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Synthesis and crystal structure of a new neodymium(III) selenate-selenite: $Nd_2(SeO_4)(SeO_3)_2(H_2O)_2$

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Abstract

The title new neodymium(III) selenate-selenite was obtained by hydrothermal reactions of neodymium(III) oxide, H_2SeO_4 and 1,10-phenanthroline at 140 °C. Its structure was established by single-crystal X-ray diffraction. The title compound crystallizes in the monoclinic space group $C2/c$ with cell parameters of a = 12.258(2) Å, b = 7.1024(15) Å, c = 13.391(3) Å, β = 104.250(2)°. The structure of $Nd_2(SeO_4)(SeO_3)_2(H_2O)_2$ is isomorphous with that of $Er_2(SeO_4)(SeO_3)_2(H_2O)_2$, which was refined in the monoclinic space group $C2$ with the disordered selenate group. It features an ordered 3D network with channels along b-axis. The selenate or selenite groups alone can form a 2D layer with the Nd(III) ions. IR spectrum, TGA and luminescent studies have also been performed.

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Keywords: Hydrothermal synthesis; Crystal structure; Neodymium selenate-selenite; Open-framework; Luminescence

1. Introduction

It is very important to design compounds with novel open framework structures and interesting physical properties. This research area is largely dominated by metal phosphates and aluminosilicate zeolites [1,2]. A few organically templated metal sulfates have also been reported recently [3–13]. As for the oxy-anions of Se, an organically templated 2D zinc selenite was first reported by Harrison et al. [14]. Organically templated 3D iron(II) and zinc(II) selenites were reported by Rao and his coworkers [15]. Both organically templated and the organically linked vanadium selenites have also been reported [16,17]. The organically templated cadmium(II) and lanthanum(III) selenates were reported by Rao and his coworkers very recently [18]. A number of novel heteropolymolybdates based on selenite group were reported by Kortz et al. [19]. In our attempt to synthesize the organically templated neodymium(III) selenate by hydrothermal reactions of Nd(III) oxide, selenic acid and 1,10-phenanthroline (phen), we obtained the title neodymium(III) selenate-selenite instead, $Nd_2(SeO_4)(SeO_3)_2(H_2O)_2$. Some selenate anions have been reduced to selenite anions by phen during the reaction. So far, only a few examples of lanthanide selenate-selenite have been reported, $La(SeO_4)(HSeO_3)(H_2O)_2$, $NaSm(SeO_4)(SeO_3)$, $Pr_4F_6(SeO_4)(SeO_3)_2$, and $Er_2(SeO_4)(SeO_3)_2(H_2O)_2$, whose structure was reportedly to be disordered for the selenate group [20–22]. Herein, we report the synthesis, crystal structure and thermal stability of $Nd_2(SeO_4)(SeO_3)_2(H_2O)_2$.

2. Experimental

All chemicals were obtained from commercial sources and used without further purification. IR spectra were recorded on a Magna 750 FT-IR spectrometer photometer as KBr pellets in the 4000–400 cm^{-1}. Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of 15 °C min^{-1} under a nitrogen atmosphere. Photoluminescence analyses were performed on an Edinburgh Analytical Instruments FLS920 fluorescence Spectrometer.

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2.1. Synthesis of $Nd_2(SeO_4)(SeO_3)_2(H_2O)_2$

Nd_2O_3 (0.5 mmol) was dissolved completely in 3 mmol of selenic acid (Aldrich, 40 wt.%), and 1.0 mmol of 1,10-phenanthroline and 10 ml of distilled water were added into the solution. The resultant mixture was then sealed into a bomb equipped with a Teflon liner (25 ml) and heated at 140 °C for 4 days. The initial and final pH values of the solution are 3.0 and 3.5, respectively. Purple crystals of the title compound were collected in a yield of 45.2%. IR data (KBr, cm^{-1}): 3445 (br), 1642 (s), 890 (s), 831 (m), 774 (m), 711 (s), 502 (m), 439 (m), 407 (m).

2.2. Crystal structure determination

A single crystal of the title compound was mounted on a Siemens Smart CCD diffractometer equipped with a graphite-monochromated MoKα radiation (λ = 0.71073 Å). Intensity data were collected by the narrow frame method at 293 K. The data sets were corrected for Lorentz and Polarization factors as well as for absorption by ψ scan technique. The space group was determined to be either $C2/c$ or Cc based on system absence. The centrosymmetric space group $C2/c$ was selected and gave a satisfactory structural solution. The structure was solved by the direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97 [23]. All atoms are ordered and showed no abnormal behaviors in the thermal and occupancy parameters. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of the aqua ligands were not included in the refinements. The data collection and refinement parameters are summarized in Table 1, atomic coordinates and displacement parameters, selected bond lengths and angles are listed in Tables 2 and 3, respectively. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: +49 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD 413943.

3. Results and discussion

The methods for the preparations of the title compound and the isostructural erbium(III) compound are also interesting. The Er(III) compound was obtained via hydrothermal reaction of hydrated erbium(III) nitrate and SeO_2, whereas the Nd(III) compound was obtained by hydrothermal reaction of neodymium(III) oxide, selenic acid and 1,10-phenanthroline. Since the reduction potential of the SeO_4^{2-}/SeO_3^{2-} is small [18], hence the selenate group in the Er(III) compound came as a result of oxidation of SeO_2 by the oxidizing nitrate anion, whereas the selenite anion in the Nd(III) compound resulted from reduction of selenate anion by the reducing 1,10-phenanthroline.

The title compound crystallizes in the monoclinic space group $C2/c$ with cell parameters of a = 12.258(2) Å, b = 7.1024(15) Å, c = 13.391(3) Å, β = 104.250(2)°. The cell is doubled (c-axis) compared with that of $Er_2(SeO_4)(SeO_3)_2(H_2O)_2$, which was refined in the non-centrosymmetric space group $C2$ with the disordered selenate group [22]. In the neodymium(III) compound, all atoms are ordered and showed no abnormal behaviors in the thermal and occupancy parameters. The disorder of the selenate group and the non-centrosymmetric space group $C2$ for the $Er_2(SeO_4)(SeO_3)_2(H_2O)_2$ may be resulted from the choice of a wrong cell which lead to a space group with a lower symmetry. The smaller cell for the Er(III) compound may be resulted from the neglect of some weak reflections during indexing. With a powerful CCD this problem can be easily corrected. It is expected that both Nd(III) and Er(III) compounds should be isostructural.

The structure of the title compound features an ordered 3D network, which is similar to that in the Er(III) compound [22]. As shown in Fig. 1, the neodymium(III) ion is eight-coordinated by seven oxygen atoms from four selenite groups and two selenate groups, and an aqua ligand, its coordination geometry can be described as a distorted square antiprism. The Nd–O distances range from 2.368(9) to 2.517(9) Å (Table 3), which are slightly longer than those in the Er(III) compound, but are comparable to those reported for other Nd(III) selenites and Nd(III) selenates [24–27]. The selenite group is pentadentate, it chelates with a Nd(III) ion (O1, O2) and also bridges with three other Nd(III) ions. O1 and O2 atoms are bidentate metal linkers whereas O3 atom is unidentate. The selenate group is tetradentate and bridges with four Nd(III) ions.

It is interesting to note that the selenite or selenate groups alone can form a 2D layer with the Nd(III) ions. The interconnection of the Nd(III) ions by chelating and bridging selenite groups resulted in a 2D layer parallel to the *bc* plane (Fig. 2). Two types of rings are formed, one is the 4-membered Nd_2O_2 ring and the other one is the 8-membered ring composed of two Nd(III) ions and two selenite groups. The second type of 2D layer is parallel to the *ab* plane. It is resulted from the interconnection of Nd(III) ions via bridging selenate groups (Fig. 3). Within the 2D layer, 16-membered rings are formed, each of which composed of four Nd(III) ions and four selenate groups, such ring is similar to that in $La(SeO_4)(HSeO_3)(H_2O)_2$ [20].

The cross-linkage of the above two types of 2D layers leads to the formation of a 3D network with tunnels running along the *b*-axis (Fig. 4). The tunnels are formed by 16-membered rings, each of which is composed of four Nd(III) ions, two selenite and two selenate groups. The lone pair electrons of the selenite group are oriented toward the free space of the tunnel. The structure of $Er_2(SeO_4)(SeO_3)_2(H_2O)_2$ differs from that of $La(SeO_4)(HSeO_3)(H_2O)_2$ in a number of ways [20]. The selenite group in the La(III) compound is 1H-protonated, hence it connects with fewer metal centers. One selenate oxygen in the La(III) compound remains non-coordinated. The

Table 1
Summary of crystal data and structure refinement for $Nd_2(SeO_4)(SeO_3)_2(H_2O)_2$

Empirical formula	$Nd_2Se_3O_{12}H_4$
Formula weight	721.39
Crystal system	Monoclinic
Space group	$C2/c$
a	12.258(3) Å
b	7.1024(15) Å
c	13.391(3) Å
β	104.250(2)°
Volume	1129.9(4) Å^3
Z	4
Density (calculated)	4.24 g/cm^3
μ	18.805 mm^{-1}
$F(0\,0\,0)$	1288
Color and habit	Purple, needle
Crystal size	0.16 mm × 0.06 mm × 0.04 mm
2θ range for data collection	6.28°–50.1°
Reflections collected	1789
Independent reflections	992 [R(int) = 0.044]
Reflections observed ($I > 2\sigma(I)$)	812
Absorption correction	Empirical
Maximum and minimum transmission	0.921 and 0.571
Solution methods	Direct methods
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	992/0/78
S (on F^2)	1.181
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0454$, $wR2 = 0.0848$
R indices (all data)	$R1 = 0.0628$, $wR2 = 0.0937$
Residual extremes/e. (Å^{-3})	2.215 (0.940 Å from Nd(1) atom) and −1.222

interconnection of La(III) ions via HSO_3 groups lead to a 1D zigzag chain in which two neighboring La(III) ions are bridged by a pair of oxygen atoms [20].

The broad IR absorption band at 3445 cm^{-1} and strong absorption band at 1642 cm^{-1} are due to the presence of aqua ligand. The absorption bands at 890, 831 and 774 and 711 cm^{-1} can be assigned to ν(Se–O) vibrations, whereas those at 502, 439, 407 cm^{-1} are originated from ν(O–Se–O) vibrations [28].

TGA curves of the title compound indicate two main steps of weight losses. The compound is stable up to 190 °C. The first step of weight loss covering the temperature range of 190–443 °C corresponds to the release of two aqua ligands. The weight loss of 5.2% is in good agreement with the calculated value (5.0%). The second weight loss occurs from 580–900 °C, corresponds to the loss of SeO_2 [28]. Since the TGA analysis was carried out under a nitrogen atmosphere, it is expected that the title neodymium selenite-selenate will be reduced to $Nd_2(SeO_3)_3$ first after the release of water molecules. The final residuals are a mixture of $Nd_2O_2(SeO_3)$ and Nd_2O_3, hence the decomposition process is not complete at 900 °C. The total weight loss of 44% is much less than the

Table 2
Atomic coordinates [×10^4] and displacement parameters [Å^2 × 10^3] for $Nd_2(SeO_4)(SeO_3)_2(H_2O)_2$

Atom	x	y	z	U(eq)[a]
Nd(1)	8040(1)	4896(1)	3255(1)	11(1)
Se(1)	7131(1)	4814(2)	705(1)	13(1)
Se(2)	5000	3381(3)	2500	16(1)
O(1)	7647(8)	3111(14)	1581(7)	16(2)
O(2)	7427(8)	6602(13)	1563(8)	18(2)
O(3)	8128(8)	4948(15)	40(7)	21(2)
O(4)	6017(8)	4789(15)	3075(8)	24(2)
O(5)	4601(9)	2071(17)	3333(9)	32(3)
O(1W)	9861(9)	3278(17)	3809(11)	40(3)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

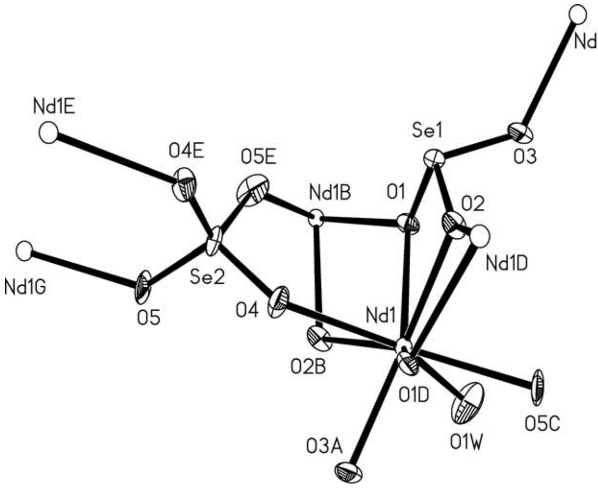

Fig. 1. ORTEP representation of the asymmetric unit in $Nd_2(SeO_4)(SeO_3)_2(H_2O)_2$. The thermal ellipsoids are drawn at 50% probability.

Table 3
Selected bond lengths (Å) and angles (°) for $Nd_2(SeO_4)(SeO_3)_2(H_2O)_2$

Nd(1)—O(3)#1	2.368(9)	Nd(1)—O(4)	2.432(9)
Nd(1)—O(2)#2	2.435(10)	Nd(1)—O(5)#3	2.442(10)
Nd(1)—O(1W)	2.457(11)	Nd(1)—O(1)#4	2.462(10)
Nd(1)—O(2)	2.516(10)	Nd(1)—O(1)	2.517(9)
Se(1)—O(3)	1.683(9)	Se(1)—O(2)	1.690(10)
Se(1)—O(1)	1.694(10)	Se(2)—O(5)#5	1.617(10)
Se(2)—O(5)	1.617(10)	Se(2)—O(4)	1.636(10)
Se(2)—O(4)#5	1.636(10)		
O(3)—Se(1)—O(2)	104.7(5)	O(3)—Se(1)—O(1)	102.2(5)
O(2)—Se(1)—O(1)	94.9(4)	O(5)#5—Se(2)—O(5)	109.8(9)
O(5)#5—Se(2)—O(4)	110.6(5)	O(5)—Se(2)—O(4)	110.6(5)
O(5)#5—Se(2)—O(4)#5	110.6(5)	O(5)—Se(2)—O(4)#5	110.6(5)
O(4)—Se(2)—O(4)#5	104.6(8)		

Symmetry transformations used to generate equivalent atoms: #1 x, $-y + 1$, $z + 1/2$ #2 $-x + 3/2$, $y - 1/2$, $-z + 1/2$ #3 $x + 1/2$, $y + 1/2$, z #4 $-x + 3/2$, $y + 1/2$, $-z + 1/2$ #5 $-x + 1$, y, $-z + 1/2$.

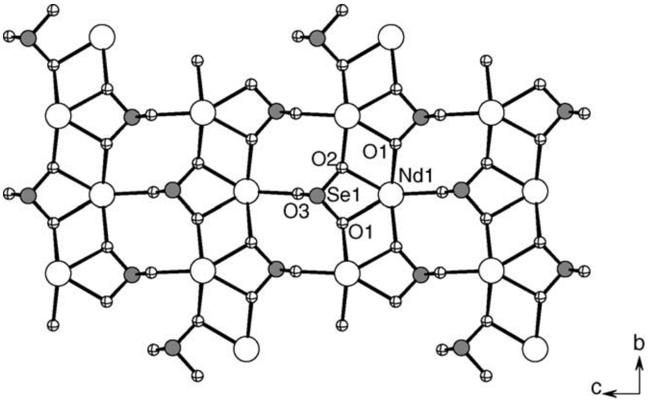

Fig. 2. A 2D layer of neodymium(III) selenite in $Nd_2(SeO_4)(SeO_3)_2(H_2O)_2$ parallel to *bc* plane. The Nd, Se and O atoms are drawn as open (large), gray and crossed circles, respectively.

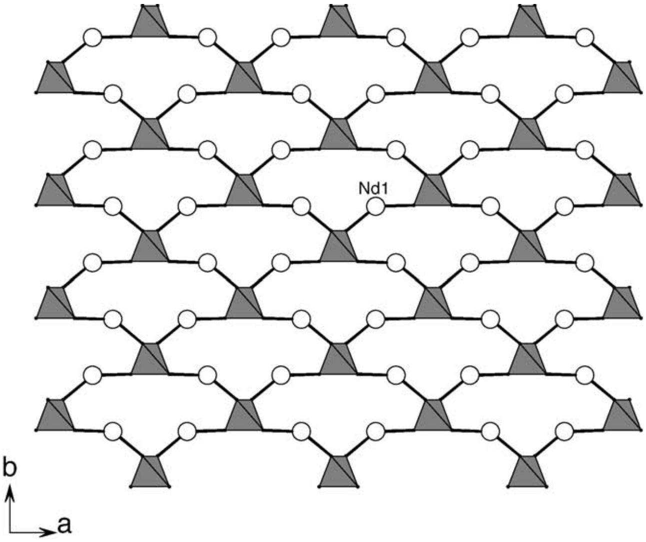

Fig. 3. A 2D layer of neodymium(III) selenate in $Nd_2(SeO_4)(SeO_3)_2(H_2O)_2$ parallel to *ab* plane. The Nd atoms are drawn as open (large) and the SeO_4 tetrahedra are shaded in gray.

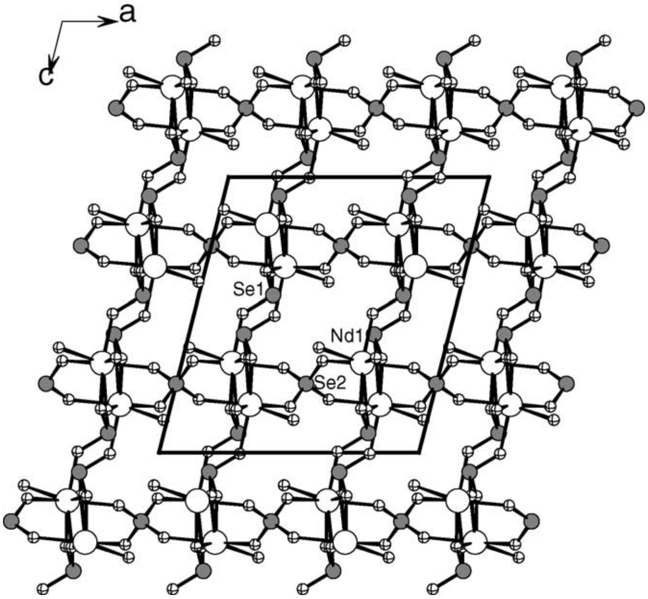

Fig. 4. View of the structure of $Nd_2(SeO_4)(SeO_3)_2(H_2O)_2$ along *b*-axis. The Nd, Se and O atoms are drawn as open (large), gray and crossed circles, respectively.

calculated value (53.4%) if the title compound is completely decomposed to be Nd_2O_3.

Luminescent spectrum of the title compound upon excitation at 356 nm indicates three emission bands at 898, 1059 and 1338 nm, respectively (Fig. 5), which correspond to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ transitions, respectively [29]. The luminescent lifetime of the title compound is about 0.9 μs, which is much longer than those of neodymium(III) complexes with organic ligands [29]. The low value of the life times of the lanthanide complexes with organic ligands compared with the ions in inorganic matrices is due to the quenching of the luminescent state by high-frequency vibrations in the ligand and the solvent. It is difficult to establish meaningful emission quantum yields at these wavelengths due to few well-established standards available.

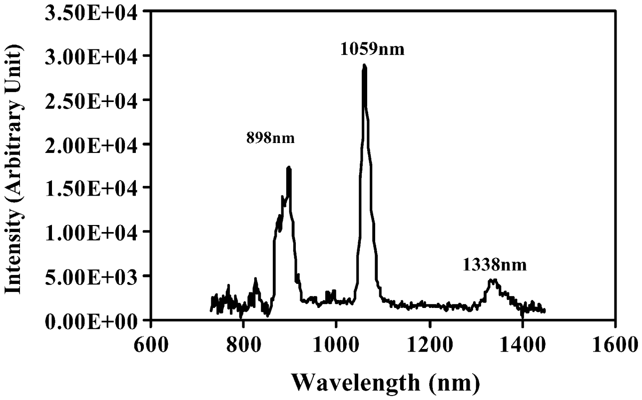

Fig. 5. Luminescent spectrum of the title compound upon excitation at 356 nm.

Acknowledgements

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