

Ammonium neodymium(III) bis[sulfate(VI)] tetrahydrate

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Key indicators

Single-crystal X-ray study

$T = 291\text{ K}$

Mean $\sigma(\text{S—O}) = 0.003\text{ Å}$

R factor = 0.024

wR factor = 0.058

Data-to-parameter ratio = 22.1

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

$(\text{NH}_4)[\text{Nd}(\text{SO}_4)_2(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$ is isotypic with other members of the $(\text{NH}_4)[\text{Ln}(\text{SO}_4)_2(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$ family (Ln = lanthanides). It contains NdO_9 polyhedra and SO_4 tetrahedra, which are linked by common edges and vertices, forming a layer-like arrangement parallel to (010). The neodymium cation is nine-coordinated in a distorted monocapped square antiprismatic geometry with two sulfate groups as chelating and two sulfate groups as bridging ligands. $\text{O—H}\cdots\text{O}$ and $\text{N—H}\cdots\text{O}$ hydrogen bonds consolidate the structure into a three-dimensional network. The dependence of unit-cell dimensions of the isotypic compounds on the lanthanide atomic number is discussed.

Comment

The unit-cell dimensions of the title compound, (I) (Fig. 1), were previously reported on the basis of an indexed powder diffraction pattern (Staritzky & Cromer, 1956), but the complete structure has never been determined. (I) is isotypic with some other ammonium bis(sulfates) of trivalent cations, viz. Y, Dy, Ho, Er (Iyer & Natarajan, 1990), Ce (Mellor, 1946), La, Tb (Kepert *et al.*, 1999), Sm (Eriksson *et al.*, 1974), and of trivalent uranium (Bullock *et al.*, 1980). The crystal structure of other neodymium sulfates are also known and include $\text{Nd}_2(\text{SO}_4)_3(\text{H}_2\text{O})_4$ (Bede, 1987), $\text{Nd}_2(\text{SO}_4)_3(\text{H}_2\text{O})_5$ (Larsson *et al.*, 1973), $\text{Nd}_2(\text{SO}_4)_3(\text{H}_2\text{O})_8$ (Bartl & Rodek, 1983) and

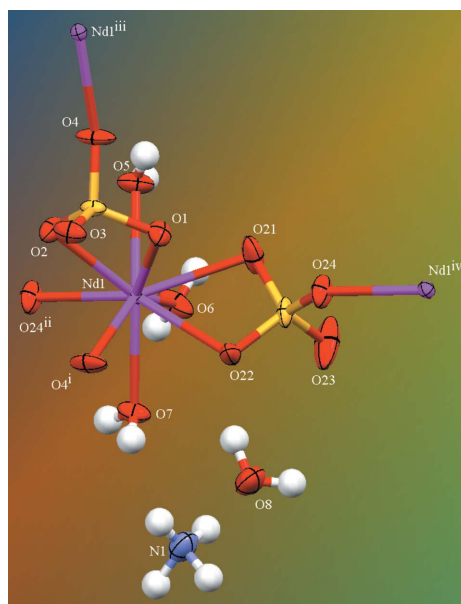


Figure 1

Part of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as white spheres of arbitrary radius. [Symmetry codes: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x + 1, y, z$; (iii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (iv) $x - 1, y, z$.]

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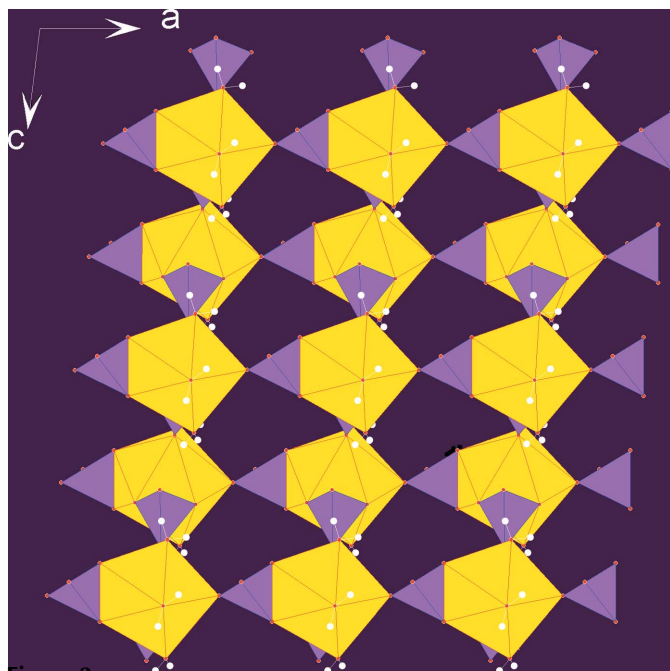


Figure 2
Part of the structure of (I) in the polyhedral representation, projected along the *b* axis. SO₄ tetrahedra are violet and NdO₉ polyhedra are yellow.

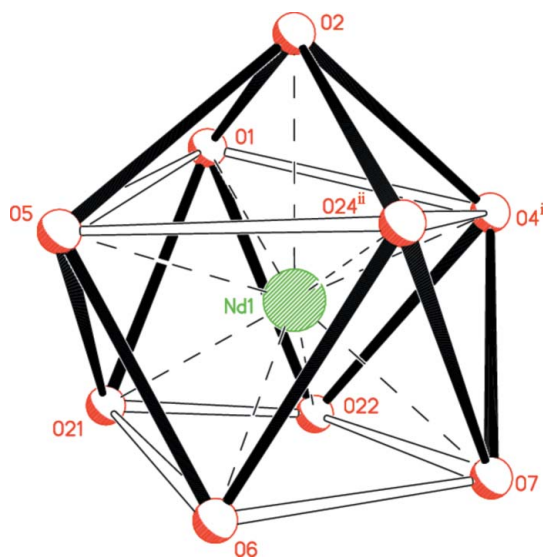


Figure 3
The coordination polyhedron around Nd. The bases of the monocapped square antiprism are indicated by hollow connections. [Symmetry codes: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x + 1, y, z$.]

(H₅O₂)(H₃O)Nd(SO₄)₃ (Wickleder, 1999). Hydrogensulfate-containing representatives are (H₃O)₂Nd(HSO₄)₃(SO₄) (Wickleder, 1999), Nd(HSO₄)₃ (Wickleder, 1998), and Nd(S₂O₇)(HSO₄) (Wickleder, 2000).

The structure of (I) (Fig. 1) contains NdO₉ polyhedra and SO₄ tetrahedra, which are linked by common edges and vertices, forming a layer-like arrangement parallel to (010) (Fig. 2). The neodymium cation in (I) is nine-coordinated with a distorted monocapped square antiprismatic geometry (Fig. 3). The nine O atoms are associated with three water

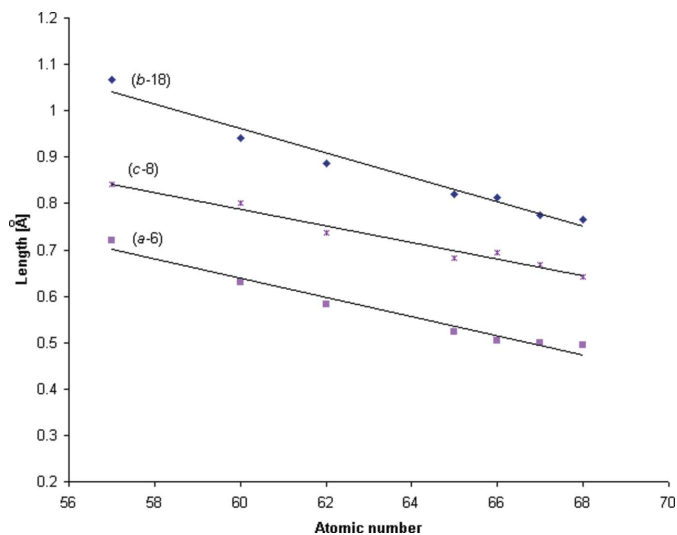


Figure 4
Lattice parameters of isotopic compounds of the formula type (NH₄)Ln(SO₄)(H₂O)₄ (*Ln* = lanthanide) plotted against the atomic numbers of the Ln elements. The integer values of the lattice parameters have been subtracted for convenience.

molecules (O5, O6, O7) and six O atoms of four sulfate groups, two of which are chelating ligands and two are bridging ligands to two neighbouring Nd polyhedra (Fig. 1). The Nd–O bond lengths, ranging from 2.402 (3) to 2.554 (3) Å (Table 1), are similar to the analogous distances found in the above-mentioned neodymium sulfates. The formal charge of trivalent neodymium was confirmed by bond-valence-sum calculations (Brown, 2002) and a total valence of 3.029 v.u. for neodymium was obtained using the calculated bond-valence parameter of 2.086 Å (Trzesowska *et al.*, 2004).

The three-dimensional structure is consolidated by O–H...O and N–H...O hydrogen bonds (Table 2).

The unit-cell parameters of isotopic lanthanide compounds are listed in Table 3. The lengths of all axes decrease linearly (regression coefficients $R^2 = 0.97$) with increasing atomic number (AN) (Fig. 4). The monoclinic angle β fluctuates slightly around 97.1° and can be considered as constant within the range of experimental errors. The dependence between the lattice parameters and AN can be described by the equations: $a = -0.0207\text{AN} + 7.8795$, $b = -0.0264\text{AN} + 20.5425$ and $c = -0.018\text{AN} + 9.8641$. These equations allow the estimation of the so-far undetermined lattice parameters of the trivalent Ce, Pr, Pm, Eu, and Gd members of this structure family. For example, only the proportion between unit-cell dimensions are known for (NH₄)[Ce(SO₄)₂(H₂O)₃](H₂O): $a:b:c = 0.3598:1:0.4670$, ($\beta = 97.16^\circ$) (Groth, 1908). The calculated lattice parameters $a = 6.679$, $b = 19.011$ and $c = 8.820$ Å ($\beta = 97.1^\circ$), give $a:b:c = 0.3513:1:0.4639$, which is in good agreement with the above-determined experimental results.

Experimental

(I) was obtained by reaction of neodymium(III) oxide (0.33648 g, 1 mmol) with 30% wt sulfuric(VI) acid (density 1.08 Mg m⁻³,

4 mmol) in the presence of hexamethylenetetraamine (hmt) (0.56070 g, 4 mmol) in 20 cm³ water. The hmt was hydrolysed to ammonia and formaldehyde in acid solution (Smolin & Rapoport, 1959). The presence of NH₄⁺ ions was confirmed by qualitative analysis. The solution was stirred at room temperature and left to crystallize at 278 K. The light-violet crystals of the title compound, obtained after several days, were removed from the solution by filtration, sealed in glass capillaries, and used for data collection. Because of the poor stability of the crystals during data collection at room temperature, we tried to collect data at lower temperature, but the crystals always broke during the cooling. IR (KBr, cm⁻¹): 3410 (*br*, νOH), 2910 (*br*, ν NH₄⁺), 1690 (*m*, νOH), 1150 (*s*, ν₃SO₄), 990 (*s*, ν₁SO₄), 750 (*w*, νOH), 650 (*m*, ν₄SO₄), 470 (*m*, ν₁SO₄ and/or O—Nd—O). Elemental analysis (calculated/found %) H 2.84/2.76, N 3.29/3.33, Nd 33.82/33.34, O 45.02/44.99, S 15.04/14.97.

Crystal data

(NH₄)[Nd(SO₄)₂(H₂O)₃].H₂O
 $M_r = 426.47$
 Monoclinic, $P2_1/c$
 $a = 6.636$ (1) Å
 $b = 18.935$ (1) Å
 $c = 8.789$ (1) Å
 $\beta = 97.06$ (1)°
 $V = 1096.0$ (2) Å³

$Z = 4$
 $D_x = 2.585$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 5.18$ mm⁻¹
 $T = 291.0$ (3) K
 Prism, light violet
 $0.06 \times 0.04 \times 0.03$ mm

Data collection

Kuma KM-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: numerical
 (*X-RED32*; Stoe & Cie, 1999)
 $T_{\min} = 0.764$, $T_{\max} = 0.869$
 3999 measured reflections
 3224 independent reflections

2939 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$
 $\theta_{\text{max}} = 30.1^\circ$
 3 standard reflections
 every 100 reflections
 intensity decay: 72.3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.058$
 $S = 1.04$
 3224 reflections
 146 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0232P)^2 + 3.8961P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.58$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.02$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0150 (4)

Table 1

Selected bond lengths (Å).

Nd1—O4 ⁱ	2.402 (3)	Nd1—O21	2.554 (3)
Nd1—O24 ⁱⁱ	2.414 (3)	Nd1—O2	2.554 (3)
Nd1—O6	2.454 (3)	S1—O3	1.459 (3)
Nd1—O5	2.494 (3)	S1—O4	1.462 (3)
Nd1—O22	2.519 (3)	S1—O2	1.477 (3)
Nd1—O1	2.520 (3)	S1—O1	1.490 (3)
Nd1—O7	2.527 (3)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5A \cdots O23 ⁱⁱⁱ	0.79	2.12	2.855 (6)	155
O5—H5B \cdots O3 ^{iv}	0.77	2.03	2.739 (4)	152
O6—H6A \cdots O8 ^v	0.76	2.11	2.808 (5)	151
O6—H6A \cdots O23 ⁱⁱ	0.76	2.57	3.159 (5)	136

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O6—H6B \cdots O21 ⁱⁱⁱ	0.90	1.82	2.713 (4)	172
O7—H7A \cdots O3 ⁱ	0.88	1.93	2.777 (4)	159
O7—H7B \cdots O23 ^v	0.81	2.56	3.067 (5)	122
N1—H1A \cdots O2 ^{vi}	0.94	1.95	2.884 (5)	171
N1—H1B \cdots O8	1.00	1.91	2.902 (6)	169
N1—H1C \cdots O22 ⁱ	0.90	2.45	3.302 (6)	158
N1—H1C \cdots O1 ⁱ	0.90	2.50	3.022 (5)	117
N1—H1D \cdots O1 ^{vii}	1.00	2.11	3.053 (5)	158
O8—H8A \cdots O22	0.93	1.89	2.785 (4)	161
O8—H8B \cdots O23 ^{viii}	0.86	2.06	2.800 (5)	144

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

Table 3

Crystal data (Å, °, Å³) for the isotopic members of the (NH₄)[Ln(SO₄)₂(H₂O)₃](H₂O) family where Ln is a trivalent cation.

Atom	Atomic number	a	b	c	β	V	Reference
Y	39	6.516 (4)	18.856 (8)	8.663 (5)	96.63 (5)	1057.2 (1)	<i>a</i> [#]
La	57	6.720 (1)	19.0680 (20)	8.841 (1)	97.50 (1)	1123.17	<i>b</i>
Nd	60	6.63	18.94	8.80	96.2	1099	<i>d</i> [#]
Sm	62	6.582 (2)	18.886 (7)	8.736 (4)	96.88 (4)	1078.13	<i>c</i>
Tb	65	6.522 (4)	18.8200 (40)	8.681 (1)	96.69 (3)	1058.29	<i>b</i>
Dy	66	6.505 (2)	18.813 (5)	8.695 (3)	97.49 (4)	1055.0 (1)	<i>a</i> [#]
Ho	67	6.499 (2)	18.774 (7)	8.667 (3)	97.28 (5)	1048.9 (1)	<i>a</i> [#]
Er	68	6.495 (4)	18.766 (8)	8.641 (5)	97.57 (5)	1044.0 (1)	<i>a</i> [#]
U	92	6.7065 (2)	19.0328 (6)	8.8305 (3)	97.337 (1)	1117.93	<i>e</i>
Pu	94	6.64 (1)	18.92 (1)	8.79 (1)	96.9 (1)	1094.4 (1)	<i>a</i> [#]

Notes: ([#]) - from powder data; (*a*) Iyer & Natarajan (1990); (*b*) Kepert *et al.* (1999); (*c*) Eriksson *et al.* (1974); (*d*) Staritzky & Cromer (1956); (*e*) Bullock *et al.* (1980).

All H atoms were found in difference Fourier syntheses. They were refined as riding on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O}, \text{N})$. The highest remaining peak in the difference Fourier map is 0.95 Å from atom O23 and the deepest hole is 0.67 Å from S2.

Data collection: *KM-4 Software* (Kuma, 1993); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Galdecki *et al.*, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP in SHELXTL* (Sheldrick, 1990), *ORTEP-3* (Farrugia, 1997) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

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