Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Yttrium triiodide, YI_3

Liesbet Jongen and Gerd Meyer*

Institut für Anorganische Chemie, Universität zu Köln, Greinstrasse 6, D-50939 Köln, Germany

Correspondence e-mail:
gerd.meyer@uni-koeln.de

Received 8 June 2005
Accepted 23 June 2005
Online 9 July 2005

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(I–Y) = 0.001 Å
R factor = 0.032
wR factor = 0.090
Data-to-parameter ratio = 32.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Single crystals of YI_3 were obtained by high-vacuum sublimation of the crude product at 1213 K. The crystal structure is that of the BiI_3 structure type. Two-thirds of the octahedral voids between every second hexagonally closest-packed layer of I^- ions are occupied by Y^{3+} ions. Thereby, the YI_6 octahedra share common edges within $B\gamma_{2/3}A$ slabs in the stacking sequence $\cdots\gamma_{2/3}A\square B\gamma_{2/3}A\square B\gamma_{2/3}A\square B\gamma_{2/3}\cdots$.

Comment

Anhydrous rare earth trihalides, MX_3, are important starting materials for a great many syntheses (Meyer & Wickleder, 2000). The preparation of pure samples of rare earth iodides MI_3 is especially demanding. The most common impurity is oxygen, since the oxyiodides, MOI, are thermodynamically favoured compounds (with respect to the binary components M_2O_3 and MI_3). As rare earth metals are available in sufficient purity and at affordable prices, the synthetic route of choice is the direct combination of the elements in stoichiometric quantities (or with a slight excess of iodine) (Corbett, 1983). A small quantity of hydrogen appears to have a catalytic effect through the formation of HI, and considerably helps to decrease the reaction temperature, such that glass ampoules can be used as reaction containers (Meyer, 1991). As oxygen appears to be ubiquitous (from air, water or oxidic impurities in the starting materials, rare earth metals and iodine), puri-

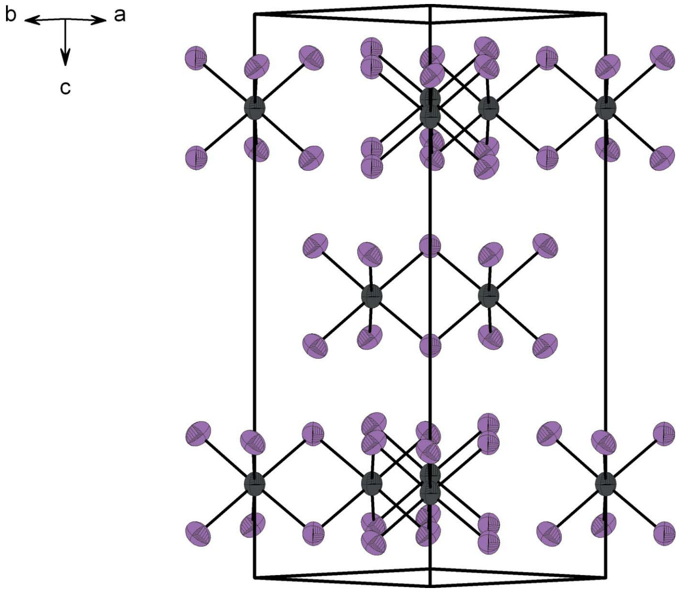

Figure 1
A perspective view of the crystal structure of YI_3 (purple denotes I and dark grey denotes Y). Displacement ellipsoids are drawn at the 50% probability level.

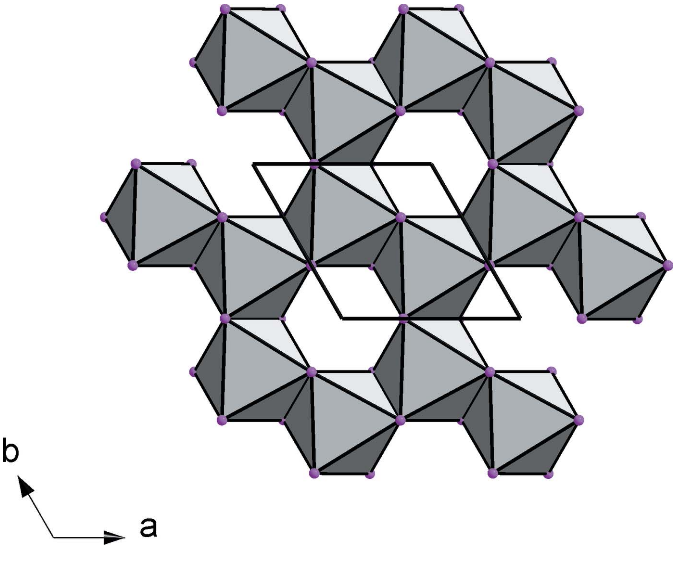

Figure 2
Part of the crystal structure of YI_3, viewed along the c axis, showing one slab $B\gamma_{2/3}A$ of edge-connected $[YI_{6/2}]$ octahedra.

fication by high-vacuum sublimation of the crude product is necessary whenever the by-product MOI is a problem in subsequent reactions. In this process, at 1213 K and 10^{-5} bar (1 bar = 100 000 Pa), single crystalline triiodides are often obtained. The quality of the crystals of such triiodides is, however, usually poor, which appears to be an intrinsic property of the corresponding crystal structure types.

In one of our routine sublimations, good quality single crystals of yttrium triiodide, YI_3, were fortuitously obtained. YI_3 crystallizes with the BiI_3 type of structure (Braekken, 1930; Ruck, 1995). The crystal structure consists of a hexagonal closest packing of I^- ions, and hence with the stacking sequence $\cdots ABABAB\cdots$. Two-thirds of the octahedral voids between every second layer are occupied by Y^{3+} ions. The complete stacking sequence can be described as follows: $\cdots\gamma_{2/3}A\square B\gamma_{2/3}A\square B\gamma_{2/3}A\square B\gamma_{2/3}\cdots$ (Fig. 1). The $[YI_6]$ octahedron is only slightly distorted, with Y—I distances of 3.0108 (7) and 3.0112 (2) Å (3 × each) and with angles deviating by at most 3° from the ideal values of 90 and 180°. Within one slab of octahedra $B\gamma_{2/3}A$, those iodide octahedra whose voids are occupied by Y^{3+} share common edges (Fig. 2).

Experimental

YI_3 was synthesized from the elements [typically 0.850 g of yttrium chips (Chempur, 99.9%) and 4.150 g of iodine (Riedel–de Häen, 99.8%)] in an evacuated glass ampoule with a temperature programme as follows: slowly heated to 373 K and kept there for 1 h, then slowly heated to 423 K (1 h), 458 K (12 h), 503 K (6 h) and then cooled to ambient temperature by turning off the power to the furnace. The glass ampoule was opened in a dry box (M. Braun, Garching, Germany) and transferred to a vacuum line, where pure crystalline YI_3 was sublimed off the crude product at 1213 K and a pressure of about 10^{-5} bar. Crystals were selected under a microscope in an argon-filled dry box and mounted in thin-walled glass capillaries.

Crystal data

YI_3
$M_r = 469.61$
Trigonal, $R\overline{3}$ (on hexagonal axes)
$a = 7.4864\ (12)$ Å
$c = 20.880\ (6)$ Å
$V = 1013.5\ (4)$ Å^3
$Z = 6$
$D_x = 4.617$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 6289 reflections
$\theta = 2.9$–$29.3°$
$\mu = 22.20$ mm^{-1}
$T = 293\ (2)$ K
Plate, colourless
0.20 × 0.10 × 0.05 mm

Data collection

Stoe IPDS-I diffractometer
φ scans
Absorption correction: numerical [*X-RED* (Stoe & Cie, 2001), after optimizing the crystal shape using *X-SHAPE* (Stoe & Cie, 1999)]
$T_{\min} = 0.023$, $T_{\max} = 0.204$
3717 measured reflections

448 independent reflections
409 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.122$
$\theta_{\max} = 26.0°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.090$
$S = 1.08$
448 reflections
14 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 2.737P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.16$ e Å^{-3}
$\Delta\rho_{\min} = -1.05$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.022 (3)

Table 1
Selected geometric parameters (Å, °).

$Y—I^{i}$	3.0108 (7)	$Y—I^{ii}$	3.0112 (7)
$I^{i}—Y—I^{iii}$	89.52 (2)	$I—Y—I^{ii}$	90.08 (2)
$I^{i}—Y—I$	92.21 (2)		

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

The highest peak and the deepest hole in the final Fourier map are located 0.79 and 0.90 Å, respectively, from I.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

References

Braekken, H. (1930). *Z. Kristallogr.* **75**, 574–575.
Brandenburg, K. (2001). *DIAMOND*. Release 2.1e. Crystal Impact GbR, Bonn, Germany.
Corbett, J. D. (1983). *Inorg. Synth.* **22**, 31–36.
Meyer, G. (1991). *Synthesis of Lanthanide and Actinide Compounds*, edited by G. Meyer & L. R. Morss, pp. 135–144. Dordrecht: Kluwer.
Meyer, G. & Wickleder, M. S. (2000). *Handbook on the Chemistry and Physics of Rare Earths*, Vol. 28, edited by K. A. Gschneider Jr & L. Eyring, ch. 177, pp. 53–129. Amsterdam: Elsevier.
Ruck, M. (1995). *Z. Kristallogr.* **210**, 650–655.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Stoe & Cie (1999). *X-SHAPE*. Version 1.06. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (2001). *X-AREA* (MainMenu Version 1.16) and *X-RED* (Version 1.22). Stoe & Cie, Darmstadt, Germany.

supporting information

Acta Cryst. (2005). E**61**, i151–i152   [https://doi.org/10.1107/S1600536805019847]

Yttrium triiodide, YI_3

Liesbet Jongen and Gerd Meyer

Yttrium triiodide

Crystal data

YI_3
$M_r = 469.61$
Hexagonal, $R\bar{3}$
Hall symbol: -R 3
$a = 7.4864$ (12) Å
$c = 20.880$ (6) Å
$V = 1013.5$ (4) Å^3
$Z = 6$
$F(000) = 1188$
$D_x = 4.617$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6289 reflections
$\theta = 2.9$–$29.3°$
$\mu = 22.20$ mm^{-1}
$T = 293$ K
Plate, colourless
0.20 × 0.10 × 0.05 mm

Data collection

Stoe IPDS-I diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ scans
Absorption correction: numerical [X-RED (Stoe & Cie, 2001), after optimizing the crystal shape using X-SHAPE (Stoe & Cie, 1999)]
$T_{min} = 0.023$, $T_{max} = 0.204$
3717 measured reflections
448 independent reflections
409 reflections with $I > 2\sigma(I)$
$R_{int} = 0.122$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.9°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.090$
$S = 1.08$
448 reflections
14 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 2.737P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.16$ e Å^{-3}
$\Delta\rho_{min} = -1.05$ e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.022 (3)

Special details

Experimental. A suitable single-crystal was carefully selected under a polarizing microscope and mounted in a glass capillary. The scattering intensities were collected with an imaging-plate diffractometer (*IPDS* I, Stoe & Cie) equipped with a fine-focus sealed-tube X-ray source (Mo Kα, λ = 0.71073 Å) operating at 50 kV and 40 mA. Intensity data for YI_3 were collected at 293 K by φ scans in 142 frames in the 2θ range 2.93–52.00°. Structure solution and refinement were carried out using the program *SHELXL97* (Sheldrick, 1997). A numerical absorption correction (*X-RED* (Stoe & Cie, 2001) was applied after optimization of the crystal shape (*X-SHAPE* (Stoe & Cie, 1999)). The final difference maps were free of any chemically significant features. The refinement was based on F^2 for ALL reflections.

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 (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
I	−0.01189 (6)	0.66558 (5)	0.08312 (2)	0.0317 (3)
Y	0.0000	1.0000	0.16627 (4)	0.0264 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I	0.0342 (4)	0.0257 (4)	0.0326 (4)	0.0130 (2)	0.00833 (14)	0.00020 (14)
Y	0.0238 (4)	0.0238 (4)	0.0315 (6)	0.0119 (2)	0.000	0.000

Geometric parameters (Å, º)

I—Y^{i}	3.0108 (7)	Y—I^{iii}	3.0108 (7)
I—Y	3.0112 (7)	Y—I^{iv}	3.0112 (7)
Y—I^{ii}	3.0108 (7)	Y—I^{v}	3.0112 (7)
Y—I^{i}	3.0108 (7)		
Y^{i}—I—Y	91.739 (17)	I^{i}—Y—I^{iv}	92.21 (2)
I^{ii}—Y—I^{i}	89.52 (2)	I^{iii}—Y—I^{iv}	88.260 (17)
I^{ii}—Y—I^{iii}	89.52 (2)	I—Y—I^{iv}	90.08 (2)
I^{i}—Y—I^{iii}	89.52 (2)	I^{ii}—Y—I^{v}	88.260 (17)
I^{ii}—Y—I	92.21 (2)	I^{i}—Y—I^{v}	177.172 (15)
I^{i}—Y—I	88.261 (17)	I^{iii}—Y—I^{v}	92.21 (2)
I^{iii}—Y—I	177.171 (15)	I—Y—I^{v}	90.08 (2)
I^{ii}—Y—I^{iv}	177.171 (15)	I^{iv}—Y—I^{v}	90.08 (2)

Symmetry codes: (i) $-x-1/3, -y+4/3, -z+1/3$; (ii) $y-1/3, -x+y+1/3, -z+1/3$; (iii) $x-y+2/3, x+4/3, -z+1/3$; (iv) $-x+y-1, -x+1, z$; (v) $-y+1, x-y+2, z$.