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Praseodymium triiodide nonahydrate

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The room temperature single-crystal X-ray structure determination of the title compound, $PrI_3 \cdot 9H_2O$, better represented as $[Pr(OH_2)_9]I_3$, shows unequivocally that it belongs to the structure type preferably adopted by hydrates of the lighter rare earth iodides (La–Ho). The praseodymium cation is coordinated by nine water molecules in the form of a tricapped trigonal prism with the metal atom situated on a site of crystallographic symmetry *mm*2.

Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(Pr–O) = 0.007 Å
H-atom completeness 0%
R factor = 0.050
wR factor = 0.136
Data-to-parameter ratio = 24.8

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

Comment

We have attempted to synthesize rare earth triiodides with a defined hydration shell of the rare earth cation in order to study quantitatively the effect of water on lifetimes and high quantum yields for luminescence of these species in ionic liquids. We have previously observed that even small amounts of water in these systems lead to a dramatic reduction, as far as total quenching of the luminescense (Arenz *et al.*, 2005).

Studies on ‘maximally’ hydrated trivalent rare earth iodides show that the lighter (and larger) rare earth elements form a nonahydrate, whereas the heavier (and smaller) rare earth elements strongly favour a lower coordination number and thus octahydrates are the maximal hydrates found for Er–Lu (Kwestroo & von Hal, 1976; Heinio *et al.*, 1980). Single-crystal structures have been so far unequivocally established for the nonahydrates of La, Sm, Gd, Dy, Ho and the octahydrates of Er, Yb and Lu (Lim *et al.*, 2000). Recently, we were able to add to the list the single-crystal structure of $NdI_3 \cdot 9H_2O$ (Timofte *et al.*, 2005).

$PrI_3 \cdot 9H_2O$ (Fig. 1) crystallizes isotypically with the other nonahydrates in the space group *Pmmn*. The nature of the

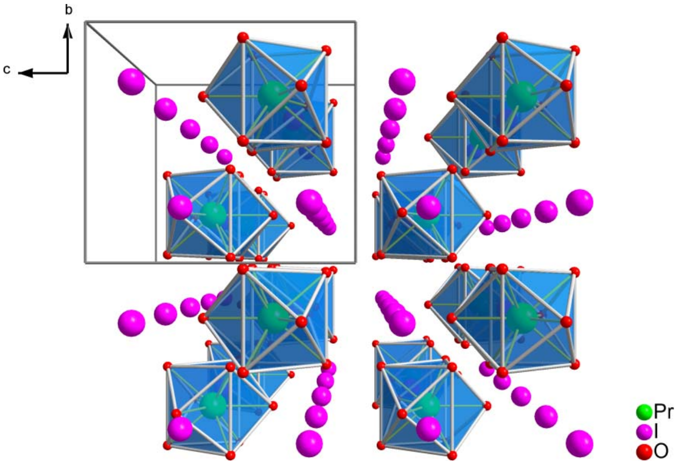

Figure 1
The unit cell contents of $PrI_3 \cdot 9H_2O$, viewed along the *a* axis.

compound is better described by the the formula $[Pr(OH_2)_9]I_3$, as nine water molecules (four independent O atoms) surround the rare earth cation in the form of a triangular tricapped prism, with the metal atom situated on a site of crystallographic symmetry *mm*2 (Fig. 2). As expected from the lanthanide contraction, the mean rare earth cation–oxygen distance in $PrI_3·9H_2O$ (Pr—O = 2.526 Å) is slightly larger than in $NdI_3·9H_2O$ (Nd—O = 2.512 Å). The iodide anions are located around the nonaaquapraseodymium cations in rows separating these.

Experimental

All reactions were carried out under an argon atmosphere. Praseodymium oxide (1 mmol; Pr_6O_{11}; 99.9% Chempur) was dissolved in multiply distilled 57% hydroiodic acid (5 ml, HI; Acros Organics). The solution was heated to 313 K and stirred for 30 min. In order to achieve complete dissolution of Pr_6O_{11} in the hydroiodic acid, the pH had to be controlled carefully (acidic, 0–1). After cooling the solution slowly to 298 K, the product crystallized within 6 d from the solution. On removing the inert atmosphere, the product decomposes and becomes liquid. The crystals obtained were placed with a small amount of mother liquor in glass capillaries and mounted on the diffractometer.

Crystal data

$[Pr(OH_2)_9]I_3$
$M_r = 683.75$
Orthorhombic, *Pmmn*
$a = 11.720$ (2) Å
$b = 8.0163$ (15) Å
$c = 8.952$ (2) Å
$V = 841.1$ (3) Å^3
$Z = 2$
$D_x = 2.700$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2000 reflections
$\theta = 1.9$–27.7°
$\mu = 8.42$ mm^{-1}
$T = 298$ (2) K
Irregular fragment, pale yellow to green
0.30 × 0.10 × 0.05 mm

Data collection

Stoe IPDS-I diffractometer
φ scans
Absorption correction: numerical [*X-RED32* (Stoe & Cie, 2002) and *X-SHAPE* (Stoe & Cie, 1999)]
$T_{min} = 0.151$, $T_{max} = 0.607$
8456 measured reflections
1016 independent reflections
870 reflections with $I > 2\sigma(I)$
$R_{int} = 0.072$
$\theta_{max} = 27.7°$
$h = -15 \rightarrow 15$
$k = -9 \rightarrow 9$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.136$
$S = 1.09$
1016 reflections
41 parameters
H-atom parameters not defined
$w = 1/[\sigma^2(F_o^2) + (0.0732P)^2 + 3.5369P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.12$ e Å^{-3}
$\Delta\rho_{min} = -1.62$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.030 (3)

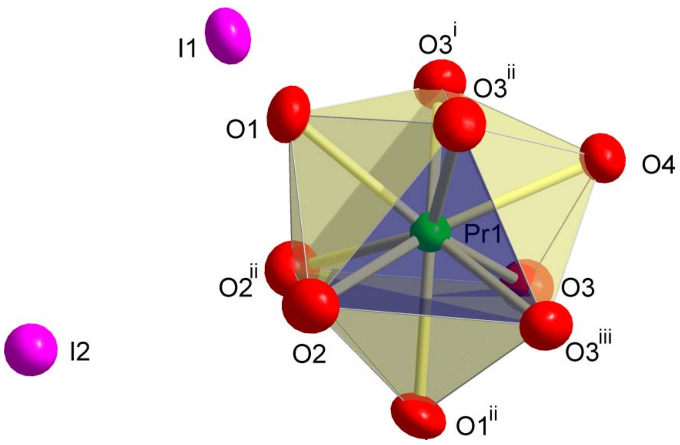

Figure 2
Coordination of praseodymium by water in $PrI_3·9H_2O$. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) = $\frac{1}{2} - x, y, z$; (ii) = $\frac{1}{2} - x, \frac{1}{2} - y, z$; (iii) = $x, \frac{3}{2} - y, z$.]

Table 1
Selected bond lengths (Å).

Pr—O3	2.520 (6)	Pr—O1	2.530 (7)
Pr—O2	2.527 (9)	Pr—O4	2.542 (11)

The maximum residual electron density is 2.34 Å from I1, and the minimum electron density is 0.78 Å from Pr.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *SHELXL97*.

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