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Cerium iron sulfide, $Ce_3Fe_{1.94}S_7$

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Tricerium(III) diiron(II,III) heptasulfide, $Ce_3Fe_{1.94}S_7$, crystallizes in the polar hexagonal space group $P6_3$ and adopts the $Ce_6Al_{3.33}S_{14}$ structure type. The Fe atoms occupy both tetrahedral and octahedral sites. Isolated FeS_4 tetrahedra, all pointing in the same direction, are stacked along the threefold rotation axes. Chains of face-sharing FeS_6 octahedra propagate along the 6_3 axis. Vacancies resulting from the partial oxidation of Fe^{2+} to Fe^{3+} occur exclusively in the octahedral Fe sites. The Ce atoms are coordinated by [7+1] S atoms, which form bicapped trigonal prisms.

Comment

In an early investigation of the pseudo-binary systems R_2S_3–MS (R is La–Nd and M is Mn–Ni), a series of compounds originally described with the formula R_4MS_7 were discovered (Collin *et al.*, 1968). The cell parameters of these compounds, determined from X-ray powder diffraction patterns indexed in the hexagonal space group $P6_3$, were reported (for 'Ce_4FeS_7', a = 10.202 Å and c = 5.657 Å). Since then, more detailed structural information has been lacking for these compounds. We report here the single-crystal structure determination of one member of the series, which has the actual formula $Ce_3Fe_{1.94}S_7$.

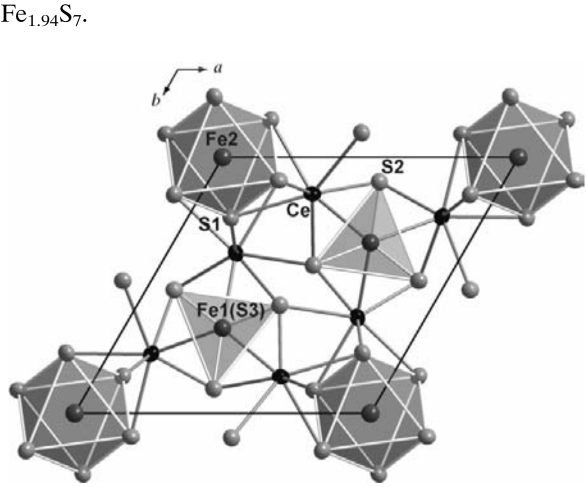

Figure 1
A view of the structure of $Ce_3Fe_{1.94}S_7$ along [00$\bar{1}$]. Displacement ellipsoids are drawn at the 95% probability level.

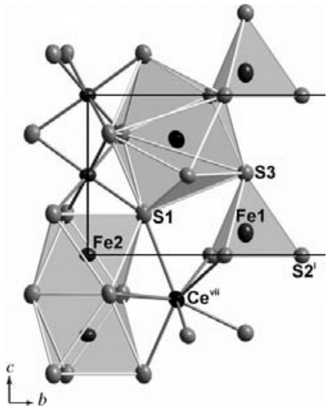

Figure 2
A view along [100] of part of the structure of $Ce_3Fe_{1.94}S_7$, showing the stacked FeS_4 tetrahedra and the $FeS_{6/2}$ chains of face-sharing octahedra, which are connected by CeS_{7+1} bicapped trigonal prisms. Displacement ellipsoids are drawn at the 95% probability level. [Symmetry codes: (i) $1 - x, 1 - y, z - \frac{1}{2}$; (vii) $x - y, x, z - \frac{1}{2}$.]

The title compound adopts the $Ce_6Al_{3.33}S_{14}$ structure type (de Saint-Giniez *et al.*, 1968), which is also sometimes referred to as the La_3CuSiS_7 structure type (Flahaut & Laruelle, 1970). Thus, $Ce_3Fe_{1.94}S_7$ belongs to a large family of compounds of general formula $R_3MM'Q_7$, where R is a rare-earth metal, M and M' are metals or metalloids, and Q is a chalcogen (Villars, 1997; Flahaut & Laruelle, 1970). Some other recently reported $R_3MM'Q_7$ compounds include Y_3NaSiS_7 (Hartenbach & Schleid, 2003), La_3CuGeQ_7 (Q is S or Se; Poduska *et al.*, 2002) and $La_3Al_{0.44}Si_{0.93}S_7$ (Yang & Ibers, 2000).

Views of the $Ce_3Fe_{1.94}S_7$ structure, highlighting the Fe-centred coordination polyhedra, are presented in Figs. 1 and 2. The Fe atoms occupy two types of sites, with tetrahedral and octahedral geometries, respectively. Isolated $Fe1S_4$ tetrahedra, all pointing in the polar [001] direction, are stacked along the threefold rotation axes (Fig. 2). The tetrahedra are trigonally compressed, with one shorter Fe1—S3 distance of 2.224 (6) Å and three longer Fe1—S2 distances of 2.265 (3) Å (Table 1). These distances are somewhat longer than those found in the FeS_4 tetrahedra of La_3MnFeS_7 (2.11–2.22 Å; Nanjundaswamy & Gopalakrishnan, 1983), but shorter than those found in the tetrahedra of $La_2Fe_2S_5$ (2.30–2.37 Å; Besrest & Collin, 1977). The S—Fe1—S angles of 106.67 (12) and 112.14 (11)° are close to the ideal tetrahedral value of 109.5°.

The $Fe2S_6$ octahedra share opposite faces to form linear $FeS_{6/2}$ chains that propagate along the 6_3 axis (Fig. 2). The Fe atoms within the slightly elongated $Fe2S1_6$ octahedra are shifted closer to one shared face than the other, yielding Fe2—S1 distances of 2.532 (4) and 2.578 (4) Å (Table 1). These distances are similar to those observed in the more distorted FeS_6 octahedra of $Ce_2Fe_{1.82}S_5$ (2.466–2.702 Å; Harms *et al.*, 2004). The *cis*-S—Fe2—S angles range from 88.40 (15) to 90.58 (5)° and the *trans* angles are 178.6 (2)°.

As in the $Ce_6Al_{3.33}S_{14}$ structure (de Saint-Giniez *et al.*, 1968), vacancies occur in the octahedral site of $Ce_3Fe_{1.94}S_7$ [Fe2, with a refined occupancy of 0.942 (16)]. The defects in $Ce_3Fe_{1.94}S_7$ are presumed to result from the partial oxidation of Fe^{2+} to Fe^{3+}, according to the charge-balanced formula

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$(Ce^{3+})_3(Fe^{3+})_{1.12}(Fe^{2+})_{0.82}\square_{0.06}(S^{2-})_7$. In support of this hypothesis, a recent Mößbauer investigation of the non-stoichiometric cerium iron sulfide $Ce_2Fe_{1.82}S_5$ established that the oxidation of Fe^{2+} to Fe^{3+} accompanies the formation of vacancies in this compound (Harms *et al.*, 2004).

The Ce atoms, located between the Fe-centred polyhedra, are coordinated by [7+1] S atoms: one S3, two S2, and three S1 atoms, at distances of 2.843 (3)–3.037 (3) Å, form a trigonal prism, capped by one S2 atom at a distance of 3.000 (3) Å and one S1 atom at a significantly longer distance of 3.414 (4) Å (Fig. 2 and Table 1). The shorter distances are within the range observed in the CeS_8 bicapped trigonal prisms of $Ce_2Fe_{1.82}S_5$ (2.887–3.142 Å; Harms *et al.*, 2004). A similar but more pronounced [7+1] coordination is observed in $Ce_6Al_{3.33}S_{14}$, where the corresponding short and long Ce—S distances are 2.83–3.03 and 3.58 (1) Å, respectively (de Saint-Giniez *et al.*, 1968).

Experimental

Hexagonal prisms of $Ce_3Fe_{1.94}S_7$ were isolated from the reaction of the elements in an alkali chloride flux. The starting reagents were cerium (rod, 99.85%, Treibacher; freshly filed prior to use), iron (powder, 99.99%, ABCR), and sulfur [powder, >99%, VEB Laborchemie; recrystallized from CS_2, then purified of C according to the method of von Wartenberg (1956)]. A 1:1 mixture of LiCl (p.a., Merck) and KCl (p.a., J. T. Baker) was used as a flux after being heated under dynamic vacuum to remove any moisture. The elements, in a ratio of 3Ce:2Fe:7S (0.25 g in total), were added to the LiCl–KCl flux (0.5 g) in a fused silica ampoule (6 cm in length, 0.8 cm in diameter), which was then sealed under vacuum (10^{-3} Torr; 1 Torr = 133.322 Pa). The reaction mixture was heated at 1170 K for 4 d and then cooled to room temperature at a rate of 10 K h^{-1}. The flux was removed by washing the sample several times with water and ethanol. The major component of the product was $Ce_3Fe_{1.94}S_7$. Energy-dispersive X-ray (EDX) analysis confirmed the presence of Ce, Fe, and S; analysis (mol. %): Ce 24 (1), Fe 14 (1), S 62 (1).

Crystal data

$Ce_3Fe_{1.94}S_7$
$M_r = 753.13$
Hexagonal, $P6_3$
$a = 10.096$ (2) Å
$c = 5.961$ (1) Å
$V = 526.2$ (2) Å^3
$Z = 2$
$D_x = 4.754$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7967 reflections
$\theta = 2.3$–28.1°
$\mu = 16.65$ mm^{-1}
$T = 293$ (2) K
Prism, black
0.16 × 0.15 × 0.12 mm

Table 1
Selected geometric parameters (Å, °).

$Ce—S2$	2.843 (3)	$Ce—S1^{v}$	3.037 (3)
$Ce—S3^{i}$	2.878 (3)	$Ce—S1^{vi}$	3.414 (4)
$Ce—S1^{ii}$	2.897 (3)	$Fe1—S3$	2.224 (6)
$Ce—S1$	2.906 (3)	$Fe1—S2^{i}$	2.265 (3)
$Ce—S2^{iii}$	2.935 (3)	$Fe2—S1^{v}$	2.532 (4)
$Ce—S2^{iv}$	3.000 (3)	$Fe2—S1$	2.578 (4)
$S2^{i}—Fe1—S2^{vii}$	106.67 (12)	$S1^{viii}—Fe2—S1^{v}$	90.43 (15)
$S3—Fe1—S2^{i}$	112.14 (11)	$S1^{v}—Fe2—S1$	90.58 (5)
$S1—Fe2—S1^{ii}$	88.40 (15)	$S1^{viii}—Fe2—S1$	178.6 (2)

Symmetry codes: (i) $1-x, 1-y, z-\frac{1}{2}$; (ii) $-x+y, -x, z$; (iii) $1-x+y, 1-x, z$; (iv) $1-x, -y, z-\frac{1}{2}$; (v) $y, -x+y, z-\frac{1}{2}$; (vi) $y, -x+y, \frac{1}{2}+z$; (vii) $x-y, x, z-\frac{1}{2}$; (viii) $-x, -y, z-\frac{1}{2}$.

Data collection

Stoe IPDS-I diffractometer
φ scans
Absorption correction: numerical [*X-RED* (Stoe & Cie, 2001) and *X-SHAPE* (Stoe & Cie, 1999)]
$T_{\min} = 0.108$, $T_{\max} = 0.246$
6903 measured reflections
865 independent reflections
856 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.107$
$\theta_{\max} = 28.2°$
$h = -13 \rightarrow 13$
$k = -12 \rightarrow 12$
$l = -7 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.135$
$S = 1.08$
865 reflections
39 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0988P)^2 + 5.9571P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 3.38$ e Å^{-3}
$\Delta\rho_{\min} = -1.54$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.035 (3)
Absolute structure: Flack (1983), 390 Friedel pairs
Flack parameter = 0.02 (6)

Since the displacement ellipsoid of the Fe2 octahedral site was initially unusually large, the occupancy of the site was refined freely, resulting in a value of 0.942 (16). Refinement of the occupancy of the Fe1 tetrahedral site confirmed that it is fully occupied. Atomic positions were standardized using the program *STRUCTURE TIDY* (Gelato & Parthé, 1987).

Data collection: *IPDS* (Stoe & Cie, 2000); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1047). Services for accessing these data are described at the back of the journal.

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