

Praseodymium dodecaiodo-ferro-octahedro-hexa-
praseodymium, Pr₇I₁₂FeAndriy Palasyuk, Ingo
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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{Pr-Fe}) = 0.0005$ Å
 R factor = 0.046
 wR factor = 0.099
Data-to-parameter ratio = 55.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Heptaprasedymium iron dodecaiodide or praseodymium dodecaiodo-ferro-octahedro-hexaprasedymium, Pr₇I₁₂Fe (= Pr{Pr₆Fe}I₁₂), was obtained as black single crystals during investigations of the Pr–Fe–I system. It crystallizes with the Sc₇Cl₁₂N-type of structure. According to the formula Pr₁{Pr₆Fe}I₁₂^{i-a}, it contains ‘isolated’ {Pr₆Fe} clusters, edge-capped by 12 I[−] ligands, with Pr1 filling the otherwise empty octahedral holes between the I[−] ions. Both Pr–Pr [3.9119 (8) and 3.9150 (8) Å] and Pr–Fe distances [2.7672 (5) Å] within the {Pr₆Fe} cluster are in good agreement with those of similar compounds, as are the Pr–I distances. One of the Pr atoms and both I atoms occupy sites with symmetry 1 (Wyckhoff position 18f). The second Pr atom (3a) and the Fe atom (3b) are situated in sites with symmetry $\bar{3}$.

Comment

During our ongoing systematic investigations of ternary Pr–I–Z systems (Z being either C or a transition metal), we have now obtained single crystals of Pr₇I₁₂Fe = Pr{Pr₆Fe}I₁₂. Besides Pr₁₂Fe₂I₁₇ (Park & Corbett, 1994), Pr₇FeI₁₂ is the second compound in the Pr–Fe–I system with a crystal structure fully determined by single-crystal X-ray diffraction.

The title compound crystallizes with a rather well explored structure type, with a crystal structure that was first determined for Sc₇Cl₁₂, where the interstitial C or N atom had not been located (Corbett *et al.*, 1978). The crystal structures of both Sc₇Cl₁₂N and Sc₇I₁₂C were determined afterwards from single-crystal data (Hwu & Corbett, 1986; Dudis *et al.*, 1986) and were refined in space groups $R\bar{3}$ and $R3$, respectively. A large number of isostructural compounds have been discovered and characterized, mostly by X-ray powder diffraction (Simon *et al.*, 1991).

The great variety of compounds with the $M_7X_{12}Z$ structure type becomes obvious when one takes into account that the rare earth elements which may be incorporated are Sc, Y, La, Ce, Pr, Gd, Tb, Dy, Ho, Er and Lu, and all tend to form interstitially stabilized octahedral clusters, { M_6Z } X_{12} . The atom Z in the centre of the isolated metal octahedron may be a C atom (other non-metals appear possible) or a transition metal atom, mostly from groups 7, 8 and 9 (Hughbanks & Corbett, 1988; Payne & Corbett, 1990). These ‘interstitial’ atoms are needed to provide electrons for M –C or M – M bonding interactions within the { M_6Z } clusters. This cluster is surrounded by 12 halide ligands X, principally Cl, Br or I atoms. In the $M_7X_{12}Z$ type of compound, a seventh metal atom resides in the centre of an octahedron formed by the halide atoms (Fig. 1). This seventh metal atom is usually of the same element as the cluster metal atoms. In Pr{Pr₆Fe}I₁₂, it provides three further electrons for cluster-based bonding.

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In $\text{Pr}\{\text{Pr}_6\text{Fe}\}\text{I}_{12}$, the $\{\text{Pr}_6\text{Fe}\}$ octahedral clusters have $\bar{3}$ symmetry, hence they deviate slightly from the ideal symmetry (Fig. 1). These octahedral clusters are isolated in the sense that the metal atoms M are not shared with other clusters. All 12 edges of the $\{\text{Pr}_6\text{Fe}\}$ clusters are capped by I ligands, to be formulated as $\{\text{Pr}_6\text{Fe}\}\text{I}_{12}^i$ [i stands for inner ligands (Schäfer & Schnering, 1964)]. Six of these ligands, perpendicular to the $\bar{3}$ axis, also serve as ‘outer’ ligands (‘a’) for neighbouring clusters, so that the formula becomes $\{\text{Pr}_2\text{Fe}\}\text{I}_6^i\text{I}_6^{i-a}$. The other six I^- ligands, I_6^i , are bound to the top and bottom triangles of the $\{\text{Pr}_6\text{Fe}\}$ octahedra (Fig. 1). A perspective view of the crystal structure is displayed in Fig. 2.

The Pr–I distances are 3.1564 (6) Å for the octahedral $\{\text{Pr}_6\text{Fe}\}$, and 3.1847 (7) and 3.2367 (7) Å for Pr2– I_6^i and Pr2– I_6^{i-a} , respectively. These distances are in good accord with those found for other Pr^{3+} – I^- interactions, for example 3.16–3.27 Å in K_2PrI_5 (Meyer *et al.*, 1985), 3.19 Å in PrI_2 –IV and 3.14 and 3.28 Å in PrI_2 –V (Gerlitzki *et al.*, 2004), or 3.18–3.27 Å in $\text{Pr}_{12}\text{Fe}_2\text{I}_{17}$ (Park & Corbett, 1994). The Pr–Pr distances within the octahedral cluster are almost identical, around 3.91 Å (Table 1). They are somewhat larger than the shortest Pr–Pr distances in $\text{Pr}_{12}\text{Fe}_2\text{I}_{17}$ of 3.81 Å (with the longest around 3.94 Å). Interestingly, the Pr–Pr distances in $\text{Pr}_7\text{I}_{12}\text{Fe}$ and in PrI_2 –V are nearly identical, although the latter contains an isolated, but empty, tetrahedron $\{\text{Pr}_4\}$. The Pr–Fe distances are 2.7672 (5) Å in $\text{Pr}\{\text{Pr}_6\text{Fe}\}\text{I}_{12}$ and 2.72–2.77 Å in $\text{Pr}_{12}\text{Fe}_2\text{I}_{17}$, an excellent agreement.

Experimental

The metals (Pr, Chempur, 99.9%; Fe, Merck, 99.5%) and iodine (Merck, 99.8%) were purchased and used without further purification. PrI_3 as a starting material was synthesized from the elements and purified by high-vacuum sublimation (Meyer, 1991). A mixture of PrI_3 , Pr and Fe (molar ratio 4:3:1) was placed under dry-box conditions (M. Braun, Garching; Ar atmosphere) in a tantalum tube, He-arc welded and jacketed by a silica ampoule. The sample was heated to 1223 K, kept there for 5 d, slowly cooled (5 K h^{-1}) to 873 K, annealed at this temperature for 10 d and finally quenched in iced water. X-ray powder diffraction revealed a single-phase product. Single crystals of $\text{Pr}_7\text{I}_{12}\text{Fe}$ were selected with the aid of a microscope in a dry box and mounted in thin-walled glass capillaries.

Crystal data

$\text{FeI}_{12}\text{Pr}_7$	Mo $K\alpha$ radiation
$M_r = 2565.02$	Cell parameters from 13127 reflections
Trigonal, $R\bar{3}$	$\theta = 2.4$ – 32.2°
$a = 15.8296$ (10) Å	$\mu = 23.02 \text{ mm}^{-1}$
$c = 10.7833$ (6) Å	$T = 293$ (2) K
$V = 2340.0$ (2) Å ³	Rhomb, black
$Z = 3$	$0.25 \times 0.15 \times 0.05 \text{ mm}$
$D_x = 5.461 \text{ Mg m}^{-3}$	

Data collection

Stoe IPDS-II diffractometer	1829 independent reflections
ω and φ scans	1593 reflections with $I > 2\sigma(I)$
Absorption correction: numerical	$R_{\text{int}} = 0.065$
[<i>X-SHAPE</i> (Stoe & Cie, 1999)	$\theta_{\text{max}} = 32.2^\circ$
and <i>X-RED</i> (Stoe & Cie, 2001)]	$h = -23 \rightarrow 23$
$T_{\text{min}} = 0.027$, $T_{\text{max}} = 0.324$	$k = -23 \rightarrow 23$
13579 measured reflections	$l = -15 \rightarrow 16$

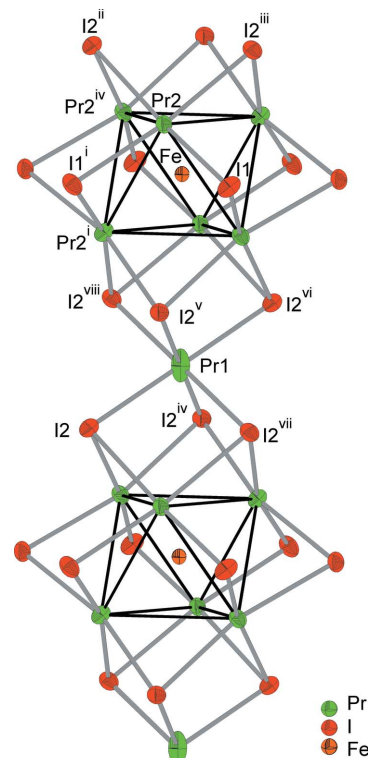


Figure 1

Two $\{\text{Pr}_6\text{Fe}\}\text{I}_{12}$ clusters and their connection *via* Pr1, which resides in an octahedral interstice. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $\frac{2}{3} + x - y, \frac{1}{3} + x, \frac{1}{3} - z$; (iv) $1 - y, 1 + x - y, z$; (v) $y - \frac{1}{3}, \frac{1}{3} - x + y, \frac{4}{3} - z$; (vi) $\frac{2}{3} - x, \frac{4}{3} - y, \frac{4}{3} - z$; (vii) $-x + y, 1 - x, z$; (viii) $\frac{2}{3} + x - y, \frac{1}{3} + x, \frac{4}{3} - z$.]

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$\Delta\rho_{\text{max}} = 3.54 \text{ e \AA}^{-3}$
$wR(F^2) = 0.099$	$\Delta\rho_{\text{min}} = -5.98 \text{ e \AA}^{-3}$
$S = 1.04$	Extinction correction: <i>SHELXL97</i>
1829 reflections	(Sheldrick, 1997)
33 parameters	Extinction coefficient: 0.00067 (3)
$w = 1/[\sigma^2(F_o^2) + (0.0261P)^2 + 153.022P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected geometric parameters (Å, °).

Pr2–I1	3.1847 (7)	Pr2–Pr2 ⁱ	3.9119 (8)
Pr2–I1 ⁱ	3.1950 (7)	Pr2–Pr2 ^{iv}	3.9150 (8)
Pr2–I2 ⁱⁱ	3.2292 (7)	Pr1–I2	3.1564 (6)
Pr2–I2 ⁱⁱⁱ	3.2367 (7)	Fe–Pr2 ^v	2.7672 (5)
Pr2 ⁱ –Pr2–Pr2 ^v	90	I2 ^{vi} –Pr1–I2 ^{iv}	180
Pr2 ^v –Pr2–Pr2 ^{iv}	60		

Symmetry codes: (i) $x - y + \frac{2}{3}, x + \frac{1}{3}, -z + \frac{1}{3}$; (ii) $x, y, z - 1$; (iii) $-x + y, -x + 1, z - 1$; (iv) $-y + 1, x - y + 1, z$; (v) $-x + y, -x + 1, z$; (vi) $y - \frac{1}{3}, -x + y + \frac{1}{3}, -z + \frac{4}{3}$.

The highest peak in the final difference Fourier map is 0.38 Å from atom Pr2 and the deepest hole is 0.86 Å from the same atom.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

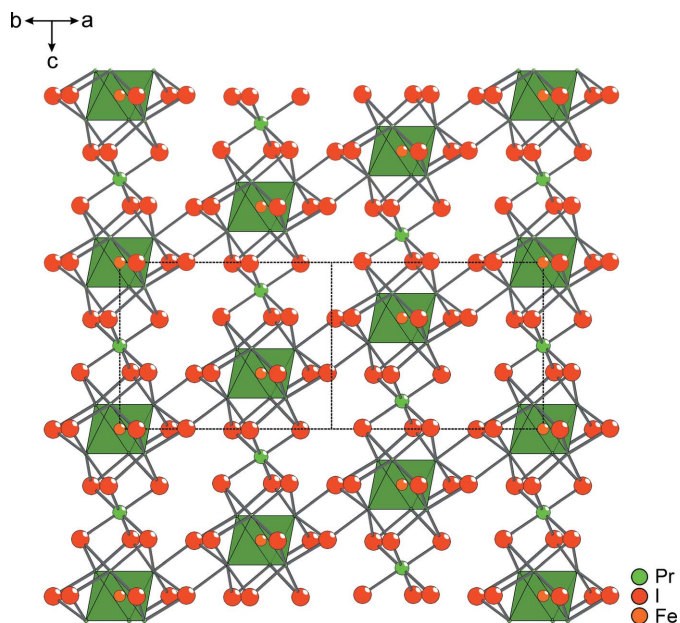


Figure 2

The arrangement of the $\{\text{Pr}_{26}\text{Fe}\}\text{I}_{12}$ clusters and their connection via Pr1 and common I^- ligands in the crystal structure of $\text{Pr}_1\{\text{Pr}_{26}\text{Fe}\}\text{I}_{16}$.

DIAMOND (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

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