metal-organic papers

Aqua[N,N′,N″,N‴-tetrakis(2-hydroxyethyl)-1,4,7,10-tetrazacyclododecane-$\kappa^4 N$]neodymium(III) tris(perchlorate) 1.25-hydrate

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The asymmetric unit of the title structure, [Nd(C₁₆H₃₆N₄O₄)(H₂O)](ClO₄)₃·1.25H₂O, (I), contains two independent Nd^III cations, six perchlorate anions and two and a half solvent water molecules. Compound (I) is a product of a program exploring the formation of polynuclear metallo-nanoclusters from oligomerization of aziridineethanol in the presence of lanthanide(III) salts. Under moderately acidic or basic solutions protonation of alcoholic sites is maintained and no oligomerization *via* bridging alcoholic sites is found. The crystal structure contains a three-dimensional network of O—H···O hydrogen bonds.

Comment

The title compound, (I), was obtained from oligomerization of 1-aziridineethanol (H2) designed to produce polynuclear lanthanide(III) nanoclusters (Thompson *et al.*, 2001). Oligomerization of 1-aziridineethanol in the presence of lanthanide(III) salts usually results in a variety of mononuclear and polynuclear complexes (Thompson *et al.*, 2003) of the dominant tetrameric product H₄L (Ham & Krause, 1978), depending on the reaction conditions. In this case, oligomerization was allowed to proceed under strongly basic conditions in which insoluble hydroxides were deposited and the mixture filtered. When allowed to evaporate, the filtrate deposited crystals of (I) in about 15% yield.

(I)
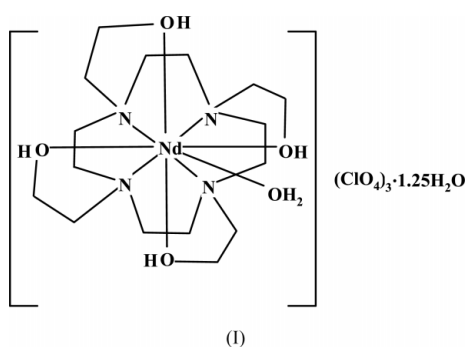
There are two independent Nd^III complexes in the asymmetric unit, which are illustrated in Figs. 1 and 2. The asymmetric unit also contains six perchlorate anions and two and a half solvent water molecules. The propensity of Ln^{3+} ions in lanthanide(III) complexes of H₄L to achieve coordination number 9 is demonstrated by coordination of a water molecule to Nd^III (O5A and O5B). The absolute stereochemistry of chelate H₄L is $\Lambda(\lambda\lambda\lambda\lambda)$ for the chelate at Nd1A, whereas it is $\Delta(\delta\delta\delta\delta)$ at Nd1B. However, the coordination polyhedra at both sites have distorted C_{4v} symmetry. Selected metal–oxy-

Figure 1
View of molecule A of (I), showing the labeling scheme and ellipsoids drawn at the 30% probability level. H atoms bonded to C atoms have been omitted.
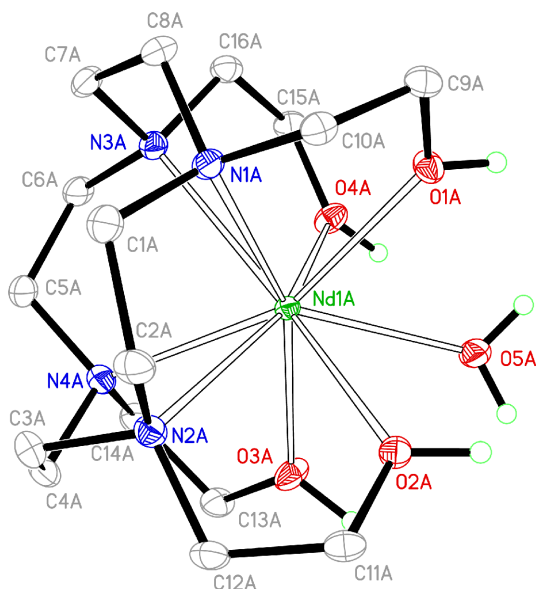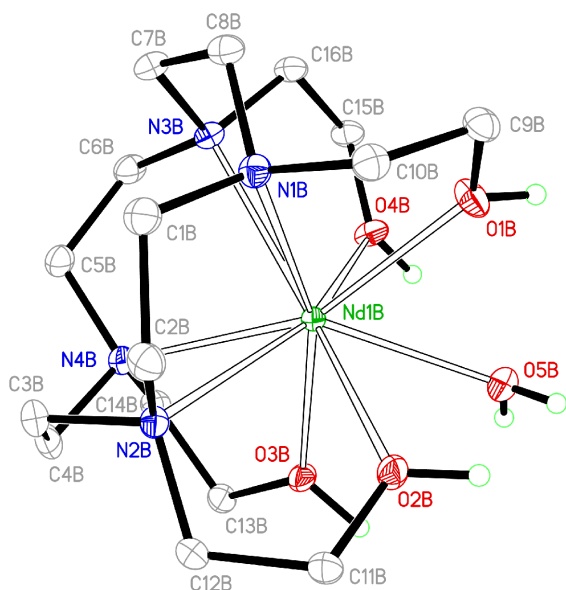

Figure 2
View of molecule B of (I), showing the labeling scheme and ellipsoids drawn at the 30% probability level. H atoms bonded to C atoms have been omitted.
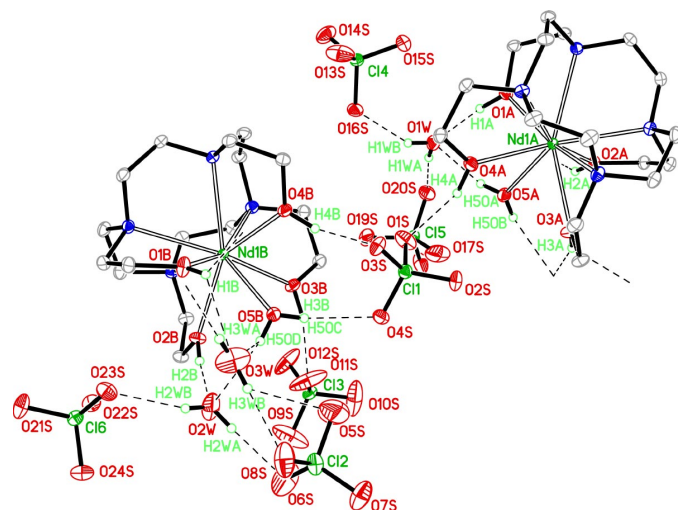

Figure 3
View of the hydrogen bonding (dashed lines) in (I) corresponding to Table 2. Ellipsoids are drawn at the 30% probability level.
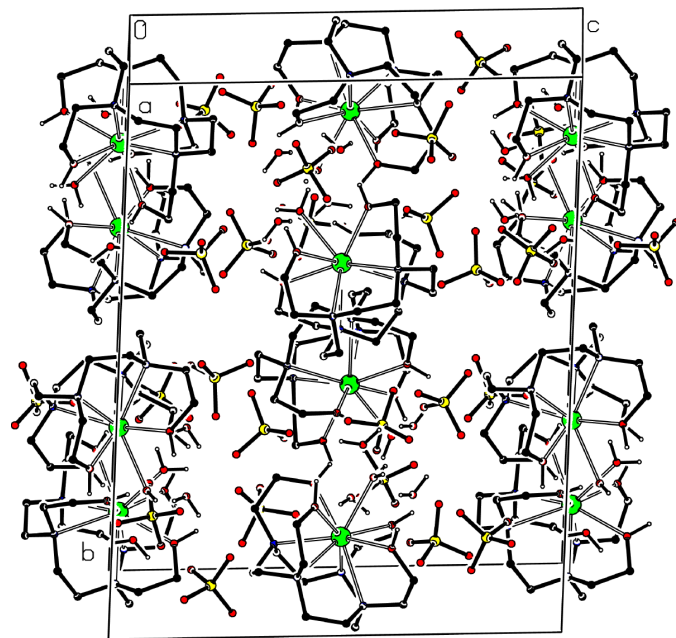

Figure 4
Packing diagram (Spek, 2003), viewed approximately along the a axis. Colour codes: green Nd, yellow Cl, red O, blue N, and black C. H atoms have been omitted for clarity.

gen bond distances are given in Table 1. The three-dimensional O—H···O hydrogen-bonding network in the crystal structure of (I) is illustrated in Fig. 3 and details of the geometry are given in Table 2. The crystal packing is illustrated in Fig. 4.

Experimental

Because of our preparative interest in nanoclusters, two solutions were used as follows. Solution A: 10 ml of a 0.39 M solution of NaOH was added dropwise to a vigorously stirring and boiling solution of Nd(ClO$_4$)$_3$·nH$_2$O (15.7 mmol) dissolved in 16 ml distilled water. The volume of the mixture was reduced to about 5 ml and filtered. Solution B: Nd(ClO$_4$)$_3$ (1.1 mmol) was dissolved in 45 ml of a 3:1 acetonitrile–methanol solution and added dropwise (2–3 h) to 2 mmol 1-aziridineethanol refluxing in 100 ml of the acetonitrile–methanol solution. Reflux was continued for 3 d, after which the volume of the solution was reduced to about 70 ml. Approximately 2.5 ml of solution A was dissolved in 20 ml of acetonitrile and added dropwise to the refluxing solution B. Reflux was continued for about one week, during which time a precipitate was deposited and filtered off; slow evaporation of the filtrate yielded purple needle-like crystals of (I) in ca 15% yield. Analysis calculated for C$_{16}$H$_{40.50}$Cl$_3$N$_4$NdO$_{18.25}$: C 23.1, H 4.9, N 6.7%; found: C 22.23, H 4.53, N 6.47%.

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Crystal data

$[Nd(C_{16}H_{36}N_4O_4)(H_2O)](ClO_4)_3\cdot$
1.25H_2O
$M_r = 831.61$
Monoclinic, $P2_1/c$
$a = 17.3365\ (2)$ Å
$b = 20.7247\ (2)$ Å
$c = 17.8135\ (2)$ Å
$\beta = 109.969\ (1)°$
$V = 6015.48\ (11)$ Å^3
$Z = 8$

$D_x = 1.837$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 13799
    reflections
$\theta = 2.6$–27.5°
$\mu = 2.08$ mm^{-1}
$T = 150\ (1)$ K
Block, purple
$0.36 \times 0.32 \times 0.32$ mm

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan
    (*DENZO–SMN*; Otwinowski &
    Minor, 1997)
$T_{min} = 0.485$, $T_{max} = 0.517$
60586 measured reflections

13750 independent reflections
11579 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 27.5°$
$h = -22 \rightarrow 22$
$k = -26 \rightarrow 26$
$l = -23 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.082$
$S = 1.05$
13750 reflections
798 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0246P)^2$
    $+ 16.909P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 2.07$ e Å^{-3}
$\Delta\rho_{min} = -1.02$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

Nd1A—O1A	2.448 (2)	Nd1B—O3B	2.441 (2)
Nd1A—O4A	2.455 (2)	Nd1B—O1B	2.445 (2)
Nd1A—O3A	2.475 (2)	Nd1B—O2B	2.446 (2)
Nd1A—O2A	2.477 (2)	Nd1B—O4B	2.467 (2)
Nd1A—O5A	2.520 (3)	Nd1B—O5B	2.566 (3)
Nd1A—N2A	2.684 (3)	Nd1B—N4B	2.679 (3)
Nd1A—N4A	2.687 (3)	Nd1B—N2B	2.688 (3)
Nd1A—N1A	2.696 (3)	Nd1B—N3B	2.692 (3)
Nd1A—N3A	2.700 (3)	Nd1B—N1B	2.692 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1A—H1A$\cdots$O1W	0.95	1.77	2.707 (3)	170
O1B—H1B$\cdots$O3W	0.95	2.42	3.100 (3)	128
O1B—H1B$\cdots$O10S^i	0.95	2.05	2.827 (5)	138
O2A—H2A$\cdots$O24S^{ii}	0.95	1.99	2.848 (4)	150
O2B—H2B$\cdots$O2W	0.95	1.70	2.648 (4)	172
O3A—H3A$\cdots$O13S^{iii}	0.95	2.18	3.096 (5)	163
O3A—H3A$\cdots$O14S^{iii}	0.95	2.19	2.916 (4)	132
O4A—H4A$\cdots$O1S	0.95	1.92	2.792 (4)	151
O5A—H5OA$\cdots$O1W	0.84	1.91	2.718 (4)	162
O5A—H5OB$\cdots$O13S^{iii}	0.84	2.14	2.923 (4)	156
O5B—H5OD$\cdots$O2W	0.84	2.19	2.957 (5)	151
O5B—H5OD$\cdots$O3W	0.84	2.12	2.741 (7)	130
O3B—H3B$\cdots$O11S	0.95	1.88	2.750 (4)	150
O4B—H4B$\cdots$O3S	0.95	1.83	2.746 (3)	163
O5B—H5OC$\cdots$O4S	0.84	2.15	2.980 (4)	172
O1W—H1WA$\cdots$O20S	0.84	1.98	2.811 (4)	172
O1W—H1WB$\cdots$O16S	0.84	2.06	2.825 (4)	152
O2W—H2WA$\cdots$O6S	0.84	2.00	2.838 (6)	175
O2W—H2WB$\cdots$O23S	0.84	2.15	2.936 (5)	155
O3W—H3WB$\cdots$O8S	0.84	2.07	2.912 (5)	180
O3W—H3WB$\cdots$O5S	0.84	2.46	2.971 (8)	120
O3W—H3WA$\cdots$O9S^i	0.84	2.00	2.844 (7)	180

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

H atoms bonded to C atoms, as well as the H atoms of the hydroxyl groups (O1, O2, O3 and O4), were placed in calculated positions with C—H distances of 0.99 Å and O—H distances of 0.95 Å. They were included in the refinement in riding-model approximation, with $U_{iso} = 1.2U_{eq}$ of the carrier atom. H atoms bonded to the O atoms of coordinated (O5) and solvent water molecules (O1W and O2W) were refined independently with isotropic displacement parameters, but the O—H distances were restrained to be 0.840 (1) Å. The intramolecular H$\cdots$H distances of both solvent water molecules were restrained to be the same. The H atoms of the half-occupancy water molecule (O3W) were placed in calculated positions so as to give sensible hydrogen-bonding geometry, but their coordinates were not refined; $U_{iso} = 1.5U_{eq}(O3W)$. The highest peak in the final difference Fourier map was 1.12 Å from O5S. However, the perchlorate anion containing O5S was not considered to be disordered despite some O atoms having relatively high anisotropic displacement parameters. A similar situation was observed for perchlorate Cl3(O9S–O12S). The deepest hole was 0.81 Å from Nd1B.

Data collection: *COLLECT* (Nonius, 1997–2002); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2001); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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