# Synthesis, Structure and Photoluminescent Properties of $[C_6N_2H_{14}][Nd_2(C_2O_4)_2(SO_4)_2(H_2O)_4] \cdot H_2O$ , a New Organically Templated Neodymium(III) Oxalate-sulfate

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Abstract. An organically templated neodymium oxalate–sulfate  $[C_6N_2H_{14}][Nd_2(C_2O_4)_2(SO_4)_2(H_2O)_4] \cdot H_2O$  (1) has been synthesized under hydrothermal conditions and structurally characterized by single-crystal X-ray diffraction analysis. In 1, the neo-

## Introduction

Compounds possessing open-framework structures have been extensively investigated in regard of their important applications in the areas of catalysis, sorption, and separation processes. A remarkable variety of open-framework organically templated inorganic materials have been reported over the last two decades [1]. The research mainly focused on the metal phosphates [2–4], phosphites [5–8], arsenates [9–11] and sulfates [12–17]. Recently, compounds with oxalate anions along with phosphate, phosphite, and arsenate units attracted much attention because of their novel extended networks formed by the combination of organic and inorganic anions [1]. However, investigations on compounds containing both, oxalate and sulfate units, have been rare.

Research activities in the area of lanthanide sulfates aroused interest because of their applications in the separation of rare earth elements [18]. Up to now, various lanthanide sulfates with open-framework structures have been reported [18–27]. The hybrid lanthanide oxalate– sulfate frameworks, on the other hand, have rarely been explored hitherto. Mao et al. synthesized La<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)-(SO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>, in which the lanthanum(III) ions are interconnected through oxalate and sulfate groups to form a novel network with a lanthanum(III)sulfate–oxalate hybrid structure [28]. Recently, the first hybrid organic–inorganic frameworks based on lanthanide(III)sulfate chains, in-situ generated oxalate and organic pillars of 1,4-piperazinediacetic acid have been reported [29]. In this work, we report dymium(III) ions are interconnected through oxalate and sulfate groups to form a neodymium oxalate-sulfate hybrid structure. A luminescence spectrum of 1 was recorded, and the luminescence decay time was also measured.

the hydrothermal synthesis, structural characterization, and photoluminescent properties of a new neodymium(III)oxalate-sulfate  $[C_6N_2H_{14}][Nd_2(C_2O_4)_2(SO_4)_2(H_2O)_4] \cdot H_2O$  (1) framework.

## **Experimental Section**

#### Materials and Methods

All chemicals used were of reagent grade and used as received from commercial sources without further purification. The X-ray powder diffraction (XRD) data were collected with a Siemens D5005 diffractometer with Cu- $K_{\alpha}$  radiation ( $\lambda = 1.5418$  Å). Elemental analyses were performed with a Perkin-Elmer 2400 element analyzer. Inductively coupled plasma (ICP) analyses were carried out with a Perkin-Elmer Optima 3300DV spectrometer. Fourier transform infrared spectra (FT-IR) were recorded within the 400-4000 cm<sup>-1</sup> region with a Nicolet Impact 410 FTIR spectrometer using KBr pellets. The thermogravimetric analyses (TGA) were performed with a Perkin-Elmer TGA 7 thermogravimetric analyzer in a nitrogen atmosphere with a heating rate of  $10 \,^{\circ}\text{C} \cdot \text{min}^{-1}$ . The luminescence excitation and emission spectra were recorded with a HO-RIBA Jobin Yvon FluoroLog-3 spectrofluorometer equipped with a 450 W Xe-lamp as an excitation source and a liquid-nitrogencooled R5509-72 PMT as a detector. The time-resolved measurement, was done by using the third harmonic (355 nm) of a Spectraphysics Nd:YAG laser with a 5 ns pulse width and 5 mJ of energy per pulse as a source, and the Near-IR emission lines were dispersed with the emission monochromator of a HORIBA Jobin Yvon FluoroLog-3 equipped with liquid-nitrogen-cooled R5509-72 PMT, and the data was analysed with a LeCroy WaveRunner 6100 1 GHz Oscilloscope. The luminescence lifetime was calculated using the Origin 7.0 software package.

(0.3365 g) and  $H_2C_2O_4 \cdot 2H_2O$  (0.8825 g) diluted sulfuric acid

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**Synthesis** 

 $[C_6N_2H_{14}][Nd_2(C_2O_4)_2(SO_4)_2(H_2O_4)] \cdot H_2O$ 

(1):

То

Nd<sub>2</sub>O<sub>3</sub>



Table 1	ι. (	Crystal	data	and	structure	refinement	for	1

Empirical formula	$C_{10}H_{24}N_2Nd_2O_{21}S_2$
Formula weight	860.93
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	monoclinic
Space group	$P2_{1}/c$
a /Å	8.523(5)
b /Å	28.628(5)
c /Å	9.306(5)
βl°	96.497(5)
Volume /Å <sup>3</sup>	2256.1(18)
Ζ	4
$D \text{calc} / \text{mg} \cdot \text{m}^{-3}$	2.535
Absorption coefficient /mm <sup>-1</sup>	4.843
<i>F</i> (000)	1672
Crystal size /mm	$0.40 \times 0.32 \times 0.28$
θrange /°	2.31 - 28.24
Limiting indices	$-11 \le h \le 5$
	$-38 \le k \le 37$
	$-12 \le l \le 12$
Reflections collected	13707
Reflections unique	5224 [R(int) = 0.0548]
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	5224 / 17 / 364
Goodness-of-fit on $F^2$	1.043
Final R indices $[I > 2\sigma (I)]$	R1 = 0.0374, wR2 = 0.0928
R indices (all data)	R1 = 0.0456, wR2 = 0.0972
Largest diff. peak and hole $/e \cdot Å^{-3}$	1.755 and -1.929

(10.0 mL; 1 mL H<sub>2</sub>SO<sub>4</sub>/10.0 mL H<sub>2</sub>O) was added under constant stirring to give solution I. 1,4-diazobicyclo[2.2.2]octane (DABCO) (0.9692 g) was added to diluted sulfuric acid (10.0 mL; 0.3 mL H<sub>2</sub>SO<sub>4</sub>/10.0 mL H<sub>2</sub>O) whilst stirring to give solution II. Afterwards, solution I was mixed with solution II under constant stirring. The resulting mixture with a molar ratio of Nd<sub>2</sub>O<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>/ DABCO/H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O/H<sub>2</sub>O = 1:24.4:4.4:7:1100 was transferred into a 30 mL Teflon-lined stainless-steel autoclave and heated at 373 K for 16 h. The resulting pink block-like single crystals of **1** were collected by filtration, washed with ethanol and dried at room temperature. Yield: 70 % (with respect to Nd). The inductively coupled plasma (ICP) and elemental analysis resulted: (C<sub>10</sub>H<sub>24</sub>N<sub>2</sub>Nd<sub>2</sub>O<sub>21</sub>S<sub>2</sub>) calcd. (%): O 39.03; Nd 33.51; C 13.95; S 7.45; N 3.25; H 2.81; found: O 39.25; Nd 33.40; C 13.83; S 7.58; N 3.12; H 2.70.

#### Crystal Structure Determination

A suitable single crystal of **1** with the dimensions  $0.40 \times 0.32 \times 0.28$  mm was selected for single-crystal X-ray diffraction analysis. The intensity data were collected with a Siemens SMART CCD diffractometer using graphite-monochromatic Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71069$  Å). Data processing was accomplished with the SAINT program [30]. All absorption corrections were performed using a multi-scan method. The structures were solved by direct methods with the SHELXTL 97 software package [31]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on oxygen and nitrogen atoms were found in Fourier difference maps and organic hydrogen atoms were placed in geometrically preset positions. Crystal and experimental data are listed in Table 1. Selected bond lengths and angles are listed in Table 2 and hydrogen bonding parameters are given in Table 3. Crystallographic information of compound **1** has been deposited

Table 2. Selected bond lengths /Å and bond angles /° for 1.

Nd(1)-O(1)	2.567(4)	Nd(2)-O(12)	2.505(4)
Nd(1) - O(2)	2.484(4)	Nd(2) - O(13)	2.511(4)
Nd(1)-O(3)#3	2.475(4)	Nd(2) - O(14)	2.429(4)
Nd(1) - O(8)	2.410(3)	Nd(2)-O(15)#4	2.486(4)
Nd(1) - O(9)	2.483(4)	Nd(2)-O(16)#4	2.526(4)
Nd(1) - O(17)	2.486(4)	S(1) - O(1)	1.492(4)
Nd(1)-O(18)#1	2.512(4)	S(1) - O(2)	1.491(4)
Nd(1) - O(19)	2.548(4)	S(1) - O(3)	1.472(4)
Nd(1)-O(20)#2	2.566(4)	S(1) - O(4)	1.448(4)
Nd(2) - O(5)	2.444(4)	S(2) - O(5)	1.484(4)
Nd(2) - O(6)	2.685(4)	S(2) - O(6)	1.485(4)
Nd(2) - O(10)	2.504(4)	S(2) - O(7)	1.462(4)
Nd(2)-O(11)	2.459(4)	S(2)-O(8)	1.470(4)
O(1) - Nd(1) - S(1)	27 95(8)	O(5) - Nd(2) - S(2)	26.81(9)
O(2) - Nd(1) - S(1)	27 59(9)	O(6) - Nd(2) - S(2)	27 78(9)
O(3)#3 - Nd(1) - S(1)	80.94(9)	O(10) - Nd(2) - S(2)	103.05(13)
O(8) - Nd(1) - S(1)	104.16(10)	O(11) - Nd(2) - S(2)	78.03(10)
O(9) - Nd(1) - S(1)	70.69(11)	O(12) - Nd(2) - S(2)	146.74(10)
O(17) - Nd(1) - S(1)	98.34(10)	O(13) - Nd(2) - S(2)	71.67(10)
O(18)#1 - Nd(1) - S(1)	149.09(9)	O(14) - Nd(2) - S(2)	100.32(11)
O(19) - Nd(1) - S(1)	95.26(9)	O(15)#4 - Nd(2) - S(2)	142.50(9)
O(20)#2-Nd(1)-S(1)	142.78(10)	O(16)#4 - Nd(2) - S(2)	92.91(10)
<u> </u>			

Symmetry transformations used to generate equivalent atoms: #1 -x+2, -y, -z+1; #2 -x+2, -y, -z+2; #3 -x+1, -y, -z+1; #4 x,  $-y+1/_2$ ,  $z+1/_2$ .

Table 3. Hydrogen bonds for 1. Lenghts /Å and angles /°.

D-H···A	d(D-H)	<i>d</i> (H···A)	<i>d</i> (D····A)	<(DHA)
N(9)-H(9)····O(16)#2	0.91	1.84	2.721(7)	161.7
N(9)-H(9)····O(13)#2	0.91	2.64	3.372(6)	138.5
N(10)-H(10)····O(1W)#1	0.91	2.09	2.905(7)	147.9
N(10) - H(10) - O(17)	0.91	2.60	3.216(6)	125.9
O(10)-H(3)····O(19)#3	0.850(19)	1.94(3)	2.770(5)	164(6)
O(10)-H(4)···O(1W)#4	0.856(19)	2.22(3)	3.006(7)	153(5)
O(1W) - H(12) - O(6)	0.842(19)	2.05(2)	2.881(6)	167(5)
O(1W)-H(11)····O(2)#1	0.845(19)	2.12(3)	2.880(6)	150(5)
O(1W)-H(11)····O(17)#1	0.845(19)	2.59(5)	3.113(6)	122(5)
O(9)-H(2)···O(4)#3	0.853(19)	1.82(3)	2.654(6)	164(5)
O(9) - H(1) - O(5)	0.820(19)	2.28(3)	3.028(6)	151(5)
O(11)-H(6)····O(18)#1	0.879(16)	2.06(2)	2.905(6)	160(4)
O(11)-H(5)···O(1)	0.861(16)	1.845(18)	2.698(5)	170(6)
O(12)-H(7)···O(20)#3	0.845(19)	1.993(19)	2.834(5)	173(5)
O(12)-H(8)····O(7)#5	0.849(19)	1.94(2)	2.781(6)	171(5)
				(0)

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

with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-695257. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

### **Results and Discussion**

The agreement between the experimental and simulated XRD patterns indicated the phase purity of **1** (Figure 1). The difference in reflection intensities between the simulated and experimental patterns was due to the variation in



Figure 1. Simulated and experimental powder X-ray diffraction patterns of 1.

preferred orientation for the powder sample during collection of the experimental XRD data.

The structure of 1 is based on a network of neodymiumcentered polyhedral NdO<sub>9</sub>, sulfur-centered tetrahedral sulfate and oxalate units. The asymmetric unit contains two neodymium atoms, two oxalate groups, two sulfate groups, one protonated 1,4-diazobicyclo[2.2.2]octane (DABCO) molecule, four coordinated and one free water molecule (Figure 2). Of the two neodymium atoms, Nd(1) is surrounded by nine oxygen atoms, in which four oxygen atoms are from two sulfates, four from two oxalates  $(C_2O_4^{2-})$ , and one from a water molecule. Nd(2), on the other hand, is nonacoordinated by two oxygen atoms from one sulfate, four from two oxalates  $(C_2O_4^{2-})$ , and three from water molecules. The average Nd-O bond lengths [Nd(1)-O =2.503 Å, Nd(2)–O = 2.505 Å], are in good agreement with those reported earlier [29]. Two sulfur atoms form the centers of the tetrahedral sulfate groups. The S-O bond lengths in the  $SO_4$  tetrahedra are in the range 1.448(4) to 1.492(4) Å, with O-S-O bond angles in the range 104.0(2) to 111.6(2)°.

As shown in Figure 3a, the neodymium atoms are linked through  $\mu_4$ -oxalate to form an infinite zigzag chain along the c direction. These neodymium oxalate chains are connected by the sulfate groups to give rise to a layer structure, as shown in Figure 3b. Finally, these layers, parallel to the ac plane, are further linked to the neodymium oxalate chains through sulfate groups, resulting in an interesting framework structure (Figure 3c). The DABCO cations and water molecules are located in the cavities of the framework. It is well known that multipoint hydrogen-bond interactions are necessary for the phase formation and stability of open architectures. This was also found for the present study, where strong interactions exist between the hydrogen atoms attached to nitrogen and the framework oxygen atoms. In addition, water molecules participate in hydrogen bonding through O<sub>Water</sub>-H···O bonds. The important hydrogen bond interactions are presented in Table 3.

The IR spectrum (Figure 4) shows the v(N-H) and v(O-H)bands in the range  $3431-2602 \text{ cm}^{-1}$ . The strong



Figure 2. ORTEP view of the structure of 1 showing the atom labeling scheme (50% thermal ellipsoids).



**Figure 3.** Structures of the zigzag chain along the *c*-axis (a), the hybrid organic-inorganic layer in the *ac* plane (b) and the framework of **1** (c). Blue dots indicate nonaconnected neodymium atoms; red, yellow, dark gray and dark blue dots suggest atoms oxygen, sulfur, carbon and nitrogen, respectively.



Figure 4. IR spectrum of 1.

absorption signals at 1598 and  $1474 \text{ cm}^{-1}$  correspond to the antisymmetric and symmetric stretching bands for the carboxylate groups of the oxalate anion. The absorption bands associated with the sulfate groups appear in the region from 1158 to 616 cm<sup>-1</sup>.

The thermogravimetric analysis (TGA) of **1** (Figure 5) displays a weight loss from room temperature to 250 °C, corresponding to the evacuation of lattice and coordinated water molecules (calcd.: 10.46 %; observed: 10.31 %). From 250 to 800 °C, two periods of sharp weight loss (calcd.: 41.16 %; observed: 40.59 %) due to the loss of protonated DABCO, CO<sub>2</sub> and SO<sub>2</sub> are observed. The powder X-ray diffraction pattern of the sample heated at 800 °C corresponds to Nd<sub>2</sub>O<sub>2</sub>(SO<sub>4</sub>) (JCPDS file card No. 48–1829).



Figure 5. TGA curve of 1.

Upon excitation at the ligands absorption band ( $\lambda_{ex} = 355 \text{ nm}$ ), the characteristic Nd<sup>3+</sup> emission is observed. The emission spectrum displays three bands in the range 800–1400 nm, the main band occurring with the maximum at 1063 nm ( ${}^{4}\text{F}_{3/2} \rightarrow {}^{4}\text{I}_{11/2}$ ); two other bands are observed at 897 nm ( ${}^{4}\text{F}_{3/2} \rightarrow {}^{4}\text{I}_{9/2}$ ) and 1335 nm ( ${}^{4}\text{F}_{3/2} \rightarrow {}^{4}\text{I}_{13/2}$ ) (Figure 6). Solid systems containing Nd<sup>3+</sup> ions have been regarded as the most popular luminescent materials for laser system applications [32, 33], since the strongest transition at 1060 nm has potential application for laser emission. The luminescence decay curve obtained from time-resolved luminescence experiments could be fitted monoexponentially, thus confirming that the chemical environment of the Nd<sup>3+</sup> ion is uniform in the materials [34]. The corresponding lifetime of the compound is 1.64 µs.

# Conclusions

In conclusion, the synthesis, the structure and the photoluminescent properties of the new compound  $[C_6N_2H_{14}][Nd_2(C_2O_4)_2(SO_4)_2(H_2O)_4] \cdot H_2O$  possessing both, the sulfate and the oxalate units, has been accomplished employing hydrothermal method. The framework is built up from a linkage involving the polyhedron of oxygen atoms around the neodymium atom, the sulfate tetrahedra, and the oxalate groups.



Figure 6. Emission ( $\lambda_{ex} = 355$  nm) spectrum for 1 in solid-state at room temperature.

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