Octahedrally Coordinated Iron in the Ba–Fe–S System: $Ba_9Fe_3S_{11}(S_2)_2$, a High-Pressure Polymorph of Ba_3FeS_5

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A reaction at pressures to 60 kbar and exceeding 1000 °C produces a previously described compound, Ba_3FeS_5, in which Fe is in the usual tetrahedral coordination. Increasing the pressure to 70 kbar and reacting a 3:1:2 mixture of BaS–Fe–S at 925 ± 25 °C produce a hexagonal polymorph, $Ba_9Fe_3S_{11}(S_2)_2$, $a = 9.218$ (1) Å, $c = 18.042$ (2) Å, $P\bar{6}c2$, $Z = 2$, $\rho_x = 4.72$ g/cm³, in which Fe is in octahedral coordination. A total of 589 three-dimensional X-ray intensities were measured, of which 446 were observed. The structure was solved from a three-dimensional Patterson synthesis and refined by least squares to $R = 0.0496$. Ba^{2+} and S^{2-} form close-packed layers and the octahedral interstices are occupied by Fe. Infinite columns of face-sharing FeS_6 octahedra exist parallel to c at each corner of the unit cell, and these create trigonal channels parallel to the threefold axes in which are located strings of S_2^{2-} units separated by S^{2-}. This phase shows the expected close packing of atomic layers and the higher coordination around Fe. Increased density is also achieved by the formation of S_2^{2-}. The Fe–S distance of 2.55 Å is consistent with high-spin Fe in an octahedral environment; Ba–S distances vary from 3.0 to 3.7 Å and S–S = 2.04 Å in S_2.

Introduction

It is well-known that high pressure stabilizes high oxidation states and increases the coordination numbers of cations. We have reported the preparation at high pressure, and the crystal structure, of Ba_3FeS_5 in which the formal oxidation state of iron is tetravalent and this phase represents also one end member of the infinitely adaptive series $Ba_3Fe_{1+x}S_5$.[1,2] In the investigation of the Ba–Fe–S system many new phases have been produced and their crystal structures determined, and in all of them iron is in tetrahedral coordination. Numerous attempts were made to prepare a compound at high pressure in which the Fe coordination would change to octahedral. Different starting compositions were employed and in particular the 3:1:2 BaS–Fe–S mixture was reacted at pressures exceeding 60 kbar. Only the orthorhombic Ba_3FeS_5 phase was observed at these pressures and at temperatures exceeding 1000 °C. When the reaction took place at a temperature below 1000 °C and at a pressure of about 70 kbar, the X-ray powder diffraction patterns showed that, in addition to orthorhombic Ba_3FeS_5, Ba_2S_3 and an unknown phase were present. Systematic variations of pressure, temperature, and time using the 3:1:2 mixture BaS–Fe–S increased the proportion of the unknown phase at the expense of the orthorhombic phase. It was also noted during the grinding of the reacted sample that the orthorhombic phase gave a brown streak while the unknown phase streaked black. A single crystal was selected from one of the reaction products and used for data collection for a structural analysis. This compound was shown to have the stoichiometry Ba_3FeS_5, a polymorph of the previously reported high-pressure phase, and contains iron in octahedral coordination. We report here the crystal structure as well as the preparative conditions which were determined after the material had been identified.

Experimental Section

Weissenberg and Buerger precession photographs of several single crystals showed that they had diffraction symmetry $6/mmm$ with systematic absences $h\bar{h}0l$, $l = 2n + 1$, consistent with space groups $P6_3/mcm$, $P6_3cm$, and $P\bar{6}c2$. The last was eventually shown to be correct. The reciprocal lattice has a pronounced subcell with $c' = \frac{1}{3}c$. Lattice constants were determined at room temperature from a least-squares refinement of precise 2θ measurements of 13 reflections between 32 and 48° from a crystal mounted on a single-crystal diffractometer using Mo radiation with λ_1 0.709 26 Å and λ_2 0.713 54 Å.[1] The lattice constants are $a = 9.218$ (1) Å and $c = 18.042$ (2) Å.

Three-dimensional X-ray diffraction intensity data to $(\sin \theta)/\lambda = 0.65$ were collected with Mo Kα radiation using a stationary-crystal, stationary-counter technique, balanced filters, and a 5° takeoff angle.

The crystal was an irregular fragment with the biggest dimension about 0.1 mm and the smallest 0.08 mm. The mosaic spread of the crystal, evaluated from an ω scan, was 0.25° measured at half-height of the peaks. Intensities and backgrounds were counted for 10 s. A total of 589 independent reflections was measured with 446 reflections considered observed on the basis that the peak count exceeded the background count by $3\sigma(I)$. Intensities were transformed into structure amplitudes after making Lorentz, polarization, and absorption corrections ($\mu l = 144$ cm⁻¹). The standard deviation of the structure factor was estimated from the equation

$$\sigma(F) = \frac{1}{2} \left(Lp \frac{1+b}{1-b} \right)^{1/2}$$

where $b = I_Y/I_Z$ is the background to peak ratio.[1]

Structure Determination

The structure was solved from an interpretation of the three-dimensional Patterson function, which yielded the position of one barium. A three-dimensional electron density map based on phased structure amplitudes yielded the positions of the other atoms and indicated that one of the S atoms had less than full occupancy. The structure was refined by the full-matrix least-squares program GENLES.[3a] The quantity minimized was $\sum w(F_o - F_c)^2$ with the weights equal to $1/\sigma^2$. The atomic scattering factors for Ba^{2+}, Fe^{3+}, and S are those from Cromer and Mann and were corrected for real and imaginary parts of dispersion.[3] For the observed reflections the final $R = 0.0496$ and $R_w = 0.0533$. For all reflections $R = 0.0681$ and $R_w = 0.0535$. The final atomic parameters are shown in Table I, and Table II contains the observed and calculated structure amplitudes.[4] A difference electron density map based on the last set of parameters showed no physically significant peaks.

Discussion

The structure of Ba_3FeS_5 is illustrated in Figures 1 and 2, and the important interatomic distances and angles are tabulated in Table III. Figure 1 shows a projection down the c axis and illustrates the distorted hexagonal close-packed layers of Ba and S. Barium and sulfur ions are nearly at the same levels, $z = 0.08$ and $z = \frac{1}{4}$, so that a close-packed unit of 3 Ba and 3 S is present around the c axis with the two levels rotated 60° with respect to each other. This arrangement creates infinite columns of face-sharing sulfur octahedra, and the interstices along the c axis are occupied by Fe. The columns are separated by the a axis dimension, 9.218 Å. The hexagonal close packing of S ions of 1.84-Å radius results in a 6-Å height giving rise to the pronounced subcell with $c' = \frac{1}{3}c$. The regularity of the close packing within a plane is limited because of the size inequality of Ba and S. The repetition of the columns at the corners of the unit cell creates

Table I. Atomic Parameters and Their Standard Deviations $(\times 10^4)^a$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba(1)	95 (7)	3841 (5)	842 (3)	39 (4)	19 (6)	12 (1)	10 (6)	4 (1)	2 (2)
Ba(2)	3897 (8)	3619 (6)	$1/4$	22 (8)	3 (7)	8 (2)	8 (7)		
Fe(1)	0	0	0	21 (21)	21	32 (12)	11		
Fe(2)	0	0	1629 (12)	33 (12)	33	12 (4)	17		
S(1)	2289 (20)	2206 (22)	841 (11)	17 (28)	4 (27)	17 (5)	1 (16)	−6 (9)	−6 (10)
S(2)	54 (37)	2205 (29)	$1/4$	0 (26)	34 (38)	6 (7)	−15 (29)		
S(3)	$1/3$	$2/3$	0	23 (36)	23	23 (16)	11		
S(4)	$1/3$	$2/3$	1936 (12)	17 (19)	17	−7 (5)	8		
S(5)	$2/3$	$1/3$	1591 (16)	26 (28)	26	21 (14)	13		
S(6)^b	$2/3$	$1/3$	179 (22)	75 (43)	75	−4 (18)	38		

^{a} The temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^{b} Occupancy factor is 0.5.
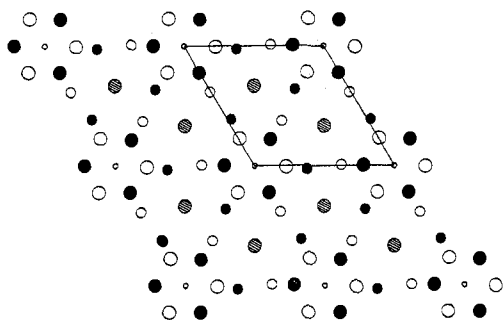
Figure 1. The (00.1) projection of the structure of $Ba_9Fe_3S_{11}(S_2)_2$. Large circles are S, intermediate size circles are Ba, and the small circles are Fe. Black and open circles not Fe are at levels $1/6c$ apart. The striped circles are the S-S_2 chains in the trigonal channels.
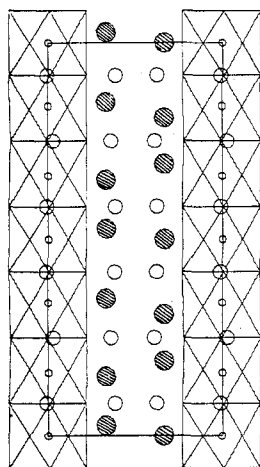
Figure 2. View of the structure along [100]. Large circles are S, intermediate are Ba, and small ones are Fe. Note the strings of S_2-S displaced $1/6c$ in the separate trigonal channels. The S at the corners of the octahedra are omitted.

Table III. Bond Distances (Å) and Angles (deg) with Standard Deviations in Parentheses

Distances

Ba(1)–S(1)	3.653 (6)	Fe(1)–6S(1)	2.569 (10)
–S(1)	3.358 (14)	Fe(2)–3S(1)	2.514 (13)
–S(1)	3.068 (18)	–3S(2)	2.550 (16)
–S(1)	3.025 (9)	Fe(1)–Fe(2)	2.940 (15)
–S(2)	3.342 (7)	Fe(2)–Fe(2)	3.142 (30)
–S(3)	3.199 (4)	S(1)–S(1)	3.612 (14)
–S(4)	3.438 (9)	–S(1)	3.741 (17)
–S(5)	3.249 (11)	–S(1)	3.590 (21)
–S(6)^a	3.187 (13)	–S(2)	3.634 (23)
Ba(2)–2S(1)	3.305 (13)	–S(2)	3.612 (22)
–S(2)	3.104 (21)	–S(5)	3.874 (16)
–S(2)	3.756 (14)	–S(6)^a	3.821 (17)
–S(2)	2.934 (21)	S(2)–S(2)	3.479 (17)
–2S(4)	3.265 (6)	–S(4)	3.829 (18)
–2S(5)	3.156 (13)	S(3)–S(4)	3.492 (14)
		S(4)–S(4)	2.037 (29)
		S(5)–S(5)	3.282 (47)
		–S(6)^a	2.546 (42)

Angles

S(1)–Fe(1)–S(1)	88.6 (6)	S(2)–Fe(2)–S(2)	86.0 (5)
	177.0 (6)	S(1)–Fe(2)–S(1)	91.1 (4)
	89.3 (6)		
	93.5 (6)		
S(2)–Fe(2)–S(1)	91.7 (3)		
	176.4 (5)		
	91.0 (7)		

^{a} Distances to S(6) are only to the two atoms at $z = 0.02$ and 0.52.

channels parallel to the threefold axes which contain sulfur not bonded to iron. The trigonal channel centered on $x = 1/3$, $y = 2/3$ contains S(3) and S(4); the latter forms the disulfide ion S_2^{2-} by reflection across the mirror plane at $z = 1/4$. Thus, an ordered infinite string of alternating S_2^{2-}–S^{2-} fills this channel. The sulfur atoms in the channel centered on $2/3$, $1/3$ present a less clear picture. The S(5)–S(5) distance between the atoms located on each side of the mirror at $z = 1/4$ is 3.28 Å. However, S(6) has a symmetry-related neighbor by the twofold axis at a distance of 0.7 Å. The occupancy factor of 0.5 clearly indicates that only two of the four equipoints are occupied and S(6) is present either at $z = 0.02$ and 0.52 or at $z = -0.02$ and 0.48. The S(6)–S(5) distance is 2.55 Å which is too long for S_2 and too short for separate S^{2-} ions. Evidently, the crystals which are obtained in these preparations are always twinned, most likely on a near-unit-cell scale. Energetically there is no difference between an S_2–S chain with S(6) near

$z = 0.02$ or a chain related to it by rotation around the twofold axis at [21.0], i.e., z of S(6) at about –0.02. The z coordinate for S(6) cannot be correct since it is a weighted average between two structures. One can postulate a reasonably ordered model. A shift of about 0.03 in the z parameter of S(6) produces a S(6)–S(5) bond of about 2 Å and the chain is comparable to that in the other channel. However, the space group cannot be $P\bar{6}c2$ for a true single crystal.

The S chains become identical in both channels if parameters $x \approx 0$ and $x \approx y$ for the various atoms in $P\bar{6}c2$ are set to $x = 0$ and $x = y$. The structure can now be accommodated in $P6_3cm$, and the channel occupancies are equalized. This model could not be refined. A model in $P6_3/mcm$ did not refine to an R value less than 0.20. It is possible that under different preparative conditions an ordered structure might exist. The X-ray powder patterns of all preparations, however, are identical, and it must be concluded that the twinned structures were always produced in our experiments.

The stoichiometric formula is perhaps best written as $Ba_9Fe_3S_{11}(S_2)_2$ to indicate explicitly the presence of S_2 in this compound. This formula implies the presence of 2 Fe^{3+} and 1 Fe^{2+} and is consistent with the two crystallographically different Fe in 2(a) and 4(g) sites of $P\bar{6}c2$. The average Fe–S distance of 2.55 Å is indicative of high-spin Fe^{2+} in octahedral coordination.[5,6] Data with regard to high-spin Fe^{3+} are somewhat more uncertain. The average Fe–S bond length is

2.418 Å in tris(*N,N*-di-*n*-butyldithiocarbamato)iron(III) where the Fe is said to be in equilibrium between the high-spin and low-spin ground states.[7] The difference in bond lengths between high- and low-spin Fe^{3+} in sixfold-coordination is 0.1 Å, and they are reported as 2.4 and 2.3 Å, respectively.[8,9] The value of the high-spin Fe^{3+}–S distance in the organometallic compounds is frequently influenced by packing considerations of the large ligands, and the sixfold-coordination polyhedron is usually described as a distorted trigonal prism or as an antiprism, i.e., a distorted octahedron. None of these influences is present in this structure and the S octahedron is very regular. It appears that the 2.5-Å bond distance might also be the proper value for high-spin Fe^{3+}–S. The Ba–S distances and S–S distance, with the exceptions noted previously, are as expected. Barium is in ninefold-coordination and the polyhedron is a distorted capped trigonal prism.

The density of this phase is 4.72 g/cm^3 as compared to 4.14 g/cm^3 for the orthorhombic Ba_3FeS_5. Increasing density is achieved by the change in coordination and near close packing of the Ba–S layers. However, size discrepancy inhibits the lateral extent of this close packing and gives rise to channels within which increased packing density is achieved by the formation of S_2 ions. It is conceivable that at even higher pressure the formation of S_3 and higher polysulfides might occur.

After the structure and stoichiometry became known, attempts were made to prepare single-phase material. Systematic experiments finally showed that the largest amount of the hexagonal phase, free of the orthorhombic polymorph,

is produced at 72 kbar and 925 ± 25 °C. The temperature stability range for this phase is very narrow and reaction temperatures outside of these limits do not yield the hexagonal phase. The best material which we prepared from a 3:1:2 mixture of BaS–Fe–S reacted for 12 h still contained Ba_2S_3. Reaction of a 9:4:6 mixture BaS–Fe–S for 5 h at 925 °C produced primarily the hexagonal phase free of Ba_2S_3 but the powder pattern contained several lines of an unknown phase.

References and Notes

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Charge Distribution and Carbonyl Site Exchange in Tricarbonyl(dienyl)iron Cations

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^{13}C NMR spectroscopy has been used to study tricarbonyl(dienyl)iron cations. The ^{13}C chemical shifts and MO calculations of atomic charge point to an alternation of charge along the dienyl chain with carbons 1, 3, and 5 being less electron deficient than carbons 2 and 4. This charge distribution is in accord with a simple frontier orbital picture of bonding in which the dominant bonding interaction involves electron donation from iron to an empty nonbonding molecular orbital of the dienyl cation ligand. The case for interpretation of chemical shift differences of the dienyl carbons in terms of atomic charge is discussed. Site exchange of the carbonyl ligands was studied by complete line-shape analysis of their ^{13}C NMR signals over the temperature range −50 to +65 °C. The measured barrier agrees closely with that calculated for rotation of the tricarbonyliron group by the extended Hückel method. Pairwise exchange has been eliminated for a triphenylphosphine substituted cation. Carbonyl site exchange must occur via tricarbonyliron rotation or via a process which approximates Berry pseudorotation.

Dienyl cations exhibit the high reactivity characteristic of carbonium ions in general. They cyclize rapidly to give cyclopentenyl cations, except when steric factors intervene, and react rapidly with nucleophiles.[2a] Yet coordination of the dienyl moiety to a transition metal such as Mn, Co, Ru, or Fe gives derivatives of considerable kinetic stability.[2b,3] Tricarbonyl(cyclohexadienyl)iron salts survive recrystallization from water![2b] The nature of bonding between transition metals and cis dienyl ligands is of interest owing to this dramatic stabilization as well as its relationship to metal–ligand bonding in transition-metal π complexes in general.

Charge distribution tells much about bonding. Thus, we have investigated charge distribution in the title cations.[4] Interpretation of ^{13}C NMR chemical shifts in terms of charge

density for carbon atoms bound to transition metals has been common in the organotransition metal literature.[5] We discuss here evidence for the validity of such an interpretation in the case of the title cations. Finally, we have studied carbonyl site exchange in the title cations and report on the mechanism and activation parameters.

^{13}C NMR Spectra

Tricarbonyl(dienyl)iron cations were generated from dienol–Fe(CO)$_3$ complexes at low temperature in $FSO_3H/SO_2/CDCl_3$ mixtures. As shown previously, ψ-exo dienol–Fe(CO)$_3$ complexes ionize stereospecifically to give syn,syn cations (eq 1), whereas ψ-endo dienol–Fe(CO)$_3$ complexes give syn,anti cations (eq 2).[6] To facilitate comparisons, data for