

Aqua(*N,N',N'',N'''*-tetrakis(2-hydroxyethyl)-1,4,7,10-tetrazacyclododecane)praseodymium(III) hexanitratopraseodymate(III) dihydrateRoxan U. Richards-Johnson,<sup>a</sup>  
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## Key indicators

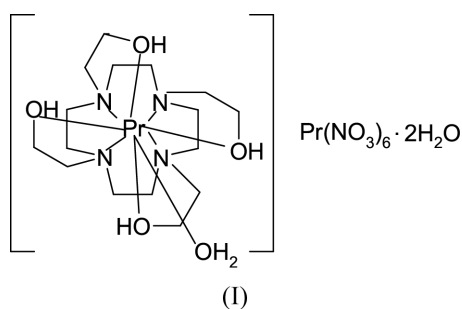
Single-crystal X-ray study  
*T* = 150 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$   
*R* factor = 0.023  
*wR* factor = 0.055  
Data-to-parameter ratio = 15.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $[\text{Pr}(\text{C}_{16}\text{H}_{36}\text{N}_4\text{O}_4)(\text{H}_2\text{O})][\text{Pr}(\text{NO}_3)_6] \cdot 2\text{H}_2\text{O}$ , was prepared as part of our search for polynuclear lanthanide(III) nanoclusters. The asymmetric unit contains two distinct metal sites, one in which the  $\text{Pr}^{3+}$  ion is in coordination number 12 and the other in coordination number 9. The cations, anions and water molecules are linked in the crystal structure by  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds

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## Comment

The title compound, (I), was obtained from the templated oligomerization of 1-aziridineethanol. The reaction was carried out under basic conditions, yielding also insoluble hydroxides. Slow evaporation of the filtrate gave needle-like crystals.



The  $\text{Pr}^{3+}$  ions are in two distinct environments (see Fig. 1). In the first case, Pr1 is coordinated by six bidentate nitrate ions, resulting in an icosahedral polyhedron with  $\text{Pr}^{3+}$  ions having a coordination number (CN) of 12. In the second case, Pr2 is encapsulated in the macrocycle *N,N',N'',N'''*-tetrakis(2-hydroxyethyl)-1,4,7,10-tetrazacyclododecane ( $\text{H}_4\text{L}$ ), bonding to four tertiary amines and four alkoxides. The stereo-

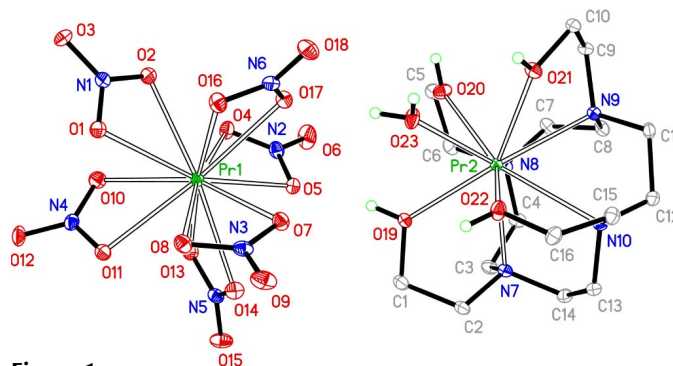
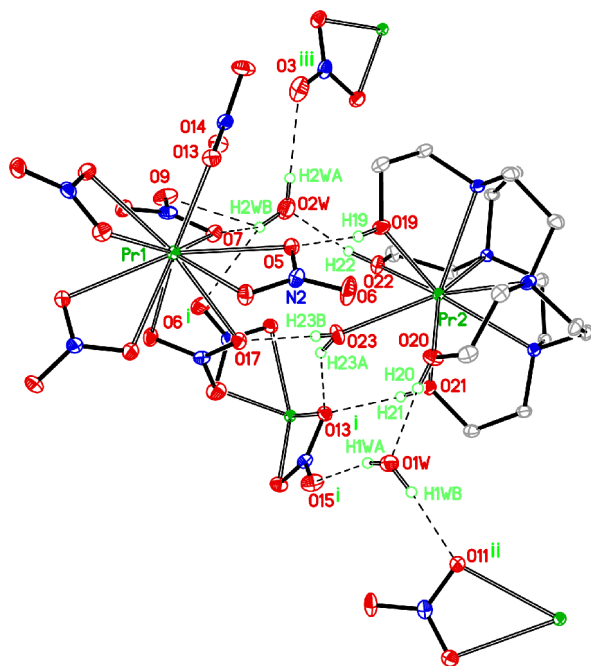
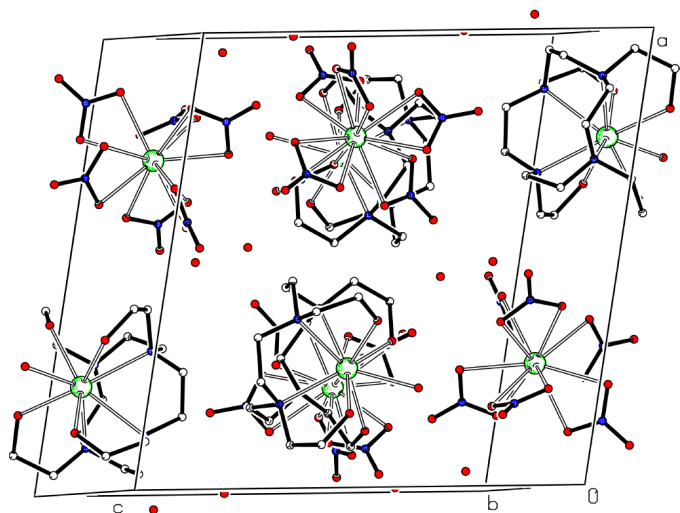


Figure 1

View of (I), showing the atom-labeling scheme, with ellipsoids drawn at the 30% probability level. H atoms and water molecules have been omitted.



**Figure 2**  
View of the hydrogen bonding in (I) corresponding to Table 2. Ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (ii)  $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$ ; (iii)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ .]



**Figure 3**  
Packing diagram (Spek, 2003), viewed approximately along the *b* axis. Atom colours are as labeled in Fig. 1.

chemistry of the chelate  $H_4L$  is  $\Delta(\delta\delta\delta\delta)$ . Atom Pr2 achieves a CN of 9 by bonding to a water molecule. The components in the crystal structure are linked by  $O-H \cdots O$  hydrogen bonds involving water molecules, nitrate ligands and the alkoxide groups (see Table 2 and Fig. 2). The crystal structure of (I) is the same as that found previously for the La analog (Thompson, 2001).

## Experimental

$Pr(NO_3)_3 \cdot 3H_2O$  (5.03 mmol) was dissolved in 100 ml of anhydrous ethanol and added dropwise to 2 mmol of 1-aziridineethanol in refluxing 50 ml of a 0.02 M solution of NaOH under reflux. Reflux

was continued for about one week, after which the reaction was filtered and slow evaporation of the filtrate yielded green needle-like crystals of (I) in ca 10% yield. Analysis calculated for  $C_{16}H_{42}N_{10}O_{25}Pr_2$ : C 18.19, H 4.14, N 13.10%; found: C 17.71, H 4.03, N 12.76%.

## Crystal data

$[Pr(C_{16}H_{36}N_4O_4)(H_2O)]_2 \cdot [Pr(NO_3)_6] \cdot 2H_2O$   
 $M_r = 1056.42$   
Monoclinic,  $P2_1/n$   
 $a = 15.5786$  (3) Å  
 $b = 14.4453$  (3) Å  
 $c = 15.5995$  (3) Å  
 $\beta = 99.7490$  (10)°  
 $V = 3459.78$  (12) Å<sup>3</sup>  
 $Z = 4$

$D_x = 2.028$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 7809 reflections  
 $\theta = 2.6$ – $27.5^\circ$   
 $\mu = 2.89$  mm<sup>-1</sup>  
 $T = 150$  (1) K  
Needle, green  
 $0.25 \times 0.25 \times 0.15$  mm

## Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  scans and  $\omega$  scans with  $\kappa$  offsets  
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)  
 $T_{min} = 0.516, T_{max} = 0.651$   
27454 measured reflections

7950 independent reflections  
7143 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.027$   
 $\theta_{max} = 27.7^\circ$   
 $h = -20 \rightarrow 20$   
 $k = -18 \rightarrow 18$   
 $l = -20 \rightarrow 19$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.023$   
 $wR(F^2) = 0.055$   
 $S = 1.09$   
7950 reflections  
519 parameters  
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + 2.2848P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.003$   
 $\Delta\rho_{max} = 1.29$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.73$  e Å<sup>-3</sup>  
Extinction correction: *SHELXL97*  
Extinction coefficient: 0.00094 (8)

**Table 1**

Selected geometric parameters (Å).

Pr1—O2	2.5568 (18)	Pr1—O13	2.7478 (17)
Pr1—O8	2.5628 (18)	Pr2—O20	2.4548 (18)
Pr1—O4	2.5687 (18)	Pr2—O22	2.4573 (18)
Pr1—O7	2.5751 (17)	Pr2—O19	2.4698 (17)
Pr1—O5	2.5910 (17)	Pr2—O21	2.4853 (17)
Pr1—O11	2.6093 (18)	Pr2—O23	2.5596 (18)
Pr1—O17	2.6287 (17)	Pr2—N7	2.677 (2)
Pr1—O1	2.6354 (18)	Pr2—N9	2.682 (2)
Pr1—O14	2.6445 (18)	Pr2—N10	2.7224 (19)
Pr1—O10	2.6620 (18)	Pr2—N8	2.745 (2)
Pr1—O16	2.6730 (18)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O23—H23A $\cdots$ O13 <sup>i</sup>	0.84 (2)	2.24 (2)	2.979 (3)	146 (2)
O20—H20 $\cdots$ O1W	0.84 (2)	1.79 (2)	2.622 (3)	174 (2)
O23—H23B $\cdots$ O17	0.84 (2)	2.02 (2)	2.835 (3)	164 (2)
O1W—H1WA $\cdots$ O15 <sup>i</sup>	0.84 (2)	2.05 (2)	2.873 (3)	165 (2)
O1W—H1WB $\cdots$ O11 <sup>ii</sup>	0.84 (2)	2.02 (2)	2.849 (3)	171 (2)
O22—H22 $\cdots$ O2W	0.84 (2)	1.78 (3)	2.599 (3)	166 (2)
O21—H21 $\cdots$ O13 <sup>i</sup>	0.84 (2)	1.93 (2)	2.768 (2)	174 (2)
O19—H19 $\cdots$ O5	0.84 (2)	1.87 (2)	2.702 (2)	169 (2)
O2W—H2WA $\cdots$ O3 <sup>iii</sup>	0.84 (2)	2.24 (2)	3.079 (4)	175 (2)
O2W—H2WB $\cdots$ O9	0.84 (2)	2.43 (2)	3.032 (3)	130 (2)
O2W—H2WB $\cdots$ O7	0.84 (2)	2.46 (2)	3.078 (3)	131 (2)
O2W—H2WB $\cdots$ O6 <sup>i</sup>	0.84 (2)	2.50 (2)	3.191 (3)	141 (2)

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

All H atoms bonded to C atoms were placed in calculated positions, with C–H distances of 0.99 Å and were included in the refinement in the riding-model approximation, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . H atoms bonded to O atoms were refined independently with isotropic displacement parameters, but the O–H distances were restrained to be 0.840 (1) Å. The maximum residual electron density peak was located 1.56 Å from atom Pr2.

Data collection: *COLLECT* (Nonius, 1997–2002); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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