

The first organically templated open-framework metal selenate with a three-dimensional architecture

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A three-dimensional metal selenate of the formula $[\text{C}_2\text{N}_2\text{H}_{10}][\text{La}_2(\text{SeO}_4)_4(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$, comprising La_2Se_4 building units and possessing 12-membered channels, has been prepared in an acidic medium under hydrothermal conditions.

Although metal silicates,¹ phosphates² and carboxylates³ constitute the majority of inorganic open-framework materials, metal sulfates⁴ and selenites⁵ with layered and three-dimensional structures have been successfully synthesized in the last few years. Thus, three-dimensional selenites of iron and zinc with well-defined channels and interesting properties have been reported.⁵ To our knowledge, three-dimensional open-framework metal selenates have not been reported hitherto, an inherent difficulty faced in making them being the small reduction potential of the $\text{SeO}_4^{2-}/\text{SeO}_3^{2-}$ couple (0.03 V) in the alkaline medium. We have therefore attempted making metal selenates in an acidic medium under hydrothermal conditions and succeeded in obtaining a three-dimensional lanthanum selenate, $[\text{C}_2\text{N}_2\text{H}_{10}][\text{La}_2(\text{SeO}_4)_4(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$, **I**, with a channel structure. In this communication, we report the synthesis and structure of this first amine-templated three-dimensional metal selenate.

I was prepared hydrothermally starting from LaCl_3 and H_2SeO_4 in the presence of ethylenediamine.[†] The asymmetric unit of **I** contains 29 non-hydrogen atoms, out of which 24 belong to the inorganic framework and 5 to the protonated amine and the water molecule.[‡] There are two crystallographically distinct La atoms and four distinct Se atoms. Of the two La atoms, La(1) is eight-coordinated by seven O atoms from seven selenate groups and one O atom from the water ligand while La(2) is nine-coordinated by seven O atoms from six selenate groups and two O atoms from water ligands, the average La–O bond length being 2.545 and 2.569 Å respectively. The Se atoms are at the centers of tetrahedral selenate ions as expected. The Se atoms form $(4 - n)$ Se–O–La bonds and n terminal Se–O bonds, the actual number of the latter differing from one to another. The average length of the Se–O bonds are 1.635 (Se–O–La) and 1.606 Å (terminal Se–O), with the O–Se–O bond angles in the range $103.8(3) - 115.3(4)^\circ$. Bond valence sum (BVS) calculations⁶ confirm the oxidation states of La and Se to be +3 and +6 respectively. The framework stoichiometry of $[\text{La}_2(\text{SeO}_4)_4(\text{H}_2\text{O})_3]^{2-}$, with a net framework charge of -2 , is balanced by the diprotonated ethylenediamine.

The complex network of LaO_8 , LaO_9 and SeO_4 moieties gives rise to a three-dimensional structure possessing channels along all the three axes. The structure is most conveniently described in terms of two small building units, both with the stoichiometry La_2Se_4 . In one, two crystallographically equivalent La(1) polyhedra are capped by four selenate ions in Q_2 connectivity (Fig. 1a) and in the other, two La(2) polyhedra are both corner and edge-linked by SeO_4 tetrahedra (Fig. 1b). Connectivity between these two units through La–O–Se–O–La linkages gives rise to infinite chains along the [100] direction (Fig. 1c), which then are connected through a bridging $\text{Se}(2)\text{O}_4$ to form a two-dimensional layer in the ab -plane, with 4- and 8-membered apertures (Fig. 2). The layers are stacked one over the other along the c -axis and connected by the $\text{Se}(4)\text{O}_4$ tetrahedra which share corners with the La(1)–O polyhedra from the adjacent layers forming the 3-dimensional network. The 3D structure has 12-membered channels along the a - and b -

axes, and 8-membered channels along the c -axis. The amine molecules reside in the 12-membered channels forming hydrogen bonds with the framework oxygens (Fig. 3). The two terminal Se–O groups pointing into the channels are involved in intraframework hydrogen bond interactions. The presence of two types of water is supported by thermogravimetric analysis and the infrared spectrum. The TGA curve shows the loss of one water molecule around 100 °C and three water molecules at 150 °C. The infrared spectrum shows the characteristic band due to coordinated water.

In conclusion, a three-dimensional La selenate with a channel structure has been synthesized hydrothermally. This result shows that the selenate ion can be usefully employed in the design of open-framework inorganic structures.

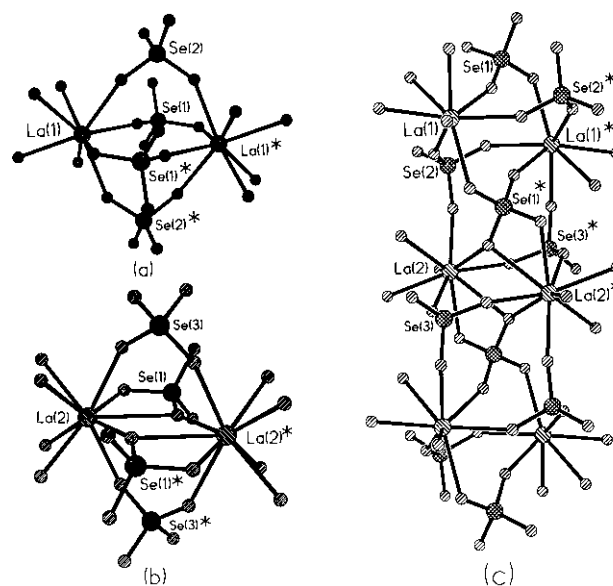


Fig. 1 (a) and (b) Ball and stick representations of the La_2Se_4 building units. (c) Connectivity between the building units creating infinite chains along the [100] direction.

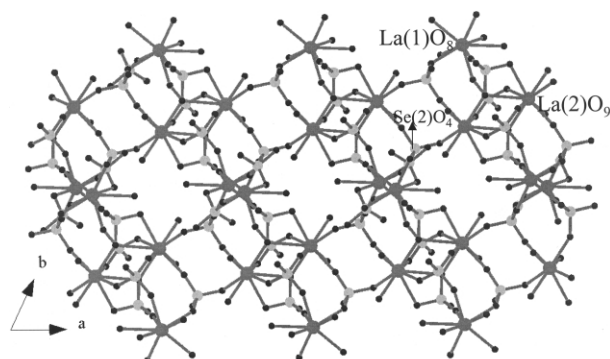


Fig. 2 The inorganic layer $[\text{La}_2(\text{SeO}_4)_3(\text{H}_2\text{O})_3]$, in the ab -plane, showing 4- and 8-membered apertures.

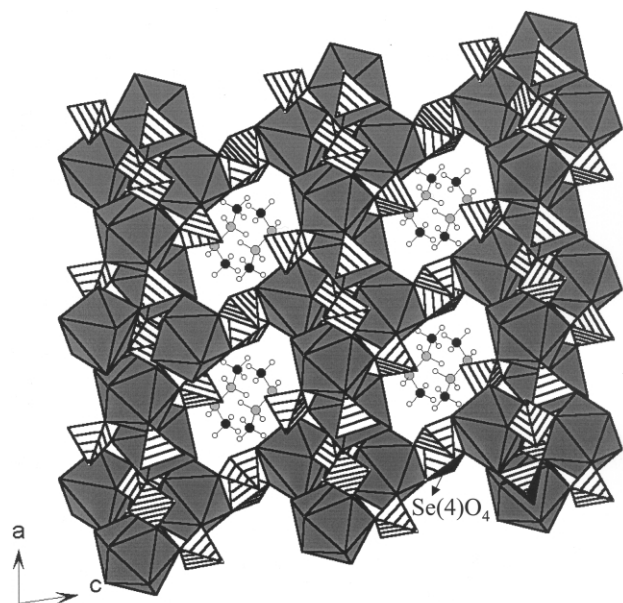


Fig. 3 Polyhedral view of the framework structure of **I** along the *b*-axis, showing 12-membered channels.

Notes and references

† *Synthesis and initial characterization*: In a typical synthesis of **I**, 0.250 g of LaCl_3 was dissolved in 1 ml of distilled water followed by the addition of 0.4 ml H_2SeO_4 (40 wt%) under continuous stirring. To this mixture, 0.2 ml of ethylenediamine was added, followed by 0.18 ml of HCl to adjust the pH to 2. The resulting gel with the molar composition $\text{LaCl}_3 \cdot 2\text{HCl} \cdot 1.5\text{H}_2\text{SeO}_4 \cdot 3\text{en} \cdot 55\text{H}_2\text{O}$ was sealed in a teflon-lined autoclave and heated at 100 °C for 120 h. The resulting colorless plate-like crystals of **I** were filtered by vacuum filtration, washed with distilled water and dried under ambient conditions. Initial characterization was carried out by powder X-ray diffraction (PXRD), energy dispersive analysis of X-rays (EDAX), thermogravimetric analysis (TGA), elemental CHN analysis and IR spectroscopy. The powder X-ray diffraction pattern was in agreement with the simulated pattern from single crystal analysis demonstrating the phase purity of the product. EDAX gave a La : Se ratio of 1 : 2 in agreement with the formula. The compound also gave satisfactory elemental analysis: Observed C 2.41%, H 1.99%, N 2.56%; Calculated C 2.44%, H 1.84%, N 2.84%. In the infrared spectrum, bands at 936, 897, and 865 cm^{-1} due to the SeO_4 units were seen.⁷ The spectrum also gave a band arising from the presence of coordinated water at 1621 cm^{-1} . Bands arising from the template cations $[\text{NH}_3(\text{CH}_2)_2\text{NH}_3]^{2+}$ were observed in the expected regions. Besides the 7.5% weight loss due to water in the range 90–160 °C, TGA showed weight loss in the 200–450 °C region due to the loss of amine and SeO_2 (obs. 18.1%, theo. 17.5%), followed by a third weight loss of rest of the selenate as SeO_2 (obs. 35.5%, theo. 41%). The final product, obtained on

heating to 900 °C, was characterized to be La_2O_3 (JCPDS file, card no: 22-0641).

‡ *Single crystal structure determination*: Single crystal data were collected on a Siemens SMART-CCD diffractometer [graphite-monochromated $\text{MoK}\alpha$ radiation, λ 0.71073 Å (*T* 298)]. An absorption correction based on symmetry-equivalent reflections was applied using SADABS.⁸ The structures were solved by direct methods using SHELXS-86⁹ and difference Fourier synthesis. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS¹⁰ package of programs. The non-hydrogen atoms were refined anisotropically.

Crystal data: $[\text{La}_2(\text{SeO}_4)_4(\text{H}_2\text{O})_3] [\text{C}_2\text{N}_2\text{H}_{10}] \cdot \text{H}_2\text{O}$, **I**, $M_r = 983.84$, triclinic, space group = $P\bar{1}$, $a = 10.0629(8)$ Å, $b = 10.4494(9)$ Å, $c = 11.1914(9)$ Å, $\alpha = 82.2070(10)^\circ$, $\beta = 78.4400(10)^\circ$, $\gamma = 63.3150(10)^\circ$, $V = 1028.7(2)$ Å³, $Z = 2$, $\rho_{\text{calc}} = 3.176$ g cm^{-3} . A total of 4340 reflections were collected in the θ range 1.86–23.27 and merged to give 2908 unique data ($R_{\text{int}} = 0.0232$) of which 2468 with $I > 2\sigma(I)$ were considered to be observed. Final $R = 0.0301$, $wR = 0.0673$ and $S = 1.02$ were obtained for 303 parameters. CCDC 228612. See <http://www.rsc.org/suppdata/cc/b4/b400120f/> for crystallographic files in .cif format.

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