(H$_3$O)Nd(SO$_4$)$_2$

Zaichao Zhang[a]* and Zhibin Zhang[b]

[a]Jiangsu Key Laboratory for the Chemistry of Low-dimensional Materials, School of Chemistry and Chemical Engineering, Huaiyin Normal University, 111 West Changjiang Road, Huai'an 223300, Jiangsu, People's Republic of China, and [b]College of Chemistry and Chemical Engineering, State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing University of Technology, Nanjing 210009, People's Republic of China
Correspondence e-mail: yanxuchem@hotmail.com

The crystal structure of oxonium neodymium bis(sulfate), (H$_3$O)Nd(SO$_4$)$_2$, shows a two-dimensional layered framework assembled from SO$_4$ tetrahedra and NdO$_9$ tricapped trigonal prisms. One independent sulfate group makes four S—O—Nd linkages, while the other makes five such connections to generate an unprecedented anhydrous anionic [Nd(SO$_4$)$_2$]$^-$ layer. To achieve charge balance, H$_3$O$^+$ cations are inserted between adjacent layers where they participate in hydrogen-bonding interactions with the sulfate O atoms of adjacent layers.

Comment

Over the past few decades, great efforts have been made to synthesize new topological solid inorganic materials because of their functional applications in ion-exchange, adsorption, catalysis and radioactive waste remediation. Recently, studies of lanthanide sulfates have yielded important advancements in this field. Compared with Zn, Al and Ge, the lanthanides can have flexible bond lengths and high coordination numbers, which offer the possibility to form solid-state materials with novel topological structures (Dan *et al.*, 2004; Doran *et al.*, 2002; Xu *et al.*, 2007; Zhou, Chen, Jiang *et al.*, 2009; Zhou, Chen, Zhu *et al.*, 2009; Zhu *et al.*, 2009). Two-dimensional lanthanide sulfates that have been reported previously include Eu$_2$(SO$_4$)$_3$(H$_2$O)$_8$ and some protonated organic amine-templated sulfates (Xu *et al.*, 2007; Zhou, Chen, Jiang *et al.*, 2009; Zhu *et al.*, 2009). To date, no oxonium cation-templated lanthanide sulfate has been reported. In this work, we designed and synthesized the title compound, which represents the first example with H$_3$O$^+$ cations inserted into a layered neodymium sulfate.

The asymmetric unit of (H$_3$O)Nd(SO$_4$)$_2$ contains ten crystallographically independent non-H atoms, including one Nd^{3+} cation, two sulfate anions and one oxonium cation (Fig. 1). The Nd^{3+} cation is coordinated by nine O atoms from seven sulfate groups with typical tricapped trigonal–prismatic coor-

dination geometry (Table 1). Atoms O3, O3^{iii}, O6, O6^v, O7^{iv} and O4^{ii} form the trigonal prism, while O2, O7 and O8^i are the face-capping atoms (symmetry codes as in Fig. 1). The sulfate group centered by S1 makes four S—O—Nd linkages where atoms O2 and O4 coordinate to one Nd atom each and atom O3 bridges two Nd atoms, while the S2 sulfate group makes five S—O—Nd connections where atom O8 coordinates to one Nd atom and atoms O7 and O7 each bridge two Nd atoms. Thus, each sulfate group has one terminal O atom that is not coordinated to the metal center. The SO$_4$ tetrahedra connect the NdO$_9$ polyhedra to generate an unprecedented anhydrous anionic Nd–O–S layer of composition [Nd(SO$_4$)$_2$]$^-$ in the *bc* plane (Fig. 2). All the previously reported Ln–O–S layers include coordinated water molecules, because of the high affinity of Ln^{3+} cations for water. To the best of our knowledge, this is the first example of an Ln–O–S layer without
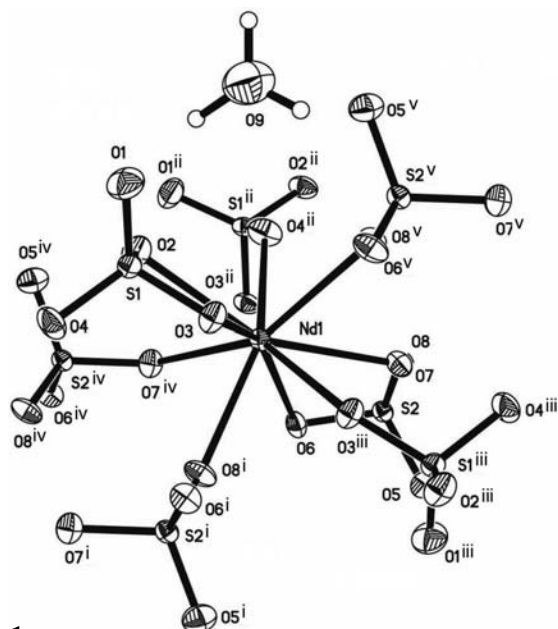
Figure 1
The molecular structure of the title compound, showing the complete coordination environment around Nd1. Displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x, -y, -z + 2$; (iv) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$; (v) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$.]
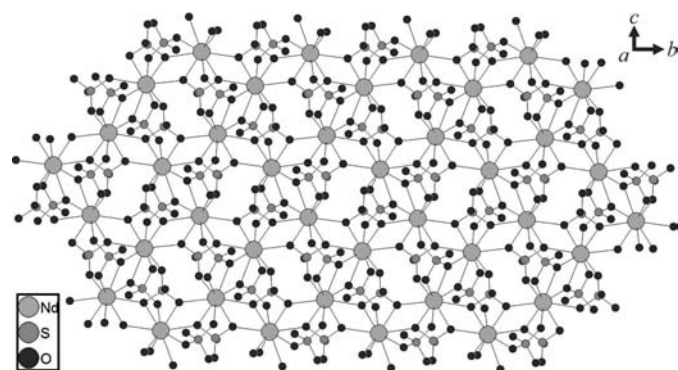
Figure 2
The structure of a single Nd–O–S layer as seen perpendicular to the layer (viewed along the *a* axis).

inorganic compounds

coordinated water molecules. In the reported layered europium sulfate $Eu_2(SO_4)_3(H_2O)_8$ (Xu *et al.*, 2007), for example, the Eu^{3+} cation coordinates to eight O atoms including four terminal water molecules; this behavior is in contrast to that of $(H_3O)Nd(SO_4)_2$, in which each Nd^{3+} cation forms nine coordination bonds with SO_4^{2-} groups without coordinated water molecules, leading to high stability of the Nd–O–S layers. The thickness of each Nd–O–S layer is about 6.48 (2) Å, which is thicker than the reported Eu–O–S layer [5.62 (3) Å] in $Eu_2(SO_4)_3(H_2O)_8$. The H_3O^+ cations are inserted between adjacent Nd–O–S layers, resulting in the novel $(H_3O)_n^{n+}$ sheet shown in Fig. 3. The distances between adjacent H_3O^+ cations are 4.20 (2)–4.26 (2) Å, indicating no direct hydrogen-bonding interactions between the cations. The H_3O^+ cations form hydrogen bonds with O atoms of sulfate groups (Fig. 4 and Table 2), the shortest interactions being to the terminal O1 and O5 atoms that are not part of the Nd coordination environment.

Thermal analysis of $(H_3O)Nd(SO_4)_2$ under an N_2 atmosphere shows a broad weight loss of 5.20% within the temperature range 323–752 K, which is attributed to the removal of water (the calculated value is 5.07%), while a subsequent weight loss of 49.78% between 753 and 1373 K may correspond to the loss of SO_3.
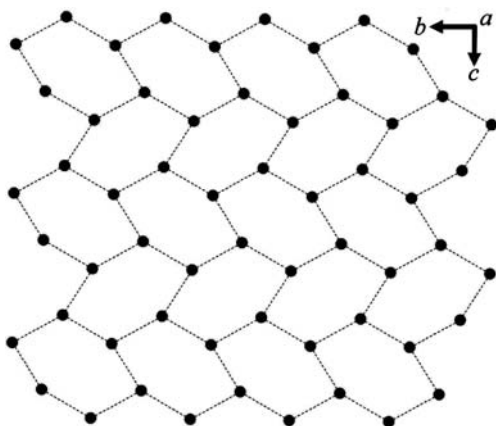

Figure 3
The arrangement of oxonium O atoms in the $(H_3O)_n^{n+}$ cation layer. The view is along the *a* axis.
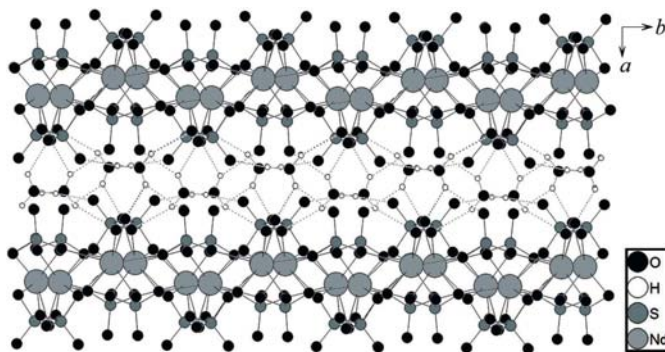

Figure 4
A view along the *c* axis showing the stacking of Nd–O–S layers with H_3O^+ cations in between. O—H···O hydrogen bonds are shown as broken lines.

Experimental

Crystals of the title compound were synthesized by hydrothermal reaction using $Nd(NO_3)\cdot6H_2O$ (0.3441 g), H_2SO_4, diethylenetriamine (0.2215 g) and water (1.1 ml). The mixture was placed in a 25 ml Teflon-lined autoclave and heated at 453 K for 7 d. After the sample was cooled to room temperature, washed with distilled water, filtered and dried in air, block-shaped pink crystals were obtained.

Crystal data

$(H_3O)Nd(SO_4)_2$	$V = 686.28$ (11) Å³
$M_r = 355.38$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 8.8593$ (8) Å	$\mu = 8.19$ mm^{-1}
$b = 7.1787$ (6) Å	$T = 293$ K
$c = 10.7955$ (10) Å	$0.10 \times 0.08 \times 0.06$ mm
$\beta = 91.671$ (1)°	

Data collection

Bruker APEXII CCD diffractometer	3416 measured reflections
	1278 independent reflections
Absorption correction: multi-scans (*SADABS*; Sheldrick, 2003)	1208 reflections with $I > 2\sigma(I)$
$T_{min} = 0.495$, $T_{max} = 0.639$	$R_{int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.056$	
$S = 1.03$	
1278 reflections	$\Delta\rho_{max} = 0.99$ e Å^{-3}
120 parameters	$\Delta\rho_{min} = -0.83$ e Å^{-3}
6 restraints	

Table 1
Selected bond lengths (Å).

Nd1—O8^i	2.4230 (19)	Nd1—O2	2.5077 (18)
Nd1—O4^{ii}	2.437 (2)	Nd1—O7	2.5095 (17)
Nd1—O3^{iii}	2.4770 (17)	Nd1—O6^v	2.5368 (16)
Nd1—O3	2.4923 (17)	Nd1—O6	2.6187 (18)
Nd1—O7^{iv}	2.5020 (17)		

Symmetry codes: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x, -y, -z+2$; (iv) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$; (v) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O9—H1···O4^{vi}	0.87 (1)	2.27 (1)	3.080 (3)	155 (2)
O9—H2···O1	0.87 (1)	2.02 (1)	2.893 (3)	175 (3)
O9—H3···O5^{vii}	0.87 (1)	2.23 (1)	2.986 (3)	146 (1)

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

The oxonium H atoms were located from a difference map and included in the refinement with the O—H bond lengths restrained to 0.87 (2) Å and the H···H distances restrained to 1.50 (2) Å. The H atoms were assigned fixed isotropic displacement parameters equal to $1.2U_{eq}$(O9).

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics:

SHELXTL (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3229). Services for accessing these data are described at the back of the journal.

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