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Holmium dodecaiodidoiron-*octahedro*-hexaholmium, $\{FeHo_6\}I_{12}Ho$

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Key indicators: single-crystal X-ray study; T = 293 K; mean σ(Ho–I) = 0.001 Å; R factor = 0.039; wR factor = 0.096; data-to-parameter ratio = 36.4.

Single crystals of $\{FeHo_6\}I_{12}Ho$ were obtained during the reaction of HoI_3 with metallic holmium and iron in a sealed tantalum container. The crystal structure consists of isolated holmium clusters encapsulating a single Fe atom, $\{FeHo_6\}$ ($\overline{3}$ symmetry). The rare earth metal atoms are surrounded by 12 edge-capping and six terminal iodide ligands that either connect the clusters to each other directly or *via* HoI_6 octahedra ($\overline{3}$ symmetry).

Related literature

Reduced rare earth metal halides without and with metal clusters have been reviewed several times, see, for example: Corbett (1973, 1996, 2000, 2006); Hughbanks & Corbett (1988); Meyer (1988, 2007); Meyer & Wickleder (2000); Simon (1981); Simon *et al.* (1991); Wiglusz *et al.* (2007). For the synthesis of the starting material HoI_3, see: Meyer (1991). Isotypic structures have been reported by Hohnstedt (1993), $\{CHo_6\}I_{12}Ho$, and Palasyuk *et al.* (2006), $\{FePr_6\}I_{12}Pr$.

Experimental

Crystal data

$FeHo_7I_{12}$
M_r = 2733.16
Trigonal, $R\overline{3}$
a = 15.2973 (17) Å
c = 10.6252 (16) Å
V = 2153.3 (5) Å^3
Z = 3
Mo $K\alpha$ radiation
μ = 32.43 mm^{-1}
T = 293 (2) K
0.2 × 0.2 × 0.2 mm

Data collection

Stoe IPDS-II diffractometer
Absorption correction: numerical [*X-RED* (Stoe & Cie, 2001) and *X-SHAPE* (Stoe & Cie, 1999)]
T_{min} = 0.027, T_{max} = 0.071
6920 measured reflections
1166 independent reflections
861 reflections with $I > 2\sigma(I)$
R_{int} = 0.115

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.096
S = 0.97
1166 reflections
32 parameters
$\Delta\rho_{max}$ = 2.36 e Å^{-3}
$\Delta\rho_{min}$ = −2.44 e Å^{-3}

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2215).

References

Brandenburg, K. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Corbett, J. D. (1973). *Rev. Chim. Miner.* **10**, 239–257.
Corbett, J. D. (1996). *J. Chem. Soc. Dalton Trans.* pp. 575–587.
Corbett, J. D. (2000). *Inorg. Chem.* **39**, 5178–5191.
Corbett, J. D. (2006). *J. Alloys Compds*, **418**, 1–20.
Hohnstedt, C. (1993). Dissertation, Universität Hannover, Germany.
Hughbanks, T. & Corbett, J. D. (1988). *Inorg. Chem.* **27**, 2022–2026.
Meyer, G. (1988). *Chem. Rev.* **88**, 93–107.
Meyer, G. (1991). *Synthesis of Lanthanide and Actinide Compounds*, edited by G. Meyer & L. R. Morss, pp. 135–144. Kluwer: Dordrecht.
Meyer, G. (2007). *Z. Anorg. Allg. Chem.* **633**, 2537–2552.
Meyer, G. & Wickleder, M. S. (2000). *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 28, edited by K. A. Gscheidner Jr. & L. Eyring, pp. 53–129. Elsevier: Amsterdam.
Palasyuk, A., Pantenburg, I. & Meyer, G. (2006). *Acta Cryst.* E**62**, i61–i63.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Simon, A. (1981). *Angew. Chem. Int. Ed. Engl.* **20**, 1–22.
Simon, A., Mattausch, Hj., Miller, G. J., Bauhofer, W. & Kremer, R. (1991). *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 15, edited by K. A. Gschneidner Jr. & L. Eyring, pp. 191–285. Elsevier: Amsterdam.
Stoe & Cie (1999). *X-SHAPE*. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (2001). *X-AREA* and *X-RED*. Stoe & Cie, Darmstadt, Germany.
Wiglusz, R., Pantenburg, I. & Meyer, G. (2007). *Z. Anorg. Allg. Chem.* **633**, 1317–1319.

supplementary materials

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Holmium dodecaiodidoiron-*octahedro*-hexaholmium, $\{FeHo_6\}I_{12}Ho$

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Comment

Rare earth cluster compounds of the general formula $\{Z(RE)_6\}I_{12}RE$, where Z is an interstitial transition metal or main group element and RE is a rare earth element, have been well explored by Hughbanks and Corbett (1988) for RE = Sc, Y, Pr and Gd. Additionally, compounds of the formula $\{Z(RE)_6\}I_{12+y}A_x$, where A is an alkali metal (Rb or Cs) with x = 1–4 and y = 0–1 and Z = C, C_2, are known for the rare earth elements Pr and Er that were compiled and studied by Meyer & Wickleder (2000) and Wiglusz *et al.* (2007). With $\{FeHo_6\}I_{12}Ho$ we were able to extend the knowledge of this structure type to the element holmium, where only $\{CHo_6\}I_{12}Ho$ had been synthesized previously by Hohnstedt (1993). Other reviews of reduced rare earth metal halides without and with metal clusters were given, for example, by Corbett (1973, 1996, 2000, 2006), Meyer (1988, 2007), Meyer & Wickleder (2000), Simon (1981) and Simon *et al.* (1991).

The structure of $\{FeHo_6\}I_{12}Ho$ is isotypic with $\{FePr_6\}I_{12}Pr$ (Palasyuk *et al.*, 2006) and consists of isolated $\{FeHo_6\}$ clusters, *i.e.* the metal atoms are not shared with other clusters. The $\{FeHo_6\}$ cluster core is surrounded by twelve edge-capping and six terminal iodide ligands that either connect the clusters to each other directly or *via* HoI_6 octahedra (Fig. 1). In $\{FeHo_6\}I_{12}Ho$, the $\{FeHo_6\}$ octahedra have $\overline{3}$ symmetry, only slightly deviating from ideal octahedral symmetry. The Ho—Ho distances range from 3.6394 (11) to 3.7297 (12) Å. The Ho—I distances vary between 3.0106 (9) and 3.3116 (12) Å.

Experimental

Black, almost cubic crystals of $\{FeHo_6\}I_{12}Ho$ were obtained by the reaction of HoI_3 (200 mg) with holmium powder (84 mg, Chempur, 99.9%) and iron powder (10 mg, Merck, p.a.) in a tantalum container at 1273 K for 200 h. HoI_3 had been synthesized from stoichiometric amounts of holmium and iodine, followed by sublimation in high vacuum for purification (Meyer, 1991). Due to air and moisture sensitivity of both reagents and products, all handlings were carried out in an argon-filled glove box (M. Braun, Garching, Germany).

Refinement

The displacement parameter for the Fe atom was refined isotropically. The highest peak (2.36 e $Å^{-3}$) in the final difference Fourier map is 1.20 Å from atom Ho1 and the deepest hole (-2.44 e $Å^{-3}$) is 2.40 Å from the same atom.

Figures

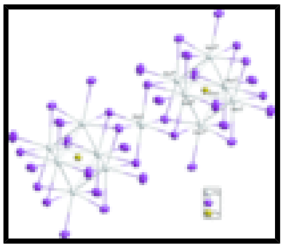

Fig. 1. : {$FeHo_6$} clusters connected *via* HoI_6 units, drawn with displacement ellipsoids at the 90% probability level [Symmetry codes: (i) 1 + *y*, 1 - *x* + *y*, 1 - *z*; (ii) 1 - *y*, -1 + *x*-*y*, *z*; (iii) -*x* + 8/3, -*y* + 1/3, -*z* + 4/3; (iv) *x*-*y*, -1 + *x*, 1 - *z*; v) 2 - *x*, -*y*, 1 - *z*; vi) 2 - *x* + *y*, 1 - *x*, *z*.]

Iron heptadysprosium dodecaiodide

Crystal data

$FeHo_7I_{12}$	$Z = 3$
$M_r = 2733.16$	$F_{000} = 3393$
Trigonal, $R\overline{3}$	$D_x = 6.323$ Mg m^{-3}
Hall symbol: -R 3	Mo *K*α radiation λ = 0.71073 Å
a = 15.2973 (17) Å	Cell parameters from 1775 reflections
b = 15.2973 (17) Å	θ = 1.9–28.2°
c = 10.6252 (16) Å	μ = 32.43 mm^{-1}
α = 90°	*T* = 293 (2) K
β = 90°	Cubic, black
γ = 120°	0.2 × 0.2 × 0.2 mm
V = 2153.3 (5) Å^3	

Data collection

Stoe IPDS-II diffractometer	1166 independent reflections
Radiation source: fine-focus sealed tube	861 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.115$
T = 293(2) K	$\theta_{max} = 28.1°$
ω scans	$\theta_{min} = 2.5°$
Absorption correction: numerical [X-RED (Stoe & Cie, 2001) and X-SHAPE (Stoe & Cie, 1999)]	$h = -20\rightarrow19$
$T_{min} = 0.027$, $T_{max} = 0.071$	$k = -19\rightarrow20$
6920 measured reflections	$l = -14\rightarrow14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.047P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$(\Delta/\sigma)_{max} = 0.001$

$wR(F^2) = 0.096$	$\Delta\rho_{max} = 2.36$ e Å^{-3}
$S = 0.97$	$\Delta\rho_{min} = -2.44$ e Å^{-3}
1166 reflections	Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/sin(2\theta)]^{-1/4}$
32 parameters	Extinction coefficient: 0.00035 (3)
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Ho1	1.15739 (5)	0.04355 (5)	0.63807 (6)	0.0153 (2)
Ho2	1.0000	0.0000	1.0000	0.0213 (4)
I1	1.05135 (6)	−0.13025 (7)	0.83941 (7)	0.0190 (2)
I2	1.31674 (7)	0.23705 (7)	0.50663 (8)	0.0242 (3)
Fe1	1.0000	0.0000	0.5000	0.0132 (9)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ho1	0.0155 (3)	0.0161 (3)	0.0147 (3)	0.0083 (3)	−0.0004 (2)	−0.0002 (2)
Ho2	0.0223 (5)	0.0223 (5)	0.0194 (7)	0.0111 (3)	0.000	0.000
I1	0.0202 (5)	0.0195 (5)	0.0183 (4)	0.0106 (4)	−0.0006 (3)	0.0010 (3)
I2	0.0167 (5)	0.0233 (5)	0.0260 (5)	0.0050 (4)	−0.0030 (3)	0.0060 (3)

Geometric parameters (Å, °)

Ho1—Fe1	2.6056 (7)	Ho2—I1^{vii}	3.0106 (9)
Ho1—I2	3.0722 (11)	Ho2—I1	3.0106 (9)
Ho1—I2^{i}	3.1144 (11)	Ho2—I1^{ii}	3.0106 (9)
Ho1—I1	3.1565 (11)	Ho2—I1^{viii}	3.0106 (9)
Ho1—I1^{ii}	3.1758 (11)	I1—Ho1^{v}	3.1758 (11)
Ho1—I2^{iii}	3.3116 (11)	I2—Ho1^{iv}	3.1144 (11)
Ho1—Ho1^{i}	3.6394 (11)	I2—Ho1^{iii}	3.3116 (11)
Ho1—Ho1^{iv}	3.6394 (11)	Fe1—Ho1^{ix}	2.6056 (7)

Ho1—Ho1^{v}	3.7297 (12)	Fe1—Ho1^{iv}	2.6056 (7)
Ho1—Ho1^{ii}	3.7297 (12)	Fe1—Ho1^{ii}	2.6056 (7)
Ho2—I1^{v}	3.0106 (9)	Fe1—Ho1^{i}	2.6056 (7)
Ho2—I1^{vi}	3.0106 (9)	Fe1—Ho1^{v}	2.6056 (7)
Fe1—Ho1—I2	100.19 (3)	I2^{iii}—Ho1—Ho1^{ii}	133.68 (2)
Fe1—Ho1—I2^{i}	99.12 (3)	Ho1^{i}—Ho1—Ho1^{ii}	90.0
I2—Ho1—I2^{i}	89.813 (17)	Ho1^{iv}—Ho1—Ho1^{ii}	59.176 (12)
Fe1—Ho1—I1	98.41 (3)	Ho1^{v}—Ho1—Ho1^{ii}	60.0
I2—Ho1—I1	161.02 (3)	I1^{v}—Ho2—I1^{vi}	180.0
I2^{i}—Ho1—I1	90.95 (3)	I1^{v}—Ho2—I1^{vii}	88.96 (2)
Fe1—Ho1—I1^{ii}	97.93 (3)	I1^{vi}—Ho2—I1^{vii}	91.04 (2)
I2—Ho1—I1^{ii}	88.28 (3)	I1^{v}—Ho2—I1	91.04 (2)
I2^{i}—Ho1—I1^{ii}	162.91 (3)	I1^{vi}—Ho2—I1	88.96 (2)
I1—Ho1—I1^{ii}	85.44 (4)	I1^{vii}—Ho2—I1	180.0
Fe1—Ho1—I2^{iii}	177.02 (3)	I1^{v}—Ho2—I1^{ii}	91.04 (2)
I2—Ho1—I2^{iii}	81.94 (3)	I1^{vi}—Ho2—I1^{ii}	88.96 (2)
I2^{i}—Ho1—I2^{iii}	82.92 (3)	I1^{vii}—Ho2—I1^{ii}	88.96 (2)
I1—Ho1—I2^{iii}	79.33 (3)	I1—Ho2—I1^{ii}	91.04 (2)
I1^{ii}—Ho1—I2^{iii}	80.00 (3)	I1^{v}—Ho2—I1^{viii}	88.96 (2)
Fe1—Ho1—Ho1^{i}	45.702 (10)	I1^{vi}—Ho2—I1^{viii}	91.04 (2)
I2—Ho1—Ho1^{i}	99.07 (3)	I1^{vii}—Ho2—I1^{viii}	91.04 (2)
I2^{i}—Ho1—Ho1^{i}	53.43 (2)	I1—Ho2—I1^{viii}	88.96 (2)
I1—Ho1—Ho1^{i}	96.59 (2)	I1^{ii}—Ho2—I1^{viii}	180.00 (3)
I1^{ii}—Ho1—Ho1^{i}	143.57 (2)	Ho2—I1—Ho1	91.20 (3)
I2^{iii}—Ho1—Ho1^{i}	136.24 (3)	Ho2—I1—Ho1^{v}	90.83 (3)
Fe1—Ho1—Ho1^{iv}	45.702 (10)	Ho1—I1—Ho1^{v}	72.17 (3)
I2—Ho1—Ho1^{iv}	54.50 (2)	Ho1—I2—Ho1^{iv}	72.07 (3)
I2^{i}—Ho1—Ho1^{iv}	96.45 (3)	Ho1—I2—Ho1^{iii}	98.06 (3)
I1—Ho1—Ho1^{iv}	144.05 (2)	Ho1^{iv}—I2—Ho1^{iii}	170.08 (3)
I1^{ii}—Ho1—Ho1^{iv}	96.25 (2)	Ho1^{ix}—Fe1—Ho1	180.00 (2)
I2^{iii}—Ho1—Ho1^{iv}	136.44 (2)	Ho1^{ix}—Fe1—Ho1^{iv}	91.403 (19)
Ho1^{i}—Ho1—Ho1^{iv}	61.65 (2)	Ho1—Fe1—Ho1^{iv}	88.597 (19)
Fe1—Ho1—Ho1^{v}	44.298 (10)	Ho1^{ix}—Fe1—Ho1^{ii}	88.597 (19)
I2—Ho1—Ho1^{v}	144.47 (2)	Ho1—Fe1—Ho1^{ii}	91.403 (19)
I2^{i}—Ho1—Ho1^{v}	96.42 (3)	Ho1^{iv}—Fe1—Ho1^{ii}	88.597 (19)
I1—Ho1—Ho1^{v}	54.16 (2)	Ho1^{ix}—Fe1—Ho1^{i}	91.403 (19)
I1^{ii}—Ho1—Ho1^{v}	94.97 (2)	Ho1—Fe1—Ho1^{i}	88.597 (19)
I2^{iii}—Ho1—Ho1^{v}	133.49 (2)	Ho1^{iv}—Fe1—Ho1^{i}	91.403 (19)
Ho1^{i}—Ho1—Ho1^{v}	59.176 (12)	Ho1^{ii}—Fe1—Ho1^{i}	180.0
Ho1^{iv}—Ho1—Ho1^{v}	90.0	Ho1^{ix}—Fe1—Ho1^{v}	88.597 (19)

Fe1—Ho1—Ho1^{ii}	44.298 (10)	Ho1—Fe1—Ho1^{v}	91.403 (19)
I2—Ho1—Ho1^{ii}	95.36 (3)	Ho1^{iv}—Fe1—Ho1^{v}	180.00 (3)
I2^{i}—Ho1—Ho1^{ii}	143.40 (2)	Ho1^{ii}—Fe1—Ho1^{v}	91.404 (19)
I1—Ho1—Ho1^{ii}	95.30 (2)	Ho1^{i}—Fe1—Ho1^{v}	88.597 (19)
I1^{ii}—Ho1—Ho1^{ii}	53.68 (2)		

Symmetry codes: (i) *y*+1, −*x*+*y*+1, −*z*+1; (ii) −*y*+1, *x*−*y*−1, *z*; (iii) −*x*+8/3, −*y*+1/3, −*z*+4/3; (iv) *x*−*y*, *x*−1, −*z*+1; (v) −*x*+*y*+2, −*x*+1, *z*; (vi) *x*−*y*, *x*−1, −*z*+2; (vii) −*x*+2, −*y*, −*z*+2; (viii) *y*+1, −*x*+*y*+1, −*z*+2; (ix) −*x*+2, −*y*, −*z*+1.

Fig. 1