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The Synthesis and Crystal Structure of LaHSe₂O₆, a Layered Anhydrous Selenite

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Abstract. Lanthanum hydrogenselenite, LaHSe₂O₆, $M_r = 393.83$, orthorhombic, $Pc2_1b$, $a = 7.139$ (6), $b = 19.008$ (9), $c = 8.469$ (9) Å, $V = 1149.24$ Å³, $Z = 8$, $D_x = 4.55$ g cm⁻³, $\mu = 199.7$ cm⁻¹, $\lambda(\text{Mo } K\alpha, \text{ graphite monochromator}) = 0.71073$ Å, $F(000) = 1392$, room temperature [298 (2) K]. Final $R = 3.61\%$, $wR = 4.21\%$ for 1701 observed reflections [$> 3\sigma(I)$]. LaHSe₂O₆ has been prepared using hydrothermal synthetic techniques and its crystal structure elucidated by single-crystal X-ray diffraction. This new structure consists of layers of LaO₁₀, HSeO₃ and SeO₃ polyhedra parallel to the ac plane; the layers are interconnected by Se—OH \cdots O—(Se,La) hydrogen bonds.

Introduction. Until recently there has been very little work, structural or otherwise, reported on phases containing rare-earth elements in combination with selenite (SeO₃²⁻) anions. The structures of PrH₃·(SeO₃)₂(Se₂O₅) (Koskenlinna & Valkonen, 1977), CeSe₂O₆ (Delage, Carpy, H'Naifi & Gourselle, 1986) and NaLa(SeO₃)₂ (Morris, Hriljac & Cheetham, 1990) have been reported in the recent literature, these being the only anhydrous examples to date. These phases consist of the lanthanide atom in typical high coordination to oxygen, the coordination number depending on its ionic radius {eightfold for cerium [$r(\text{Ce}^{4+}) = 1.28$ Å], ninefold for praseodymium [$r(\text{Pr}^{3+}) = 1.32$ Å] and tenfold for lanthanum [$r(\text{La}^{3+}) = 1.40$ Å]}, linked into a three-dimensional structure *via* the sharing of faces and/or edges with other Ln—O (Ln = lanthanide) poly-

hedra, and vertices with the trigonal-pyramidal SeO₃ units. This paper reports the synthesis, using hydrothermal techniques, and structure of a new layered lanthanum selenite, LaHSe₂O₆.

Experimental. LaHSe₂O₆ was prepared from lanthanum nitrate, La(NO₃)₃·9H₂O (2 g), selenium dioxide, SeO₂ (5 g), and 15 cm³ of water in a Teflon-lined steel autoclave. The autoclave was heated to 473 K for 48 h and then allowed to cool to room temperature. Colorless, plate-like crystals (maximum dimensions 3 × 1 × 0.5 mm) were recovered from the autoclave by suction filtration. A small crystal (0.5 × 0.1 × 0.05 mm) was mounted on a glass fibre using cyano-acrylate glue, and intensity data were collected on an Enraf-Nonius CAD-4 diffractometer (graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å). The unit-cell constants were determined from 25 centered reflections ($12 < \theta < 18^\circ$) and then refined by the method of least squares. 3750 intensity data were collected in the range $0 < 2\theta < 60^\circ$, using the ω - 2θ scan mode [scan width = $(1.0 + 0.35\tan\theta)^\circ$, minimum scan speed = $1.3^\circ \text{ min}^{-1}$, maximum scan speed = $6.7^\circ \text{ min}^{-1}$, $0 \leq h \leq 10$, $0 \leq k \leq 28$, $0 \leq l \leq 12$]. The systematic absences ($0kl$, l ; $hk0$, k) were consistent with the space groups $Pcmb$ (No. 57; standard setting $Pbcm$) and $Pc2_1b$ (non-standard setting of $Pca2_1$, No. 29). No model could be established in the centrosymmetric space group, and all subsequent calculations assumed the structure was noncentrosymmetric, as confirmed by the successful course of the refinement. ψ -scan data on 2 reflections

with $\chi \sim 90^\circ$ were recorded in order to apply an empirical absorption correction (minimum correction = 1.34, maximum correction = 7.12) and the raw data were prepared for structure solution and refinement using the program *RC85* (Baird, 1987), resulting in 1701 observed reflections, according to the criterion $I > 3\sigma(I)$. After the usual corrections for Lorentz and polarization effects were made, the heavy-atom positions were located from a super-sharpened Patterson function using the program *SHELXS86* (Sheldrick, 1986), and the O-atom positions were located by repeated Fourier difference syntheses following refinement of the known atom positions.

All the least-squares and subsidiary calculations were performed using the Oxford *CRYSTALS* system (Watkin, Carruthers & Betteridge, 1986) and all programs were executed on a VAX 3800 computer. The origin with respect to the polar y direction was fixed as the centroid of the structure (Waser, 1974). The last cycle of full-matrix refinement on F (1701 reflections, 164 independent parameters, final $\sigma/e.s.d. < 0.01$), including anisotropic thermal parameters for La, Se and O, converged to final agreement factors of $R = 3.61\%$, $wR = 4.21\%$ using complex neutral-atom scattering factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The weighting scheme used was that of Tukey & Prince (Carruthers & Watkin, 1979), fitted using a Chebyshev polynomial [coefficients 22 (2), -17 (2) and 16 (2)]. A final difference Fourier synthesis revealed no peaks that were refineable as the H atoms (maximum peak height = 2.0, minimum = $-1.8 e \text{ \AA}^{-3}$).

Discussion. Table 1* gives the final atomic positional and thermal parameters and Table 2 gives selected bond distances and angles for the structure. The structure of LaHSe_2O_6 (Figs. 1 and 2) consists of layers of LaO_{10} and $(\text{H})\text{SeO}_3$ groups parallel to the ac plane, these sheets being held together through hydrogen bonding. The structure contains two crystallographically independent La atoms, both of which are deca-coordinated to O in irregular geometry [ave. $\text{La}(1)\text{—O}$ distance 2.615 (3) Å, ave. $\text{La}(2)\text{—O}$ distance 2.622 (3) Å], similar to that found in $\text{NaLa}(\text{SeO}_3)_2$ [$d_{\text{ave}}(\text{La—O}) = 2.635$ (3) Å] (Morris, Hriljac & Cheetham, 1990), and four crystallographically distinct Se atoms, all of which form their characteristic pyramidal coordination with three

* Lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54917 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0356]

Table 1. Atomic positional parameters and U_{eq} values
$$U_{eq} = (U_1U_2U_3)^{1/3}.$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
La(1)	0.41902 (8)	0.4108 (1)	0.84339 (7)	0.0082
La(2)	0.91735 (8)	0.4997 (1)	0.94737 (7)	0.0082
Se(1)	0.9347 (1)	0.3586 (2)	0.6924 (1)	0.0084
Se(2)	0.4304 (1)	0.5516 (2)	1.0944 (1)	0.0089
Se(3)	0.4390 (2)	0.2601 (2)	0.6264 (2)	0.0140
Se(4)	0.9217 (2)	0.6508 (2)	1.1708 (1)	0.0144
O(1)	0.768 (1)	0.3923 (5)	0.817 (1)	0.0064
O(2)	0.863 (1)	0.3826 (6)	0.509 (1)	0.0151
O(3)	1.097 (1)	0.4293 (4)	0.715 (1)	0.0063
O(4)	0.361 (1)	0.5316 (6)	1.277 (1)	0.0161
O(5)	0.593 (1)	0.4873 (5)	1.075 (1)	0.0096
O(6)	0.264 (1)	0.5217 (5)	0.971 (1)	0.0195
O(7)	0.367 (2)	0.2751 (5)	0.811 (1)	0.0124
O(8)	0.472 (1)	0.3473 (5)	0.581 (1)	0.0110
O(9)	0.672 (2)	0.2366 (6)	0.665 (1)	0.0156
O(10)	0.983 (1)	0.5719 (5)	1.210 (1)	0.0071
O(11)	0.816 (2)	0.6383 (6)	0.998 (1)	0.0216
O(12)	1.129 (2)	0.6878 (7)	1.089 (1)	0.0300

Table 2. Bond distances (Å) and angles ($^\circ$)

La(1)—O(1)	2.528 (8)	La(1)—O(2 a)	2.51 (1)
La(1)—O(3 b)	2.571 (7)	La(1)—O(4 c)	2.84 (1)
La(1)—O(5)	2.738 (9)	La(1)—O(5 d)	2.702 (9)
La(1)—O(6)	2.61 (1)	La(1)—O(7)	2.622 (9)
La(1)—O(8)	2.55 (1)	La(1)—O(8 e)	2.477 (9)
La(2)—O(1)	2.553 (9)	La(2)—O(2 f)	2.77 (1)
La(2)—O(3)	2.702 (8)	La(2)—O(3 g)	2.632 (8)
La(2)—O(4 h)	2.53 (1)	La(2)—O(5)	2.564 (8)
La(2)—O(6 i)	2.52 (1)	La(2)—O(10)	2.658 (9)
La(2)—O(10 j)	2.533 (9)	La(2)—O(11)	2.76 (1)
Se(1)—O(1)	1.713 (8)	Se(1)—O(2)	1.697 (9)
Se(1)—O(3)	1.783 (8)		
Se(2)—O(4)	1.671 (9)	Se(2)—O(5)	1.694 (8)
Se(2)—O(6)	1.68 (1)		
Se(3)—O(7)	1.67 (1)	Se(3)—O(8)	1.717 (9)
Se(3)—O(9)	1.76 (1)		
Se(4)—O(10)	1.599 (9)	Se(4)—O(11)	1.66 (1)
Se(4)—O(12)	1.78 (1)		
O(2 a)—La(1)—O(1)	144.1 (3)	O(3 b)—La(1)—O(1)	149.9 (3)
O(3 b)—La(1)—O(2 a)	63.2 (3)	O(4 c)—La(1)—O(1)	63.2 (3)
O(4 c)—La(1)—O(2 a)	136.6 (4)	O(4 c)—La(1)—O(3 b)	107.6 (3)
O(5)—La(1)—O(1)	71.9 (3)	O(5)—La(1)—O(2 a)	94.4 (3)
O(5)—La(1)—O(3 b)	129.6 (3)	O(5)—La(1)—O(4 c)	57.3 (3)
O(5 d)—La(1)—O(1)	91.9 (3)	O(5 d)—La(1)—O(2 a)	124.1 (3)
O(5 d)—La(1)—O(3 b)	62.7 (2)	O(5 d)—La(1)—O(4 c)	54.3 (2)
O(5 d)—La(1)—O(5)	109.4 (3)	O(6)—La(1)—O(1)	124.5 (3)
O(6)—La(1)—O(2 a)	66.6 (3)	O(6)—La(1)—O(3 b)	71.7 (3)
O(6)—La(1)—O(4 c)	70.4 (3)	O(6)—La(1)—O(5)	57.9 (3)
O(7)—La(1)—O(1)	89.7 (3)	O(7)—La(1)—O(2 a)	74.6 (3)
O(7)—La(1)—O(3 b)	87.9 (3)	O(7)—La(1)—O(4 c)	148.7 (3)
O(7)—La(1)—O(5)	131.5 (3)	O(8)—La(1)—O(1)	73.3 (3)
O(8)—La(1)—O(2 a)	120.2 (3)	O(8)—La(1)—O(3 b)	80.1 (3)
O(8)—La(1)—O(4 c)	97.4 (3)	O(8)—La(1)—O(5)	143.7 (3)
O(8 e)—La(1)—O(1)	72.1 (1)	O(8 e)—La(1)—O(2 a)	72.1 (3)
O(8 e)—La(1)—O(3 b)	133.9 (3)	O(8 e)—La(1)—O(4 c)	112.3 (3)
O(8 e)—La(1)—O(5)	62.2 (3)	O(6)—La(1)—O(5 d)	84.3 (3)
O(7)—La(1)—O(5 d)	115.9 (3)	O(7)—La(1)—O(6)	140.9 (3)
O(8)—La(1)—O(5 d)	61.8 (3)	O(8)—La(1)—O(6)	143.4 (3)
O(8)—La(1)—O(7)	57.6 (3)	O(8 e)—La(1)—O(5 d)	163.4 (3)
O(8 e)—La(1)—O(6)	101.0 (3)	O(8 e)—La(1)—O(7)	69.5 (3)
O(8 e)—La(1)—O(8)	115.5 (3)		
O(2 f)—La(2)—O(1)	71.1 (3)	O(3)—La(2)—O(1)	59.1 (3)
O(3)—La(2)—O(2 f)	58.2 (3)	O(3 g)—La(2)—O(1)	87.2 (3)
O(3 g)—La(2)—O(2 f)	56.7 (2)	O(3 g)—La(2)—O(3)	113.2 (3)

Table 2 (cont.)

O(4 ^a)—La(2)—O(1)	67.5 (3)	O(4 ^a)—La(2)—O(2 ^a)	138.2 (4)
O(4 ^a)—La(2)—O(3)	94.3 (3)	O(4 ^a)—La(2)—O(3 ^a)	125.7 (3)
O(5)—La(2)—O(1)	74.5 (3)	O(5)—La(2)—O(2 ^a)	111.0 (3)
O(5)—La(2)—O(3)	133.5 (3)	O(5)—La(2)—O(3 ^a)	63.7 (2)
O(5)—La(2)—O(4 ^a)	63.4 (3)	O(6 ^a)—La(2)—O(1)	125.2 (3)
O(6 ^a)—La(2)—O(2 ^a)	64.0 (3)	O(6 ^a)—La(2)—O(3)	71.0 (3)
O(6 ^a)—La(2)—O(3 ^a)	93.0 (3)	O(6 ^a)—La(2)—O(4 ^a)	141.0 (3)
O(10)—La(2)—O(1)	148.1 (3)	O(10)—La(2)—O(2 ^a)	98.9 (3)
O(10)—La(2)—O(3)	141.4 (3)	O(10)—La(2)—O(3 ^a)	63.1 (3)
O(10)—La(2)—O(4 ^a)	119.6 (3)	O(10 ^b)—La(2)—O(1)	101.9 (3)
O(10 ^b)—La(2)—O(2 ^a)	115.2 (3)	O(10 ^b)—La(2)—O(3)	63.8 (3)
O(10 ^b)—La(2)—O(3 ^a)	165.4 (3)	O(10 ^b)—La(2)—O(4 ^a)	68.7 (3)
O(11)—La(2)—O(1)	136.1 (3)	O(11)—La(2)—O(2 ^a)	152.0 (3)
O(11)—La(2)—O(3)	135.0 (3)	O(11)—La(2)—O(3 ^a)	110.0 (3)
O(11)—La(2)—O(4 ^a)	69.8 (3)	O(6 ^a)—La(2)—O(5)	150.3 (3)
O(10)—La(2)—O(5)	81.7 (3)	O(10)—La(2)—O(6 ^a)	70.9 (3)
O(10 ^b)—La(2)—O(5)	129.4 (3)	O(10 ^b)—La(2)—O(6 ^a)	72.4 (3)
O(10 ^b)—La(2)—O(10)	109.6 (3)	O(11)—La(2)—O(5)	77.7 (3)
O(11)—La(2)—O(6 ^a)	94.9 (3)	O(11)—La(2)—O(10)	54.9 (3)
O(11)—La(2)—O(10)	71.3 (3)		
O(2)—Se(1)—O(1)	104.6 (5)	O(3)—Se(1)—O(1)	95.9 (4)
O(3)—Se(1)—O(2)	95.2 (4)		
O(5)—Se(2)—O(4)	97.6 (5)	O(6)—Se(2)—O(4)	106.8 (5)
O(6)—Se(2)—O(5)	100.3 (4)		
O(8)—Se(3)—O(7)	94.9 (5)	O(9)—Se(3)—O(7)	99.3 (6)
O(9)—Se(3)—O(8)	99.1 (5)		
O(11)—Se(4)—O(10)	100.1 (5)	O(12)—Se(4)—O(10)	103.0 (6)
O(12)—Se(4)—O(11)	95.1 (6)		

Symmetry codes (a) $1 - x, y, \frac{1}{2} + z$; (b) $-1 + x, y, z$; (c) $1 - x, y, -\frac{1}{2} + z$; (d) $2 - x, y, \frac{1}{2} + z$; (e) $1 + x, y, z$; (f) $2 - x, y, -\frac{1}{2} + z$.

O-atom neighbors. The twelve crystallographically distinct O atoms can be classified into four groups with respect to the number and types of their nearest neighbour atoms: six O atoms, O(1), O(2), O(4), O(6), O(8) and O(10), which are coordinated with two La and one Se atom each; atoms O(3) and O(5) are coordinated with three La atoms and one Se atom; atoms O(7) and O(11) bond to one La atom and one Se atom; two more atoms, O(9) and O(12), which are protonated (confirmed by bond-strength/bond-length analysis) are coordinated with an Se atom. The possible H-bonding scheme is discussed below.

The La atoms are both shifted from the centroids of their coordinating O polyhedra: La(1) by 0.15 (1) and La(2) by 0.11 (1) Å, the distortion being largely in the direction of the polar axis of the unit cell (*i.e.* the *b* axis). The program *MISSYM* (Le Page, 1988) which checks a crystallographic atomic model for 'missing' (unmodeled) symmetry, did not detect that this polyhedral asymmetry was the result of a distortion from a possible centrosymmetric prototype structure, allowing all the atoms to move up to 1 Å to assume their possible new positions. All four Se atoms exhibit the usual trigonal pyramidal geometry with an (unobserved) stereochemically active lone pair of electrons [ave. Se—O distance 1.702 (3) Å, ave. O—Se—O bond angle 99.3 (2)^o]. These values

compare satisfactorily with the average geometrical parameters [$\langle d(\text{Se—O}) \rangle = 1.709 (10) \text{ \AA}$, $\langle \theta(\text{O—Se—O}) \rangle = 100.2 (1.3)^\circ$; values in parentheses = r.m.s. deviations] derived by Hawthorne, Groat & Ercit (1987) for a large number of (H)SeO₃ species.

One La(1)O₁₀ polyhedron is linked *via* the sharing of two triangular faces with two other La(2)O₁₀ units, and with two more La(1)O₁₀ groups *via* the sharing of edges, forming an infinite layer. The layers incorporate the Se atoms in two ways: Se(1) and Se(2) share all three O-atom vertices with neighboring LaO₁₀ units, while Se(3) and Se(4) share only two of their O vertices with La atoms. The two remaining O atoms of the Se(3) and Se(4) selenite groups [O(9) and O(12), respectively] are protonated and point into the interlamellar region, and it is through these atoms that the hydrogen bonding which binds the layers together occurs. The proton positions were not located in the diffraction study, but reasonable interlayer hydrogen-bonding O...O distances include O(9)H...O(11) [$d(\text{O—O}) = 2.541 (15) \text{ \AA}$] and O(12)H...O(9) [$d(\text{O—O}) = 2.686 (15) \text{ \AA}$]. If an O—H distance of 1.0 Å, and linear O—H—O bonds between layers are assumed,

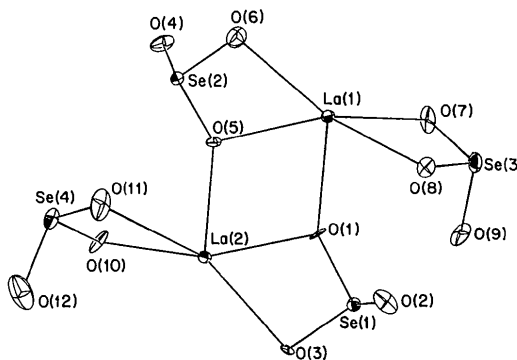


Fig. 1. Detail of the La/Se/O sheet in LaHSe₂O₆ showing the atom-labeling scheme. Thermal ellipsoids are at the 50% probability level.

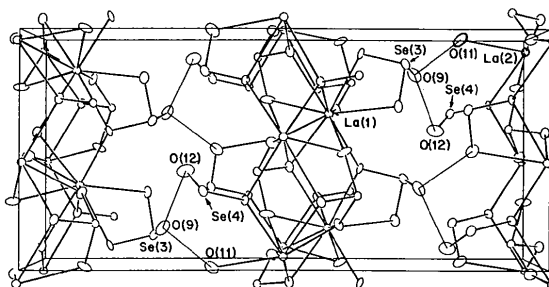


Fig. 2. Packing diagram for LaHSe₂O₆, viewed down the *a* direction, showing the proposed interlayer hydrogen-bonding scheme, indicated by thin lines.

Se—O—H angles of 106 and 118° would result from these interactions. Both these hydrogen bonds also lead to short non-bonding Se to H distances of less than 2.4 Å.

This compound is the first layered anhydrous selenite to be discovered, complementing the layered praseodymium selenite/diselenite phase $\text{PrH}_3(\text{SeO}_3)_2(\text{Se}_2\text{O}_5)$ (Koskenlinna & Valkonen, 1977), and layered hydrated selenite phases such as $\text{CaSeO}_3 \cdot \text{H}_2\text{O}$ (Hawthorne, Ercit & Groat, 1986) and the recently discovered $\text{LnHSe}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, Ln = Y, Pr—Yb (except Pm) (Morris, Harrison, Srdanov, Stucky & Cheetham, 1991). The two-dimensional structure of LaHSe_2O_6 , which is layered with respect to the polar crystallographic direction, combined with the acidic protons which must be present, leads to interesting possibilities for ion exchange and intercalation chemistry. Studies of these reactions are now being undertaken.

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The Structure of Hexaaquaaluminium(III) Bromate Trihydrate, [Al(H₂O)₆](BrO₃)₃·3H₂O

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Abstract. Hexaaquaaluminium(III) bromate trihydrate, $[\text{Al}(\text{H}_2\text{O})_6](\text{BrO}_3)_3 \cdot 3\text{H}_2\text{O}$, $M_r = 572.84$, triclinic, $P\bar{1}$, $a = 9.536$ (2), $b = 11.095$ (4), $c = 9.291$ (2) Å, $\alpha = 106.58$ (2), $\beta = 100.42$ (2), $\gamma = 113.01$ (2)°, $V = 818.1$ (4) Å³, $Z = 2$, $D_x = 2.33$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 74.58$ cm⁻¹, $F(000) = 560$, $T = 296$ K, $R = 0.050$ for 3777 unique reflections having $I > \sigma_I$. The single type of Al ion is coordinated by six inequivalent water O atoms which form a slightly distorted octahedron. The average Al—O distance within the octahedron is 1.872 (11) Å. Each of the three inequivalent bromate groups has three inequivalent O atoms. The average Br—O distances and O—Br—O angles for these ions are: 1.652 (25) Å and 104.1 (17)° for Br(1)O₃; 1.650 (9) Å and 104.4 (18)° for Br(2)O₃; 1.643 (9) Å

and 103.6 (14)° for Br(3)O₃. The aluminium—oxygen complex conformed to rigid-body behavior but the bromate groups did not. Corrected for rigid-body motion, the average Al—O distance becomes 1.880 (10) Å. Least-squares refinement of the positional parameters of the 18 inequivalent H atoms permitted a detailed analysis of the hydrogen bonding.

Introduction. Continuing interest in structures of simple hydrated oxyhalogen salts led to the present study of hydrated aluminium bromate. As in our previous studies, it was of particular interest to refine H-atom coordinates in order to carry out a detailed analysis of the hydrogen bonding.

Experimental. Metathetical reaction of aqueous solutions of $\text{Al}_2(\text{SO}_4)_3$ (Aldrich Chemical Company) and

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