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

Although metal silicates,\(^1\) phosphates\(^2\) and carboxylates\(^3\) constitute the majority of inorganic open-framework materials, metal sulfates\(^4\) and selenites\(^5\) 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 \(\text{SeO}_3^{2-}\) to \(\text{SeO}_2^{2-}\) 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, \([\text{C}_2\text{N}_2\text{H}_{10}]_2[\text{La}_2(\text{SeO}_4)_4(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}\), \(\text{I}\), 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 \(\text{LaCl}_3\) and \(\text{H}_2\text{SeO}_3\) in the presence of ethylenediamine.\(^\dagger\) The asymmetric unit of \(\text{I}\) contains 29 non-hydrogen atoms, out of which 24 belong to the inorganic framework and 5 to the protonated amine and the water molecule.\(^\ddagger\) There are two crystallographically distinct \(\text{La}\) atoms and four distinct \(\text{Se}\) atoms. Of the two \(\text{La}\) atoms, \(\text{La}(1)\) is eight-coordinated by seven \(\text{O}\) atoms from seven selenate groups and one \(\text{O}\) atom from the water ligand while \(\text{La}(2)\) is nine-coordinated by seven \(\text{O}\) atoms from six selenate groups and two \(\text{O}\) atoms from water ligands, the average \(\text{La}\)–\(\text{O}\) bond length being 2.545 and 2.569 Å respectively. The \(\text{Se}\) atoms are at the centers of tetrahedral selenate ions as expected. The \(\text{Se}\) atoms form (4 – \(n\)) \(\text{Se}\)–\(\text{O}\)–\(\text{La}\) bonds and \(n\) terminal \(\text{Se}\)–\(\text{O}\) bonds, the actual number of the latter differing from one to another. The average length of the \(\text{Se}\)–\(\text{O}\) bonds are 1.635 (\(\text{Se}\)–\(\text{O}\)–\(\text{La}\)) and 1.606 Å (terminal \(\text{Se}\)–\(\text{O}\)), with the \(\text{O}\)–\(\text{Se}\)–\(\text{O}\) bond angles in the range 103.8(3) – 115.3(4)°. Bond valence sum (BVS) calculations\(^6\) confirm the oxidation states of \(\text{La}\) and \(\text{Se}\) to be +3 and +6 respectively. The framework stoichiometry of \([\text{La}_2(\text{SeO}_4)_4(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}\), with a net framework charge of \(–2\), is balanced by the diprotonated ethylenediamine.

The complex network of \(\text{LaO}_8\), \(\text{LaO}_9\) and \(\text{SeO}_4\) 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 \(\text{La}_2\text{Se}_4\). In one, two crystallographically equivalent \(\text{La}(1)\) polyhedra are capped by four selenate ions in \(Q_2\) connectivity (Fig. 1a) and in the other, two \(\text{La}(2)\) polyhedra are both corner and edge-linked by \(\text{SeO}_4\) tetrahedra (Fig. 1b). Connectivity between these two units through \(\text{La}(1)\)–\(\text{O}\)–\(\text{La}(2)\) linkages gives rise to infinite chains along the [100] direction (Fig. 1c), which then are connected through a bridging \(\text{SeO}_4\) 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 \(\text{La}(1)\)–\(\text{O}\) 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 \(\text{Se}\)–\(\text{O}\) 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 \(\text{La}\) 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.
SeO$_4$ units were seen. The spectrum also gave a band arising from the selenate as SeO$_2$ (obs. 35.5%, theo. 41%). The final product, obtained on heating to 900 °C, was characterized to be La$_2$O$_3$ (JCPDS file, card no: 22-6041).

† Single crystal structure determination: Single crystal data were collected on a Siemens SMART-CCD diffractometer [graphite-monochromated MoK$_\alpha$ radiation, $\lambda$ 0.71073 Å (T 293 K)]. An absorption correction based on symmetry-equivalent reflections was applied using SADABS. The structures were solved by direct methods using SHELXS-86 and difference Fourier synthesis. Full-matrix least-squares structure refinement against $F^2$ was carried out using the SHELXL-PLUS package of programs. The non-hydrogen atoms were refined anisotropically.

Crystal data: [La$_2$(SeO$_4$)$_4$(H$_2$O)$_3$][C$_2$N$_2$H$_{10}$], $M_r$ = 983.84, triclinic, space group = $P1$, $a$ = 10.0629(8) Å, $b$ = 10.4494(9) Å, $c$ = 11.1914(9) Å, $\alpha$ = 82.2070(10)°, $\beta$ = 87.4400(10)°, $\gamma$ = 63.3150(10)°, $V$ = 1028.7(2) Å$^3$, $Z$ = 2, $\nu$ = 3.176 g cm$^{-3}$. A total of 4340 reflections were collected in the $\theta$ range 1.86–23.27 and merged to give 2908 unique data ($R$_{int} = 0.0232) of which 2408 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 238612. See http://www.rsc.org/suppdata/cc/b4/b400120f/ for crystallographic files in .cif format.

8 (a) G. M. Sheldrick, SADABS: Siemens Area Detector Absorption Correction program, University of Göttingen, Göttingen, Germany, 1994.
10 G. M. Sheldrick, SHELXL-PLUS Program for Crystal Structure Solution and Refinement, University of Göttingen, Göttingen, Germany.