systematic absences were *hkl*, $h + k = 2n + 1$, and *h*0*l*, $l = 2n + 1$, consistent with the space groups *C2/c* and *Cc*. A small platelike crystal measuring 0.135 × 0.135 × 0.037 mm (0.037 mm = [010]) was selected from the BaS–Fe–S reaction product and mounted about the "*b*" axis on a GE single-crystal orienter. Twenty-four reflections were carefully centered on the $K\alpha_1$ and $K\alpha_2$ components of the molybdenum radiation (λ_1 0.70926 Å, λ_2 0.71354 Å) using a 1° takeoff angle and a 0.02° slit. The 2θ measurements, made at room temperature, 25 ± 0.5°, were used in a least-squares refinement for the determination of the lattice parameters $a = 25.490$ (2) Å, $b = 8.244$ (1) Å, $c = 14.949$ (2) Å, and $\beta = 118.852$ (6)°. Three-dimensional data to $(\sin\theta)/\lambda = 0.60$ were collected with Mo $K\alpha$ radiation using balanced filters and the stationary-crystal, stationary-counter method, a 5° takeoff angle, and the window of the pulse height analyzer set to accept 85% of the incident radiation. Peak heights were counted for 10 sec using a zirconium filter, and then background was counted for 10 sec using a yttrium

---

* To whom correspondence should be addressed.

[1] This research was supported in part by the National Science Foundation and in part by the Robert A. Welch Foundation, Houston, Texas.

[2] I. G. Grey and H. Steinfink, to be submitted for publication.

[3] I. E. Grey and H. Steinfink, *J. Amer. Chem. Soc.*, **92**, 5093 (1970).

[4] J. T. Maynard, U. S. Patent 2,770,528 (1956).

TABLE I

FINAL ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS IN PARENTHESES ($\times 10^4$) FOR $Ba_7Fe_6S_{14}$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba_1	$^1/_2$	1753 (2)	$^1/_4$	7 (0.4)	54 (2)	18 (1)	0	4 (0.6)	0
Ba_2	1815 (0.6)	312 (1)	3733 (0.8)	5 (0.3)	50 (2)	16 (0.7)	−3 (0.6)	3 (0.4)	−2 (0.9)
Ba_3	97 (0.6)	2123 (1)	753 (0.9)	6 (0.3)	47 (2)	20 (0.7)	−4 (0.7)	1 (0.4)	−2 (1)
Ba_4	3260 (0.6)	395 (1)	2656 (0.9)	7 (0.3)	46 (2)	18 (0.7)	3 (0.7)	6 (0.4)	5 (1)
Fe_1	1357 (1)	2653 (3)	148 (2)	3 (0.6)	30 (4)	10 (2)	2 (1)	2 (0.9)	2 (2)
Fe_2	1373 (1)	4232 (3)	4509 (2)	1 (0.6)	34 (4)	9 (2)	−0.8 (1)	−0.5 (1)	−2 (2)
Fe_3	3601 (1)	4473 (3)	4110 (2)	4 (0.7)	28 (4)	12 (2)	−2 (1)	4 (1)	−2 (2)
S_1	2990 (2)	2608 (6)	4301 (4)	5 (1)	32 (8)	15 (3)	0.3 (2)	3 (1)	6 (3)
S_2	704 (2)	4709 (6)	−2 (4)	4 (1)	37 (8)	20 (3)	4 (3)	5 (2)	6 (4)
S_3	850 (2)	3411 (6)	2879 (3)	4 (1)	52 (8)	7 (3)	−4 (3)	−2 (1)	−7 (3)
S_4	3074 (2)	1400 (6)	524 (4)	3 (1)	55 (8)	15 (3)	4 (3)	2 (1)	8 (4)
S_5	4132 (2)	3551 (6)	3343 (3)	2 (1)	53 (8)	7 (3)	3 (2)	−3 (1)	4 (4)
S_6	1936 (2)	1770 (6)	1792 (3)	4 (1)	41 (8)	8 (3)	1 (2)	−1 (1)	3 (3)
S_7	4242 (2)	4453 (6)	746 (4)	4 (1)	32 (8)	17 (3)	−1 (2)	3 (1)	1 (3)

[a] The temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

filter. A total of 2420 independent reflections was measured of which 2074 were considered observed on the basis that the peak measurement exceeded background by 4 counts in 10 sec. Lorentz and polarization corrections were applied and an absorption correction was made. The equation

$$\sigma(F) = {}^1/_2\left[K\frac{1 + I_Y/I_{Zr}}{1 - I_Y/I_{Zr}}\right]^{1/2}$$

was used to estimate the variance for the structure factors where I_Y is the background, I_{Zr} is the peak count, and K is the product of the Lorentz, polarization, absorption, α splitting, and tube current corrections.

Structure Determination

The direct method for the determination of phases was used in the solution of the structure. A Wilson plot was constructed which provided an approximate scale factor and also indicated a centric distribution of intensities so that the space group $C2/c$ was chosen. The sequence of computer programs FAME–MAGIC–LINK–SYMPL[5] was used to generate 300 phases from five symbol-assigned reflections. Four E maps were generated using different sign combinations for the symbolic assignments and the correct map was ascertained by checking interactions between the largest peaks against the Patterson map. The correct E map also displayed a uniform distribution of peak heights and they were in the appropriate ratio of atomic numbers of the atoms. Four barium atoms and three iron atoms were clearly visible; the sulfur atoms could not be unambiguously assigned as there were a number of spurious peaks with heights equivalent to those of the sulfur atoms.

From a structure factor calculation based on the barium and iron positions, a discrepancy value R of 0.28 was obtained. A Fourier map immediately revealed the positions of seven independent sulfur atoms. The atom parameters and scale and isotropic temperature factors were then refined using a least-squares program XFLS, a modification of ORFLS.[6] The function minimized was $\Sigma w(KF_o - F_c)^2$ with $w = 1/\sigma^2$. After three cycles of refinement the value of R was 0.060. At this stage the isotropic temperature factors were converted to anisotropic factors and three more cycles of refinement led to a final R value of 0.049 for all observed reflections and a weighted $R = 0.053$ $\{R = \Sigma||F_o - |F_c||/\Sigma|F_o|,\ wR = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}\}$. For all reflections the final R was 0.065. The scattering factors used for Ba, Fe^{2+}, and S^{2-} are those published in ref 7 and were not corrected for dispersion effects. The final atomic parameters and anisotropic temperature factors with standard deviations are shown in Table I, and the set of calculated and observed structure factors is listed in Table II. A three-dimensional difference electron density function was calculated with this last set of parameters and no physically significant peaks were observed. The largest peak was 1.5 e$^-$ Å^{-3}.

Discussion

The structure of $Ba_7Fe_6S_{14}$ is illustrated in Figures 1 and 2. The basic structural unit is a trinuclear iron cluster, $Fe_3S_6S_{2/2}$, which consists of three FeS_4 tetrahedra, where the central tetrahedron shares its two opposing edges with two other tetrahedra. The trinuclear groups link together by corner sharing of the tetrahedra to produce infinite zigzag chains in the general direction of the "b" axis. The chains are held together by the packing of barium ions.

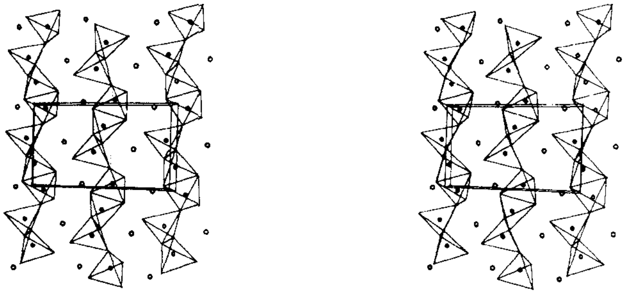


Figure 1.—Stereographic view of $Ba_7Fe_6S_{14}$ with the b axis vertical and the a axis horizontal; only $^1/_4$ c of the unit cell is shown.

Within a Fe_3S_7 group, the Fe–Fe distances are unequal, with Fe_1 distances to the two terminal iron atoms

---

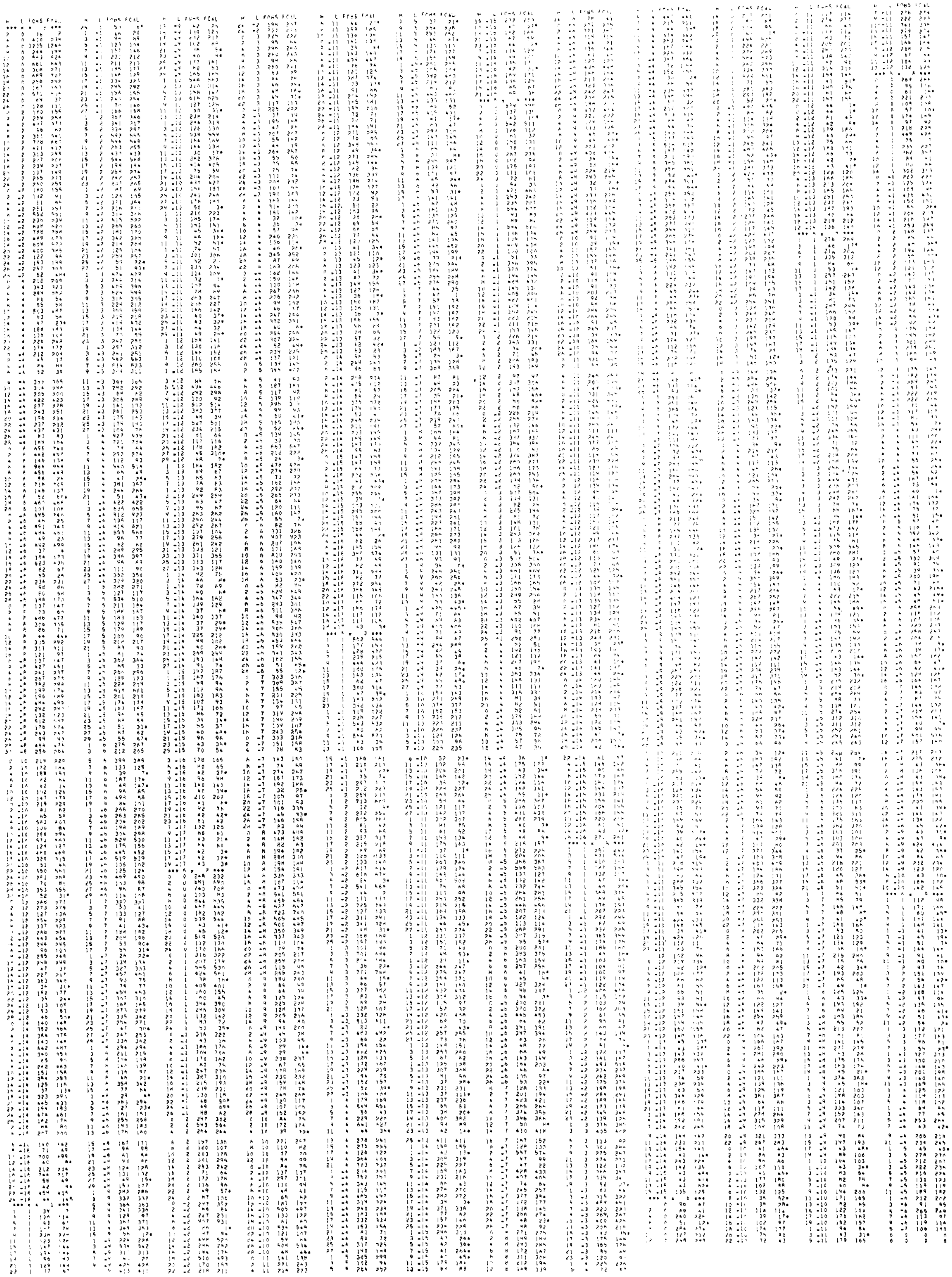
(5) R. Dewar and A. Stone, The University of Chicago, personal comnication.

(6) W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-35, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(7) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $Ba_7Fe_6S_{14}$[a]



---

[a] Structure factors marked with an asterisk were not used in the structure refinement.

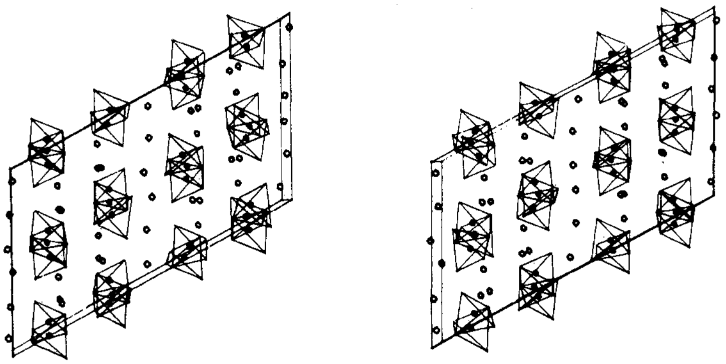


Figure 2.—View of the $Ba_7Fe_6S_{14}$ structure along [010]; the *c* axis is vertical. The open circles within the tetrahedra are iron atoms and the others are barium.

2.747 (7) and 2.829 (7) Å. The bridging angles Fe–S–Fe are in the range 72–75° and the sequence Fe_2–Fe_1–Fe_3 is almost linear (177.1 (2)°). These distances and angles are closely similar to those observed in $KFeS_2$,[8] containing infinite chains of edge-sharing tetrahedra. Each of the FeS_4 tetrahedra is considerably distorted as reflected in the large variation in the tetrahedral angles and in the Fe–S bond lengths as shown in Table III. In the two terminal tetrahedra of each trinuclear grouping the Fe–S bond to the sulfur atom not involved in bridging is shorter than the bond to the sulfur atom involved in corner sharing, which in turn is shorter than the bonds to the two sulfur atoms involved in edge sharing (the only exception is Fe_2–S_4). The distance between adjacent iron atoms of two corner-shared trinuclear groups is 3.670 (7) Å which is considerably greater than the distances between irons within a cluster. It is, however, shorter than the Fe–Fe separation in Ba_2FeS_3 which is isostructural with Ba_2ZnS_3[9] and whose structure consists of infinite chains of corner-sharing tetrahedra. In that structure the Fe–Fe distance is equal to the *b*-axis dimension, 4.29 Å.

The sum of the ionic radii for Ba^{2+} and S^{2-} is 3.29 Å and it is seen that the Ba^{2+}–S^{2-} distances are all quite close to this value. Of the four independent barium ions, two have eightfold, one has sevenfold, and one has sixfold coordination to sulfur.

TABLE III

BOND DISTANCES AND ANGLES IN $Ba_7Fe_6S_{14}$

Distances, Å

Ba_1–S_2(2)	3.485 (10)	Fe_1–S_2	2.31 (1)	Fe_3–S_1	2.30 (1)
Ba_1–S_3(2)	3.380 (9)	Fe_1–S_4	2.26 (1)	Fe_3–S_5	2.28 (1)
Ba_1–S_5(2)	3.373 (9)	Fe_1–S_6	2.29 (1)	Fe_3–S_6	2.34 (1)
Ba_1–S_7(2)	3.267 (9)	Fe_1–S_7	2.27 (1)	Fe_3–S_7	2.36 (1)
Ba_2–S_1	3.290 (9)	S_2–S_4	3.67 (1)	S_1–S_5	3.89 (1)
Ba_2–S_1	3.227 (9)	S_2–S_6	3.85 (1)	S_1–S_6	3.84 (1)
Ba_2–S_3	3.343 (9)	S_2–S_7	3.63 (1).	S_1–S_7	3.75 (1)
Ba_2–S_4(2)	3.378 (10)	S_4–S_6	3.76 (1)	S_5–S_6	3.73 (1)
Ba_2–S_4	3.342 (10)	S_4–S_7	3.79 (1)	S_5–S_7	3.83 (1)
Ba_2–S_5	3.215 (9)	S_6–S_7	3.66 (1)	S_6–S_7	3.66 (1)
Ba_2–S_6	3.290 (9)				
Ba_2–S_7	3.224 (9)	Fe_2–S_1	2.30 (1)	Fe_2–Fe_1	2.747 (7)
		Fe_2–S_2	2.32 (1)	Fe_1–Fe_3	2.829 (7)
Ba_3–S_2	3.146 (10)	Fe_2–S_3	2.24 (1)	Fe_3'–Fe_2'	3.670 (7)
Ba_3–S_2	3.168 (10)	Fe_2–S_4	2.29 (1)		
Ba_3–S_3	3.005 (9)			Some Nonbonded Fe–Fe Distances	
Ba_3–S_5	3.284 (9)	S_1–S_2	3.81 (1)		
Ba_3–S_6	3.436 (9)	S_1–S_3	3.89 (1)	Fe_1–Fe_1'	6.060 (7)
Ba_3–S_7	3.093 (10)	S_1–S_4	3.73 (1)	Fe_2–Fe_2'	7.486 (7)
		S_2–S_3	3.70 (1)	Fe_3–Fe_3'	8.827 (7)
Ba_4–S_1	3.388 (9)	S_2–S_4	3.80 (1)	Fe_2–Fe_1'	6.232 (7)
Ba_4–S_2	3.264 (10)	S_3–S_4	3.60 (1)	Fe_2–Fe_3'	5.992 (7)
Ba_4–S_3	3.195 (9)			Fe_3–Fe_1'	7.023 (7)
Ba_4–S_4	3.100 (10)				

Angles, Deg

S_2–Fe_1–S_4	106.8 (4)	S_1–Fe_2–S_2	110.8 (4)	S_1–Fe_3–S_5	116.1 (4)
S_2–Fe_1–S_6	113.5 (4)	S_1–Fe_2–S_3	117.9 (4)	S_1–Fe_3–S_6	111.6 (4)
S_2–Fe_1–S_7	104.8 (4)	S_1–Fe_2–S_4	108.6 (4)	S_1–Fe_3–S_7	107.0 (4)
S_4–Fe_1–S_6	111.5 (4)	S_2–Fe_2–S_3	108.2 (4)	S_5–Fe_3–S_6	107.6 (4)
S_4–Fe_1–S_7	113.2 (4)	S_2–Fe_2–S_4	105.4 (4)	S_5–Fe_3–S_7	111.3 (4)
S_6–Fe_1–S_7	106.9 (4)	S_3–Fe_2–S_4	105.1 (4)	S_6–Fe_3–S_7	102.3 (4)
Fe_1–S_2–Fe_2	72.7 (4)	Fe_1–S_7–Fe_3	75.2 (4)	Fe_2–Fe_1–Fe_3	177.1 (2)
Fe_1–S_4–Fe_2	74.2 (4)	Fe_2–S_1–Fe_3'	105.6 (4)	Fe_1–Fe_2–Fe_3'	125.6 (2)
Fe_1–S_6–Fe_3	75.2 (4)				

In $Ba_7Fe_6S_{14}$, as in Fe_3S_4· and $Cu^IFe_2S_3$, the iron atoms have a formal oxidation state which is nonintegral. The last two compounds have been formulated as $Fe^{II}Fe^{III}_2S_4$ and $Cu^IFe^{II}Fe^{III}S_3$, respectively, containing both divalent and trivalent iron. Similarly $Ba_7Fe_6S_{14}$ may be expressed as $Ba_7[Fe^{III}_2Fe^{II}_4]S_{14}$ with the iron having an average oxidation number of 2.33. It was of interest to examine carefully the bonds associated with the three independent iron atoms in the structure to determine if iron existed in both oxidation states in this compound. The average Fe–S bond lengths for Fe_1, Fe_2, and Fe_3 are 2.28 (2), 2.29 (2), and 2.32 (2) Å, respectively, which are equal within the accuracy of the experiment; *i.e.*, in $Ba_7Fe_6S_{14}$, each of the iron atoms has an averaged oxidation state probably due to rapid electron exchange between Fe^{2+} and Fe^{3+} as is postulated for orthorhombic cubanite.[10] This is further supported by the results of Mössbauer studies,[11] which may be interpreted on the basis of three iron atoms in different environments but with the same oxidation state.

(8) J. W. Boon and C. H. MacGillavry, *Recl. Trav. Chim. Pays-Bas*, **61**, 910 (1942).

(9) H. G. Schnering and R. Hoppe, *Z. Anorg. Allg. Chem.*, **312**, 99 (1961).

(10) N. N. Greenwood and H. S. Whitfield, *J. Chem. Soc. A*, 1697 (1968).

(11) W. Reiff, I. E. Grey, H. Hong, and H. Steinfink, to be submitted for publication.