The First Amine-Templated Layered Metal Selenates

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Although a few open-framework metal sulfates and selenites have been synthesized and characterized recently, it has not been possible to prepare the corresponding selenates, probably because of the instability of the +6 oxidation state of Se in alkaline media. We have been able to synthesize, for the first time, organically templated open-framework rare earth selenates with the general formula $0.5[C_2N_2H_{10}][Ln(H_2O)_2(SeO_4)_2]$ (**I**) (Ln = La, Nd or Pr) and $0.5[C_4N_2H_{14}][La(SeO_4)_2]\cdot 0.5H_2O$ (**II**), under hydrothermal conditions in an acidic medium. Crystal data: **I** (Ln = La): triclinic, space group = $P\bar{1}$, Mr = 491.91, a = 7.0105(8) Å, b = 7.3772(9) Å, c = 9.526(1) Å, α = 82.014(2), β = 84.514(2), γ = 84.247(2)°, V = 483.76(1) Å^3, Z = 2; **II**: triclinic, space group = $P\bar{1}$, Mr = 478.91, a = 5.94(2), b = 7.408(3), c = 11.048(2) Å, α = 86.899(2), β = 75.971(1), γ = 79.456(2)°, V = 463.7(2) Å^3, Z = 4. Being the first report of complex layered selenates, it is likely to stimulate efforts to synthesize other novel open-framework structures making use of the selenate ion as the building unit.
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Introduction

A wide variety of organically templated inorganic open-framework materials are known today. Although metal silicates,[1] phosphates[2] and carboxylates[3−5] dominate this area, several organically templated open-framework metal sulfates[6−8] and selenites[9−11] have also been prepared more recently. The first organically templated layered selenite was synthesized by Harrison et.al,[9] followed by the reports of three-dimensional as well as other layered metal selenites.[10−11] To the best of our knowledge, no organically templated layered metal selenates are known hitherto. While the most stable oxidation state of S is +6 as in SO_4^{2-}, that of Se is +4 (SeO_3^{2-} or $Se_2O_5^{2-}$). The reduction potential of the SO_4^{2-}/SO_3^{2-} couple is 0.119V while that of the SeO_4^{2-}/SeO_3^{2-} couple is only 0.03V in alkaline media. This has direct implications on the stability of the compounds of oxy anions of selenium. Selenites are thus commonly obtained as products even though one may start with H_2SeO_4 as source of Se. This has been encountered by us in few instances[10] and it is probably because of this difficulty that it has not been possible to prepare open-framework metal selenates in the presence of amines. In this article, we report the first successful synthesis and characterization of organically templated open-framework lanthanum selenates, $0.5[C_2N_2H_{10}][Ln(H_2O)_2(SeO_4)_2]$ (**I**) (Ln = La, Nd or Pr) and $0.5[C_4N_2H_{14}][La(SeO_4)_2]\cdot 0.5H_2O$ (**II**), prepared hydrothermally under acidic conditions.

Results and Discussion

$0.5[C_2N_2H_{10}][Ln(H_2O)_2(SeO_4)_2]$ (I) (Ln = La, Nd or Pr)

We shall discuss the structure of the La compound as a representative of this isomorphous group of compounds. The asymmetric unit of **I** contains 14 non-hydrogen atoms of which twelve belong to the inorganic framework and two to the amine (ethylenediamine) as shown in Figure 1 (a). There are two crystallographically distinct Se atoms and a unique La atom, with half of the amine appearing in the asymmetric unit. The lanthanum atoms are nine-coordinate with seven oxygen atoms from two selenate anions [Se(1)X2, Se(2)X5] and two oxygen atoms from water ligands. Each La is connected to two neighboring La atoms by La−μ-O−La linkages, through three-coordinate oxygen atoms (O2 and O6). The $Se(1)O_4$ tetrahedron shares corners (O1 and O3) with two adjacent LaO_9 polyhedra. The remaining two oxygen atoms O7 and O8 are part of terminal Se=O groups. The Se2 atom forms five Se−O−La linkages via a two-coordinate O10 atom, and the three-coordinate O2 and O6 atoms. We thus observed three types of Se−O bonds: Se−O, Se=O and Se−μ$_3$-O, with average bonds lengths of 1.637 Å, 1.62 Å and 1.645 Å respectively. Bond Valence Sum (BVS) calculations for the La and Se atoms [La(1) = 3.13, Se(1) = 6.14 and Se(2) = 5.98] clearly show the oxidation states of the La and Se to be +3 and +6 respectively. The framework stoichiometry of $La(H_2O)_2(SeO_4)_2$ creates a net framework charge of −1, which is balanced by the presence of half of the diprotonated ethylenediamine.

The structure of **I** involves a two-dimensional covalently bonded framework built up of LaO_9 polyhedra and SeO_4 tetrahedra, the former being connected through La−μ$_3$-

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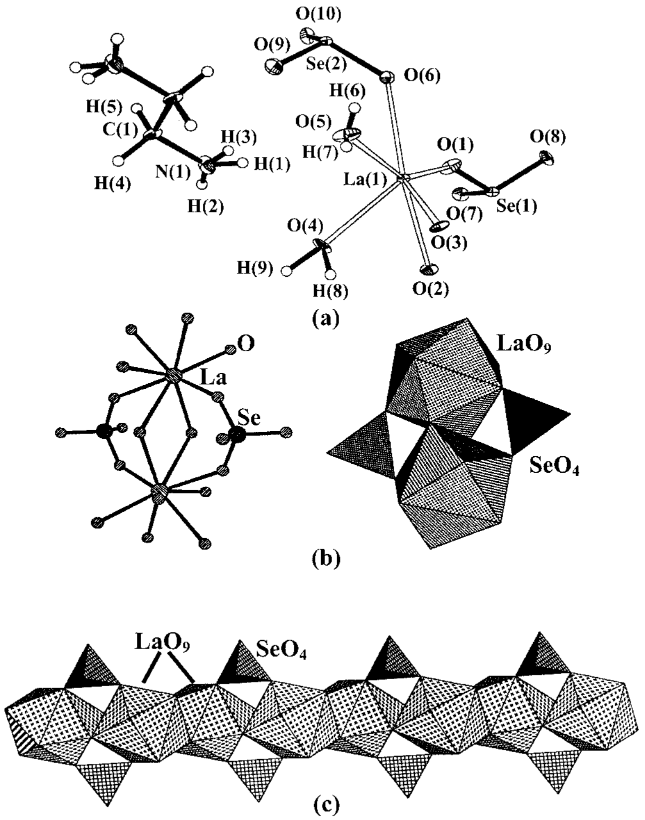

Figure 1. (a) ORTEP plot of $0.5[C_2N_2H_{10}][La(H_2O)_2(SeO_4)_2]$ (**I**); the asymmetric unit is labeled; thermal ellipsoids are given at the 50% probability level; (b) ball and stick, and polyhedral representation of the secondary building unit, SBU-4 in **I**; note the presence of two three-membered rings (La_2Se); c) connectivity between the SBU-4 units creating an infinite chain of edge-shared LaO_9 polyhedra

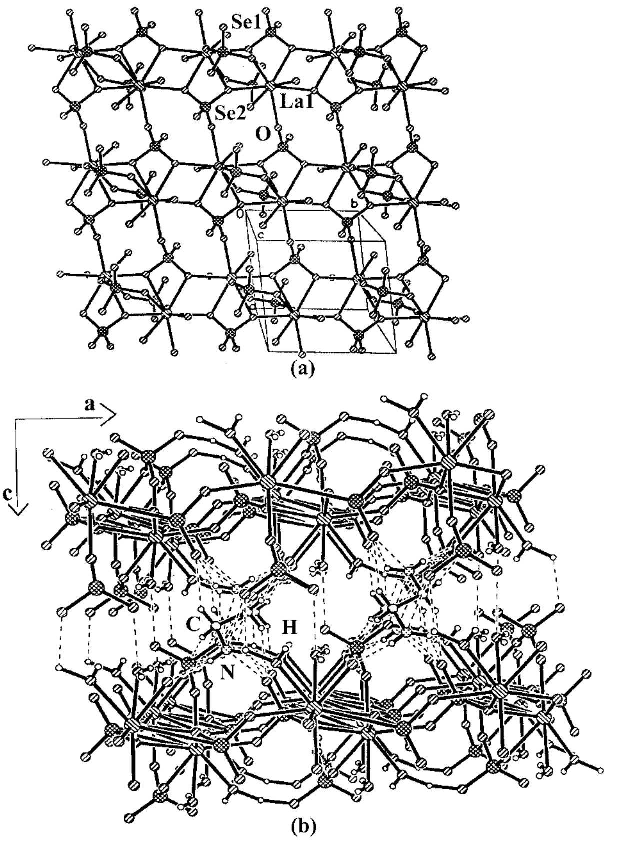

Figure 2. (a) Ball and stick representation of the inorganic layer of **I**, in the *ab* plane; note the presence of two different types of chains; (b) view down the crystallographic *b* axis showing the packing of layers in **I**; hydrogen-bonding interactions between the amine and the framework oxygen atoms are shown by dotted lines

O−La linkages. The topology of the layer in **I** can be described in terms of a secondary building unit (SBU), constructed by capping the two edge-shared LaO_9 polyhedra by two $Se(1)O_4$ groups as shown in Figure 1 (b). Such SBUs, described as SBU-4 by Ferey,[15] have been observed in several metal phosphate systems.[16] The SBU-4 units are linked by three-coordinate oxygen atoms (O2 and O6) forming an infinite chain-like structure consisting of edge-shared LaO_9 polyhedra propagating in a zig-zag fashion as shown in Figure 1 (c). Such a chain can be considered as a tetrahedrally decorated rutile type chain as in a recently reported FePO system.[17] The chains run parallel to the *b* axis and are covalently connected by the $Se(2)O_4$ groups via La−O−Se linkages creating edge-shared four-membered rings (ladder). The $Se(2)O_4$ units also share an edge with neighboring LaO_9 polyhedra along the chain, where as the $Se(1)O_4$ units are involved only in capping the LaO_9 polyhedra along the chain. The structure of **I** is thus made of two types of chains arranged in an ABAB fashion in the *ab* plane (Figure 2, a). The ethylenediamine cations occupy the interlayer sites, forming hydrogen bonds with the framework oxygen atoms (Figure 2, b).

$0.5[C_4N_2H_{14}][La(SeO_4)_2]\ 0.5H_2O$ (II)

The asymmetric unit of **II** (Figure 3, a) contains fifteen non-hydrogen atoms of which eleven belong to the inorganic framework and three to the amine (piperazine). There are two crystallographically distinct Se atoms and a unique La atom, with half of the amine appearing in the asymmetric unit. Two bidentate and five monodentate selenate anions give rise to the nine-coordination of the La atoms. In the framework structure, each lanthanum atom is connected to three neighboring lanthanum centers by La−μ-O−La linkages through three-coordinate oxygen atoms (O3, O4 and O8). The average La−O bond length is 2.61(8) Å. The Se1 atom makes four Se−O−La linkages with the three neighboring La atoms through a three-coordinate oxygen atom O3 ($Se-\mu_3-O-La_2$ bridge), and two two-coordinate oxygen atoms O1 and O5 (Se−O−La bridge). The Se2 atom is connected to four neighboring La atoms through Se−O−La linkages via two three-coordinate oxygen atoms, O4 and O8 ($Se-\mu_3-O-La_2$), and a two-coordinate oxygen atom, O2 (Se−O−La bridge). The O6 and O7 atoms form terminal Se=O groups. The average Se−O bond lengths, which are in the range 1.609(9)−1.665(8) Å, are in agreement with the literature value.[18,19] The coordination environments of La and Se are shown in Figure 3 (b). Bond Valence Sum (BVS) calculations show the La and Se atoms to be in +3 and +6 oxidation states, respectively. The framework stoichiometry of La $(SeO_4)_2$ creates a net framework charge of −1, which is compensated by the +1 charge of half of the diprotonated piperazine.

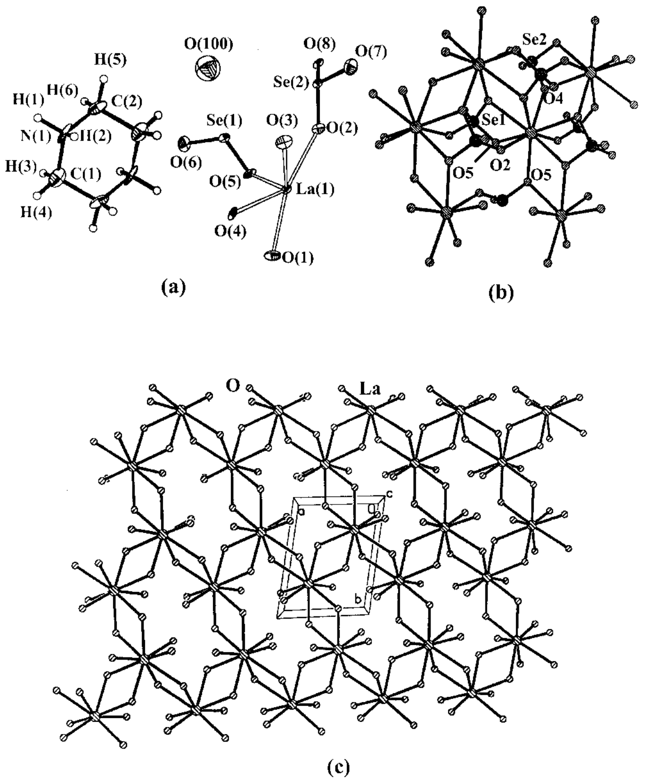

Figure 3. (a) ORTEP plot of $0.5[C_2N_2H_{14}][La(SeO_4)_2]\cdot0.5H_2O$ (**II**); the asymmetric unit is labeled; thermal ellipsoids are given at the 50% probability level; (b) ball and stick representation showing the coordination environment of La and Se atoms in **II**; (c) the LaO layer in **II**; note the presence of six-membered rings made up of edge-shared LaO_9 polyhedra

The structure of **II** is constructed from macro-anionic framework layers of $[La(SeO_4)_2]^{-1}$, held together by hydrogen-bonding interactions with the amine molecules located in the interlamellar space. The structure involves LaO sheets formed by the edge-sharing LaO_9 polyhedra in the *ab* plane (Figure 3, c). The LaO_9 polyhedra are connected by La−μ-O−La linkages forming chains running parallel to the *b* axis with the alternate La atoms of the chains being bridged by La−μ-O−La linkages along the perpendicular direction. Such connectivity between the chains creates hexanuclear lanthanide rings as shown in Figure 3 (c). Along the chain two LaO_9 polyhedra are capped on either side by the $Se(2)O_4$ units alternatively, which are also connected to the two La atoms in the neighboring chains through a three-coordinate oxygen (O8). In the perpendicular direction, the bridging La atoms are capped by two $Se(1)O_4$ units which share an edge with a LaO_9 polyhedron of the neighboring chains. Accordingly, the SeO_4 units are involved in both capping and bridging the La atoms in the LaO sheets. Such a dual connectivity of the SeO_4 units produces corner-shared four-membered rings (La_2Se_2) propagating along the *a* direction as shown in Figure 4 (a).

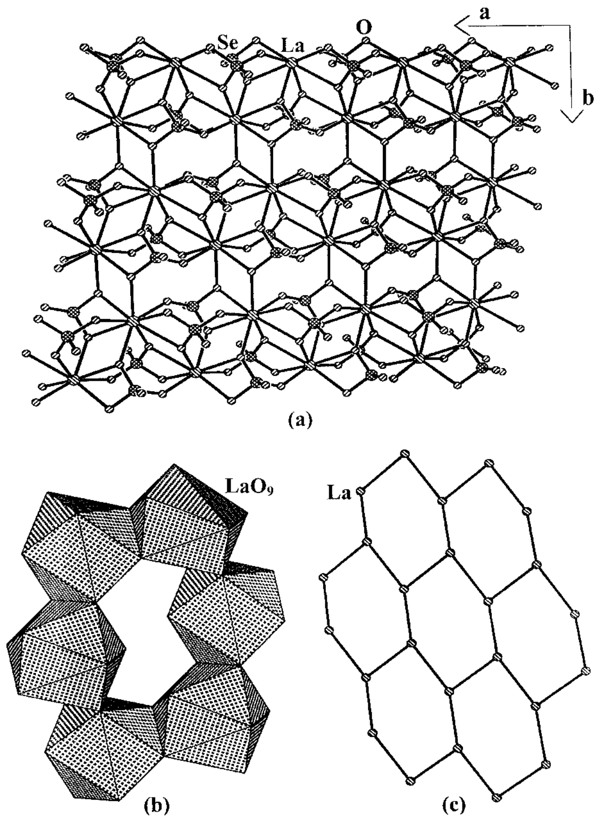

Figure 4. (a) The inorganic layer in **II**; note the capping and bridging of the LaO_9 dimers by two selenate units, resulting in corner-shared four-membered rings along the *a* axis; (b) polyhedral view of a hexanuclear lanthanide ring in **II**; (c) the (6,3) net in **II**

The thermogravimetric analyses (TGA) of **I** and **II** were carried out under N_2 from 30−900 °C at a heating rate of 5 °C/min. Compound **I** decomposes to the selenite in the temperature range 100−330 °C, with the removal of the amine, water and SeO_2 (wt.loss: calcd. 33.02%, obsd. 33.89%) which on further heating, decomposes to a mixture of La_2Se_3 and La_2O_3 (JC, PDS file, card nos: 22-0369, 19-0659), as indicated by the PXRD of the residue at 950 °C. Such thermal decomposition of selenate to selenite has been observed in the case of simple lanthanum selenate hydrates,[20] but the reduction to selenide is unusual. A similar decomposition scheme was observed for **II**, except that in the final stage, all the selenium was lost as SeO_2 to give La_2O_3 as the residue. The overall weight losses for **I** and **II** are 55.94% (calcd. 55.55%) and 57.25% (57.12%), respectively.

Besides being the first examples of two-dimensional organically templated metal selenates, **I** and **II** exhibit several interesting structural features. The La atoms are nine-coordinate in both **I** and **II**, but there are definitive differences between their structures. The layer structure of **I** is constructed from two types of chains: type A consisting of chains formed by the SBU-4 units and type B chains consisting of ladders, arranged in an ABAB fashion. **I** appears to be a unique case whereby the layer structure is formed by alternating chains of SBU-4 units and ladders. An important feature of **II** is the two-dimensional network of edge-sharing LaO_9 polyhedra to form a hexanuclear lanthanide ring (Figure 4, b). The hexanuclear lanthanide rings are surrounded by six similar rings resulting in the (6,3) net shown in Figure 4 (c). This is probably the first such layer architecture in the open-framework compounds containing XO_4^{2-} units. Similar rings containing twelve and 14 edge-shared MO_6 octahedra (M = Mn, Co) occur in metal-organic hybrid compounds containing dicarboxylate units.[21] These organic moieties covalently connect the neighboring metal atoms of the ring through C−O−M bonds. A similar connectivity occurs in **II** whereby the two selenate units connect the La atoms in a ring through Se−μ_3-O−La_2 linkages. The zig-zag chains made from edge-sharing LaO_9 polyhedra run parallel in **I** (Figure 2, b), but the chains in **II**, shifted along the *a* direction, are linked to form the LaO sheet in the *ab* plane (Figure 4, c).

Conclusion

In conclusion, the successful synthesis of amine-templated open-framework metal selenates with layered structures has been demonstrated. The results suggest that it may indeed be possible to prepare other complex metal selenates with 2-D and 3-D networks.

Experimental Section

Synthesis and Initial Characterization: Compounds **I** and **II** were synthesized by employing the hydrothermal method in the presence of organic amines. In a typical synthesis of **I** with Ln = La, $LaCl_3$ (0.25 g) was dissolved in water (2 mL) in a Teflon beaker. To this solution selenic acid (0.26 mL, 40 wt%) was added with stirring followed by ethylenediamine (0.08 mL) and the stirring continued for a further 20 min until a homogeneous gel was obtained. The resultant gel with the molar ratio $LaCl_3/H_2SeO_4$/1.2en/111H_2O was transferred to a 7 mL capacity PTFE-lined stainless steel autoclave and heated at 150 °C for 48 h. The pH of the starting reaction mixture was 4, and there was no change in pH after the completion of the reaction. Colorless plate-like crystals of **I** were collected, washed with de-ionized water, and dried under ambient conditions. For the synthesis of the Nd and Pr analogues of compound **I**, Nd_2O_3 and $Pr_2(CO_3)_3$ were used as metal sources, respectively. The Nd analogue of **I** was obtained by heating a mixture of molar composition Nd_2O_3/6H_2SeO_4/4en/600H_2O at 100 °C for 120 h whereas the Pr analogue of **I** was synthesized starting with the following mixture: $Pr_2(CO_3)_3$ (0.23 g), H_2SeO_4 (0.78 mL), en (0.1 mL), and H_2O (1.8 mL) at 150 °C for 48 h. For the synthesis of **II**, hydrothermal reactions were carried out at 150 °C for 70 h starting with the following composition, $LaCl_3$ (0.25 g, 1 mmol)/H_2SeO_4 (0.4 mL, 1.5 mmol)/PIP (0.17 g, 2 mmol)/H_2O (1.8 mL, 100 mmol) (PIP = piperazine). Initial characterization of both **I** and **II** was carried out by powder X-ray diffraction (PXRD), energy dispersive analysis of X-rays (EDAX), elemental CHN analysis and thermogravimetric analysis (TGA).

The compounds gave satisfactory elemental analysis. The experimental and calculated (in wt%) values for C, H, and N are as follows: **I** (Ln = La): calcd. C 2.43, N 2.80, H 1.84; found C 2.4, N 2.69, H 1.86; **II**: calcd. C 5.02, N 2.94, H 1.67; found: C 5.12, N 2.92, H 1.61. EDAX indicated that the ratios of Ln (Ln = La, Nd or Pr) and Se are 1: 2 for **I** and **II**, which is in agreement with

Table 1. Crystal data and structure refinement parameters **I** and **II**

	I[a]	**II**
Empirical formula	$0.5[C_2N_2H_{10}][La(H_2O)_2(SeO_4)_2]$	$0.5[C_4N_2H_{14}][La(SeO_4)_2]\cdot 0.5H_2O$
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
T [K]	293(2)	293(2)
a [Å]	7.0105(8)	5.94(2)
b [Å]	7.3772(9)	7.408(3)
c [Å]	9.526(1)	11.048(2)
α [°]	82.014(2)	86.899(2)
β [°]	84.514(2)	75.971(1)
γ [°]	84.247(2)	79.456(2)
Volume [Å^3]	483.76(1)	463.7(2)
Z	2	4
Formula mass	491.91	478.91
$\rho_{calcd.}$ [g cm^{-3}]	3.453	3.358
μ [mm^{-1}]	11.986	12.476
Total data collected	2032	1956
Unique data	1359	1316
λ(Mo-K_α) [Å]	0.071073	0.071073
R_{int}	0.0329	0.0383
R [$I > 2\sigma(I)$]	$R1 = 0.0435$, $wR2 = 0.1083$[b]	$R_1 = 0.0456$, $wR_2 = 0.1128$
R (all data)	$R1 = 0.0482$, $wR2 = 0.1105$	$R_1 = 0.0610$, $wR_2 = 0.1193$

[a] The lattice parameters of the corresponding Nd and Pr compounds were comparable. [b] $R1 = \|F_o| - |F_c\|/|F_o|$; $wR2 = [\{w(F_o^2 - F_c^2)^2\}/\{w(F_o^2)^2\}]^{1/2}$, $w = 1/[\sigma^2(F_o)^2 + (aP)^2]$, $P = [F_o^2 + 2F_c^2]/3$, where $a = 0.0710$ for **I** and $a = 0.0623$ for **II**.

the molecular formulae. The formula masses of **I** and **II** are 491.91 and 478.91, respectively.

Single-Crystal Structure Determination: Suitable single-crystals of each compound were carefully selected under a polarizing microscope and mounted on the tip of a thin glass fiber using cyanoacrylate (super glue) adhesive. Single-crystal structure determinations by X-ray diffraction were performed with a Siemens SMART-CCD diffractometer equipped with a normal focus, 2.4 kW sealed-tube X-ray source (Mo-K_α radiation, $\lambda = 0.71073$ Å) operating at 50 kV

Table 2. Selected bond lengths and angles for $0.5[C_2N_2H_{10}][La(H_2O)_2(SeO_4)_2]$ (**I**)

Moiety	Distance [Å]
La(1)−O(1)	2.449(7)
La(1)−O(2)	2.476(7)
La(1)−O(3)	2.498(7)
La(1)−O(10)$^{\#1}$	2.521(7)
La(1)−O(4)	2.556(8)
La(1)−O(5)	2.586(9)
La(1)−O(6)	2.609(7)
La(1)−O(6)$^{\#2}$	2.637(7)
La(1)−O(2)$^{\#3}$	2.842(7)
La(1)−Se(2)$^{\#2}$	3.4747(1)
Se(1)−O(7)	1.617(8)
Se(1)−O(1)	1.623(7)
Se(1)−O(8)	1.627(7)
Se(1)−O(3)$^{\#3}$	1.647(7)
Se(2)−O(9)	1.608(8)
Se(2)−O(10)	1.637(7)
Se(2)−O(2)$^{\#4}$	1.646(7)
Se(2)−O(6)	1.668(7)
Se(2)−La(1)$^{\#2}$	3.4747(1)
O(2)−Se(2)$^{\#5}$	1.646(7)
O(2)−La(1)$^{\#3}$	2.842(7)
O(3)−Se(1)$^{\#3}$	1.647(7)
O(6)−La(1)$^{\#2}$	2.637(7)
O(10)−La(1)$^{\#1}$	2.521(7)

Moiety	Angle [°]
O(1)−La(1)−O(2)	74.5(3)
O(1)−La(1)−O(3)	131.4(2)
O(2)−La(1)−O(3)	78.2(2)
O(1)−La(1)−O(10)$^{\#1}$	85.2(3)
O(2)−La(1)−O(10)$^{\#1}$	93.7(2)
O(3)−La(1)−O(10)$^{\#1}$	136.3(2)
O(1)−La(1)−O(4)	135.6(3)
O(2)−La(1)−O(4)	72.5(3)
O(3)−La(1)−O(4)	68.2(3)
O(10)$^{\#1}$−La(1)−O(4)	68.4(3)
O(1)−La(1)−O(5)	150.4(3)
O(2)−La(1)−O(5)	135.1(3)
O(3)−La(1)−O(5)	67.4(3)
O(10)$^{\#1}$−La(1)−O(5)	92.0(3)
O(4)−La(1)−O(5)	68.5(3)
O(1)−La(1)−O(6)	75.3(2)
O(2)−La(1)−O(6)	148.2(2)
O(3)−La(1)−O(6)	130.6(2)
O(10)$^{\#1}$−La(1)−O(6)	74.2(2)
O(4)−La(1)−O(6)	126.1(3)
O(5)−La(1)−O(6)	75.6(3)
O(1)−La(1)−O(6)$^{\#2}$	82.2(3)
O(2)−La(1)−O(6)$^{\#2}$	119.2(2)
O(3)−La(1)−O(6)$^{\#2}$	77.1(2)
O(10)$^{\#1}$−La(1)−O(6)$^{\#2}$	139.7(2)
O(4)−La(1)−O(6)$^{\#2}$	140.4(3)
O(5)−La(1)−O(6)$^{\#2}$	81.0(3)
O(6)−La(1)−O(6)$^{\#2}$	65.5(3)
O(1)−La(1)−O(2)$^{\#3}$	67.5(2)
O(2)−La(1)−O(2)$^{\#3}$	63.7(3)
O(3)−La(1)−O(2)$^{\#3}$	64.5(2)
O(10)$^{\#1}$−La(1)−O(2)$^{\#3}$	147.8(2)
O(4)−La(1)−O(2)$^{\#3}$	120.0(2)
O(5)−La(1)−O(2)$^{\#3}$	120.2(3)
O(6)−La(1)−O(2)$^{\#3}$	112.4(2)
O(6)$^{\#2}$−La(1)−O(2)$^{\#3}$	55.5(2)
O(1)−La(1)−Se(2)$^{\#2}$	74.3(2)
O(2)−La(1)−Se(2)$^{\#2}$	91.6(2)
O(3)−La(1)−Se(2)$^{\#2}$	67.1(2)
O(10)$^{\#1}$−La(1)−Se(2)$^{\#2}$	156.6(2)
O(4)−La(1)−Se(2)$^{\#2}$	134.7(2)
O(5)−La(1)−Se(2)$^{\#2}$	100.2(2)
O(6)−La(1)−Se(2)$^{\#2}$	89.5(2)
O(6)$^{\#2}$−La(1)−Se(2)$^{\#2}$	27.6(2)
O(2)$^{\#3}$−La(1)−Se(2)$^{\#2}$	27.98(1)
O(7)−Se(1)−O(1)	109.2(4)
O(7)−Se(1)−O(8)	111.3(4)
O(1)−Se(1)−O(8)	108.3(4)
O(7)−Se(1)−O(3)$^{\#3}$	106.8(4)
O(1)−Se(1)−O(3)$^{\#3}$	112.2(4)
O(8)−Se(1)−O(3)$^{\#3}$	108.9(4)
O(9)−Se(2)−O(10)	112.7(4)
O(9)−Se(2)−O(2)$^{\#4}$	112.6(4)
O(10)−Se(2)−O(2)$^{\#4}$	109.3(4)
O(9)−Se(2)−O(6)	110.4(4)
O(10)−Se(2)−O(6)	110.2(4)
O(2)$^{\#4}$−Se(2)−O(6)	101.0(4)
O(9)−Se(2)−La(1)$^{\#2}$	128.0(3)
O(10)−Se(2)−La(1)$^{\#2}$	119.0(3)
O(2)$^{\#4}$−Se(2)−La(1)$^{\#2}$	54.1(3)
O(6)−Se(2)−La(1)$^{\#2}$	47.0(2)
Se(1)−O(1)−La(1)	144.6(4)
Se(2)$^{\#5}$−O(2)−La(1)	145.7(4)
Se(2)$^{\#5}$−O(2)−La(1)$^{\#3}$	97.9(3)
La(1)−O(2)−La(1)$^{\#3}$	116.3(3)
Se(1)$^{\#3}$−O(3)−La(1)	134.3(4)
La(1)−O(4)−H(8)	119(8)
La(1)−O(5)−H(5)	130(1)
Se(2)−O(6)−La(1)	129.5(4)
Se(2)−O(6)−La(1)$^{\#2}$	105.4(3)
La(1)−O(6)−La(1)$^{\#2}$	114.5(3)
Se(2)−O(10)−La(1)$^{\#1}$	141.4(4)

Organic moiety

Moiety	Distance [Å]	Moiety	Angle [°]
N(1)−C(1)	1.479(14)	N(1)−C(1)−C(1)$^{\#6}$	109.4(11)
C(1)−C(1)$^{\#6}$	1.55(2)		

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, -y + 1, -z + 2$; $^{\#2}$ $-x + 1, -y + 1, -z + 2$; $^{\#3}$ $-x + 1, -y + 2, -z + 2$; $^{\#4}$ $x, y - 1, z$; $^{\#5}$ $x, y + 1, z$; $^{\#6}$ $-x, -y + 1, -z + 1$

Table 3. Selected bond lengths and angles for $0.5[C_4N_2H_{14}][La(SeO_4)_2]\cdot0.5H_2O$ (**II**)

Moiety	Distance [Å]	Moiety	Angle [°]	Moiety	Angle [°]
La(1)−O(1)	2.479(9)	O(1)−La(1)−O(2)	150.6(3)	O(8)#1−La(1)−O(4)$^{\#3}$	115.7(2)
La(1)−O(2)	2.480(8)	O(1)−La(1)−O(3)	140.4(3)	O(8)#2−La(1)−O(4)$^{\#3}$	57.0(2)
La(1)−O(3)	2.533(8)	O(2)−La(1)−O(3)	67.6(3)	O(1)−La(1)−O(3)$^{\#4}$	117.9(3)
La(1)−O(4)	2.534(7)	O(1)−La(1)−O(4)	73.2(3)	O(2)−La(1)−O(3)$^{\#4}$	78.1(3)
La(1)−O(5)	2.554(8)	O(2)−La(1)−O(4)	136.0(3)	O(3)−La(1)−O(3)$^{\#4}$	65.0(3)
La(1)−O(8)$^{\#1}$	2.605(7)	O(3)−La(1)−O(4)	71.5(3)	O(4)−La(1)−O(3)$^{\#4}$	70.4(2)
La(1)−O(8)$^{\#2}$	2.614(7)	O(1)−La(1)−O(5)	84.1(3)	O(5)−La(1)−O(3)$^{\#4}$	56.6(2)
La(1)−O(4)$^{\#3}$	2.665(8)	O(2)−La(1)−O(5)	85.8(3)	O(8)$^{\#1}$−La(1)−O(3)$^{\#4}$	119.1(2)
La(1)−O(3)$^{\#4}$	2.795(8)	O(3)−La(1)−O(5)	119.5(2)	O(8)$^{\#2}$−La(1)−O(3)$^{\#4}$	160.8(3)
O(4)−La(1)$^{\#3}$	2.665(8)	O(4)−La(1)−O(5)	100.9(3)	O(4)$^{\#3}$−La(1)−O(3)$^{\#4}$	125.2(2)
O(8)−La(1)$^{\#1}$	2.605(7)	O(1)−La(1)−O(8)$^{\#1}$	72.9(3)	La(1)−O(3)−La(1)$^{\#4}$	115.0(3)
O(8)−La(1)$^{\#5}$	2.614(7)	O(2)−La(1)−O(8)$^{\#1}$	77.8(3)	La(1)−O(4)−La(1)$^{\#3}$	115.7(3)
O(3)−La(1)$^{\#4}$	2.795(8)	O(3)−La(1)−O(8)$^{\#1}$	143.6(3)	La(1)$^{\#1}$−O(8)La(1)$^{\#5}$	116.7(3)
Se(1)−O(6)	1.609(9)	O(4)−La(1)−O(8)$^{\#1}$	144.8(3)	O(2)−Se(2)−O(7)	113.9(4)
Se(1)−O(1)$^{\#5}$	1.628(8)	O(5)−La(1)−O(8)$^{\#1}$	66.7(2)	O(2)−Se(2)−O(4)$^{\#4}$	111.9(4)
Se(1)−O(5)	1.645(8)	O(1)−La(1)−O(8)$^{\#2}$	81.3(3)	O(7)−Se(2)−O(4)$^{\#4}$	110.1(4)
Se(1)−O(3)$^{\#4}$	1.660(8)	O(2)−La(1)−O(8)$^{\#2}$	84.3(2)	O(2)−Se(2)−O(8)	109.4(4)
Se(2)−O(2)	1.600(8)	O(3)−La(1)−O(8)$^{\#2}$	101.3(3)	O(7)−Se(2)−O(8)	112.1(4)
Se(2)−O(7)	1.614(9)	O(4)−La(1)−O(8)$^{\#2}$	119.7(2)	O(4)$^{\#4}$−Se(2)−O(8)	98.6(4)
Se(2)−O(4)$^{\#4}$	1.657(7)	O(5)−La(1)−O(8)$^{\#2}$	130.0(2)	O(6)−Se(1)−O(1)$^{\#5}$	109.7(4)
Se(2)−O(8)	1.665(7)	O(8)$^{\#1}$−La(1)−O(8)$^{\#2}$	63.3(3)	O(6)−Se(1)−O(5)	110.5(5)
O(1)−Se(1)$^{\#2}$	1.628(8)	O(1)−La(1)−O(4)$^{\#3}$	76.7(3)	O(1)$^{\#5}$−Se(1)−O(5)	110.3(4)
O(3)−Se(1)$^{\#4}$	1.660(8)	O(2)−La(1)−O(4)$^{\#3}$	115.8(3)	O(6)−Se(1)−O(3)$^{\#4}$	113.5(4)
O(4)−Se(2)$^{\#4}$	1.657(7)	O(3)−La(1)−O(4)$^{\#3}$	72.4(2)	O(1)$^{\#5}$−Se(1)−O(3)$^{\#4}$	111.9(5)
		O(4)−La(1)−O(4)$^{\#3}$	64.3(3)	O(5)−Se(1)−O(3)$^{\#4}$	100.7(4)
		O(5)−La(1)−O(4)$^{\#3}$	158.4(3)		
Organic moiety Moiety	Distance [Å]	Moiety	Angle [°]		
N(1)−C(2)	1.46(2)	N(1)−C(1)−C(2)$^{\#6}$	111.9(12)		
N(1)−C(1)	1.47(2)	N(1)−C(2)−C(1)$^{\#6}$	112.4(11)		
C(1)−C(2)$^{\#6}$	1.48(2)				
C(2)−C(1)$^{\#6}$	1.48(2)				

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, -y, -z$; $^{\#2}$ $x + 1, y, z$; $^{\#3}$ $-x + 1, -y + 1, -z$; $^{\#4}$ $-x, -y + 1, -z$; $^{\#5}$: $x - 1, y, z$; $^{\#6}$: $-x + 1, -y, -z - 1$

and 40 mA. The structures were solved by direct methods using SHELXS-86,[12] which readily revealed all the heavy atom positions (La, Se) and enabled us to locate the other non-hydrogen (C, N and O) positions from the difference Fourier maps. Empirical absorption corrections based on symmetry-equivalent reflections were applied using SADABS.[13] All the hydrogen positions were found in the difference Fourier maps. For the final refinements, hydrogen atoms for both the framework as well as the amine were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. However hydrogen positions for the extra-framework water (O100) for **II** were not included in the final refinement because of disorder at that site. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS[14] package of programs. Details of the structure determinations and final refinements for **I** (M = La) and **II** are listed in Table 1. Selected bond lengths and bond angles in **I** and **II** are given in Tables 2 and 3, respectively. Various hydrogen-bonding interactions in **I** and **II** are listed in Table 4. The powder X-ray diffraction patterns of **I** and **II** were in good agreement with the simulated patterns based on single-crystal data, indicative of their phase purity. CCDC-212329 (**I**) and -212330 (**II**) contain the supplementary crystallographic data for this paper. These data can be

Table 4. Hydrogen-bonding interactions in **I** and **II**

Moiety	D−H [Å]	H···A [Å]	D···A [Å]	D−H···A [°]
I				
N(1)−H(1)···O(7)	0.92(2)	2.07(2)	2.83(2)	138.8(1)
N(1)−H(2)··· O(6)	0.92(2)	2.00(1)	2.92(1)	171.2(1)
C(1)−H(3)··· O(1)	0.99(2)	2.51(2)	3.31(2)	138.1(1)
C(1)−H(4)··· O(7)	0.99(2)	2.52(2)	3.24(2)	129.9(1)
C(2)−H(5) ···O(5)	0.99(2)	2.46(2)	3.44(2)	171.8(1)
N(1)−H(1)···O(100)	0.92(2)	2.23(1)	2.91(1)	130.7(1)
II				
N(1)−H(1)···O(9)	0.861(16)	2.501(14)	2.823(14)	103.1(11)
N(1)−H(2)···O(3)	0.860(16)	2.125(14)	2.981(14)	173.8(13)
N(1)−H(3)···O(9)	0.64(12)	2.29(12)	2.823(14)	143(14)
N(1)−H(3)···O(10)	0.64(12)	2.57(12)	3.048(14)	134(13)
*O(5)−H(6)···O(8)	0.71(14)	2.46(14)	3.049(15)	142(13)
O(5)−H(7)···O(8)	0.5(3)	2.4(3)	2.858(13)	158(38)
*O(4)−H(8)···O(8)	0.91(13)	2.17(13)	3.010(12)	153(11)
O(4)−H(9)···O(7)	1.04(15)	1.70(14)	2.709(12)	162(13)
C(1)−H(4)···O(9)	0.970(17)	2.327(15)	3.099(15)	136.0(11)

* Intramolecular hydrogen bonding

obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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