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*Acta Cryst.* (1994). C**50**, 1384–1386

# $Sm(HSeO_3)(SeO_3).2H_2O$

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(*Received* 20 *December* 1993; *accepted* 2 *March* 1994)

## Abstract

The structure of samarium hydrogenselenite selenite dihydrate is characterized by layers parallel to the *xy* plane consisting of $SmO_8$ polyhedra linked by selenite and hydrogenselenite ions. A selenite ion links one Sm atom to three other Sm atoms while the hydrogenselenite ion acts as a monodentate bridging ligand to two Sm atoms. The layers are held together by hydrogen bonds and van der Waals forces. The coordination polyhedron of Sm is a distorted square antiprism.

## Comment

Several different crystalline phases in the system Ln–$SeO_2$ (where Ln is a lanthanide) have been structurally characterized. The unit-cell parameters and powder diffraction data for a compound with the formula $LnH(SeO_3)_2.2.5H_2O$ have been reported previously (Immonen, Koskenlinna, Niinistö & Pakkanen, 1976). Several single-crystal structures of this type of compound, *e.g.* $PrH_3(SeO_3)_2(Se_2O_5)$ (Koskenlinna & Valkonen, 1977*a*), $Sc(HSeO_3)_3$ (Valkonen & Leskelä, 1978), $CeSe_2O_6$ (Delage, Carpy, H'Naïfi & Goursolle, 1986) and $LaHSe_2O_6$ (Morris, Harrison, Stucky & Cheetham, 1992), or with an alkali metal added to the system, *e.g.* $NaLa(SeO_3)_2$ (Morris, Hriljac & Cheetham, 1990), have been reported also. In addition, anions other than selenite can be incorporated in the structures as in the compounds $Y(Se_2O_5)NO_3.3H_2O$ (Valkonen & Ylinen, 1979) and $Er(SeO_3)(SeO_4).0.5H_2O$ (Morris, Wilkinson & Cheetham, 1992). The structure of the title compound has remained unsolved until now because of the severe twinning and multiple twinning of the crystals. The tendency for the crystals to be twinned may be the reason why the unit cell reported here differs from that reported earlier (Immonen, Koskenlinna, Niinistö & Pakkanen, 1976).

The title compound contains both selenite and hydrogenselenite ions. The bond distances in the selenite ion [1.680 (13)–1.717 (14) Å] are normal compared to those in other lanthanide selenites. The hydrogenselenite ion has one elongated Se—O bond [1.75 (2) Å] due to the bonded H atom. This bond is slightly shorter in the title compound than that in $LaHSe_2O_6$ (1.783 Å; Morris, Harrison, Stucky & Cheetham, 1992) or in $PrH_3(SeO_3)_2(Se_2O_5)$ (Koskenlinna & Valkonen, 1977*a*), in which they vary between 1.766 and 1.805 Å.

The hydrogenselenite ion acts as a bridge between two Sm atoms. The selenite ion bridges four Sm atoms through monodentate coordination by O6 to one Sm atom, bidentate coordination by O1 and O5 to a second Sm atom and the coordination of O1 and O5 to two other Sm atoms. Thus the three-coordinate O atoms O1 and O5 are bonded to Se1 and two Sm atoms. Each $OSeSm_2$ group is tetrahedral in shape with an O atom at the apex. The angles Sm–HO–Se vary between 100.2 (6) and 132.9 (7)° for O5 and 101.8 (7) and 136.4 (8)° for O1. Three-coordinate O atoms are not uncommon in selenite compounds and are found in the structures of $PrH_3(SeO_3)_2(Se_2O_5)$ (Koskenlinna & Valkonen, 1977*a*), $LaHSe_2O_6$ (Morris, Harrison, Stucky & Cheetham, 1992), $MnSeO_3.D_2O$ (Koskenlinna & Valkonen, 1977*b*) and $Ag_2SeO_3$ (Okkonen, Hiltunen, Koskenlinna & Niinistö, 1994). In $MnSeO_3.D_2O$ (Koskenlinna

*Acta Crystallographica Section C*
ISSN 0108-2701 ©1994

& Valkonen, 1977*b*) the Mn—O—Se angles vary between 97.9 and 125.0°.

The structure of the title compound consists of $SmO_8$ coordination polyhedra arranged in layers parallel to the *xy* plane. Se1 connects a group of three polyhedra to one polyhedron in the *x* direction. The hydrogenselenite ion connects Sm atoms in the *y* direction. The O atoms in each $SmO_8$ coordination polyhedron belong to five selenite ions, two hydrogenselenite ions and one water molecule. The Sm coordination polyhedron is a distorted square antiprism, the Sm—O bond lengths being normal for eight-coordinate samarium.

The second water molecule of crystallization is situated in the cavity between the layers of $SmO_8$ polyhedra and Se1 atoms and is connected to O7 [2.69 (2) Å] and O6 (at $x+\frac{1}{2}$, $\frac{1}{2}-y$, $-z$) [2.87 (2) Å]. The half water molecule observed by chemical analysis of the powder samples could not be located in the single-crystal structure.

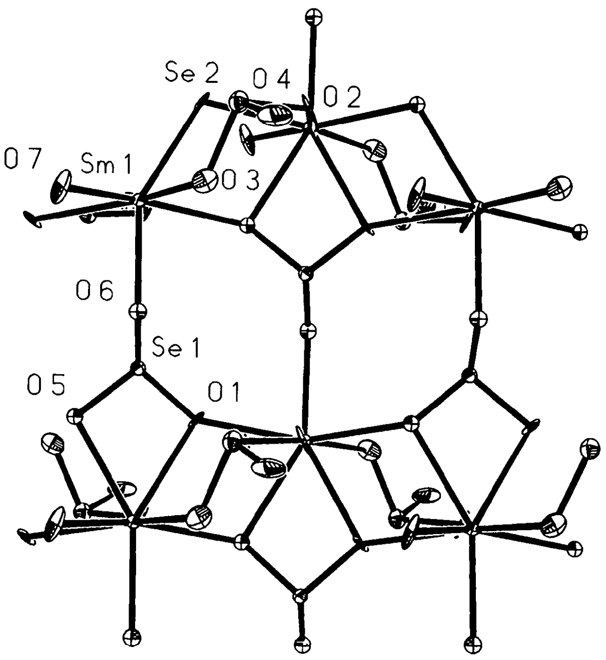

Fig. 1. O5 and O6 were refined isotropically. The H atoms and O8 are omitted for clarity.

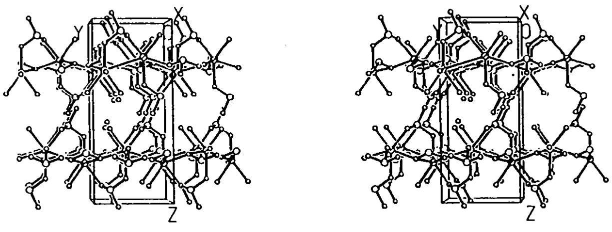

Fig. 2. A stereoview of the structure viewed along **a**.

## Experimental

The title compound can be crystallized from aqueous solutions of $SeO_2$ and $SmCl_3$ within a wide range of concentration (0.1–1.0 *M*) and stoichiometric ratios (Sm:$SeO_2$ between 1:1 to 1:4). The crystals thus obtained are always very small and display severe twinning and multiple twinning. In order to avoid twinning the crystallization was performed in a long narrow tube by pouring a layer of 0.1 *M* $H_2SeO_3$ solution onto a 0.1 *M* $SmCl_3$ solution and carefully avoiding the mixing of the layers. After a few days at room temperature tiny needle-shaped crystals precipitated. These were washed with water, ethanol and ether. After several attempts a small single crystal suitable for data collection was obtained.

*Crystal data*

$Sm(HSeO_3)(SeO_3).2H_2O$
$M_r = 441.31$
Orthorhombic
$P2_12_12_1$
$a = 6.6670\ (10)$ Å
$b = 7.0310\ (10)$ Å
$c = 16.426\ (3)$ Å
$V = 770.0\ (2)$ Å$^3$
$Z = 4$
$D_x = 3.807$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–$15°$
$\mu = 17.083$ mm$^{-1}$
$T = 293\ (2)$ K
Transparent needle
0.175 × 0.030 × 0.025 mm
Colourless

*Data collection*

Rigaku AFC-7*S* diffractometer
$\omega$–$2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.755$, $T_{max} = 1.000$
953 measured reflections
953 independent reflections
730 observed reflections [$I > 2\sigma(I)$]

$\theta_{max} = 26.50°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 20$
3 standard reflections monitored every 200 reflections
intensity variation: none

*Refinement*

Refinement on $F^2$
$R(F) = 0.0456$
$wR(F^2) = 0.0926$
$S = 1.063$
953 reflections
93 parameters
H-atom positions refined using a riding model with $U$(H) = 1.5 × $U$ of atom to which it is bonded
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0358P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$\Delta\rho_{max} = 2.433$ e Å$^{-3}$ (near Sm)
$\Delta\rho_{min} = -1.503$ e Å$^{-3}$
Extinction correction: none
Atomic scattering factors, dispersion corrections and absorption coefficients from *International Tables for Crystallography* (1992, Vol. C, Tables 6.1.1.4, 4.2.6.8 and 4.2.4.2, respectively)
Absolute configuration: Flack (1983)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å$^2$)

$U_{\rm iso}$ for O5 and O6; $U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all others.

| | $x$ | $y$ | $z$ | $U_{\rm eq}/U_{\rm iso}$ |
|---|---|---|---|---|
| Sm1 | 0.8739 (2) | 0.1095 (2) | 0.78517 (7) | 0.0098 (3) |
| Se1 | 0.3451 (3) | 0.1143 (3) | 0.72696 (12) | 0.0113 (4) |
| Se2 | 1.1459 (3) | −0.1895 (3) | 0.92008 (13) | 0.0157 (5) |
| O1 | 0.189 (2) | −0.065 (2) | 0.7564 (9) | 0.017 (4) |
| O2 | 1.146 (2) | −0.387 (2) | 0.8606 (8) | 0.021 (3) |
| O3 | 0.917 (2) | −0.096 (3) | 0.9019 (9) | 0.022 (4) |
| O4 | 1.085 (2) | −0.295 (3) | 1.0135 (9) | 0.028 (4) |
| O5 | 0.192 (2) | 0.293 (2) | 0.7619 (8) | 0.011 (3) |
| O6 | 0.5240 (18) | 0.105 (2) | 0.7989 (8) | 0.013 (3) |
| O7 | 0.890 (3) | 0.307 (2) | 0.9049 (10) | 0.031 (4) |
| O8 | 0.889 (3) | 0.190 (3) | 1.0607 (10) | 0.051 (6) |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| Sm1—O6 | 2.344 (12) | Sm1—O5$^{\rm iii}$ | 2.396 (14) |
| Sm1—O2$^{\rm i}$ | 2.398 (14) | Sm1—O7 | 2.41 (2) |
| Sm1—O3 | 2.42 (2) | Sm1—O1$^{\rm iv}$ | 2.423 (14) |
| Sm1—O1$^{\rm ii}$ | 2.479 (15) | Sm1—O5$^{\rm ii}$ | 2.513 (14) |
| Sm1···Sm1$^{\rm i}$ | 4.0647 (12) | O6—O8$^{\rm v}$ | 2.87 (2) |
| O7—O8 | 2.69 (2) | Se1—O6 | 1.680 (13) |
| Se1—O1 | 1.706 (14) | Se1—O5 | 1.717 (14) |
| Se2—O3 | 1.69 (2) | Se2—O2 | 1.70 (2) |
| Se2—O4 | 1.75 (2) | | |
| O6—Sm1—O5$^{\rm iii}$ | 80.5 (5) | O6—Sm1—O2$^{\rm i}$ | 92.4 (5) |
| O5$^{\rm iii}$—Sm1—O2$^{\rm i}$ | 71.3 (5) | O6—Sm1—O7 | 88.5 (6) |
| O5$^{\rm iii}$—Sm1—O7 | 143.7 (5) | O2$^{\rm i}$—Sm1—O7 | 144.1 (5) |
| O6—Sm1—O3 | 91.9 (5) | O5$^{\rm iii}$—Sm1—O3 | 73.9 (5) |
| O2$^{\rm i}$—Sm1—O3 | 143.6 (5) | O7—Sm1—O3 | 72.1 (5) |
| O6—Sm1—O1$^{\rm iv}$ | 82.5 (5) | O5$^{\rm iii}$—Sm1—O1$^{\rm iv}$ | 138.9 (5) |
| O2$^{\rm i}$—Sm1—O1$^{\rm ii}$ | 82.1 (5) | O7—Sm1—O1$^{\rm ii}$ | 113.8 (6) |
| O1$^{\rm iv}$—Sm1—O1$^{\rm ii}$ | 124.1 (4) | O5$^{\rm iii}$—Sm1—O5$^{\rm ii}$ | 125.7 (3) |
| O2$^{\rm i}$—Sm1—O5$^{\rm ii}$ | 83.6 (5) | O7—Sm1—O5$^{\rm ii}$ | 77.9 (5) |
| O3—Sm1—O5$^{\rm ii}$ | 109.1 (5) | Sm1$^{\rm iii}$—O1—Sm1$^{\rm vi}$ | 112.0 (5) |
| Sm1$^{\rm iv}$—O5—Sm1$^{\rm vi}$ | 111.8 (5) | Se1—O1—Sm1$^{\rm iii}$ | 136.4 (8) |
| Se1—O1—Sm1$^{\rm vi}$ | 101.8 (7) | Se2—O2—Sm1$^{\rm vii}$ | 125.8 (7) |
| Se2—O3—Sm1 | 118.7 (7) | Se1—O5—Sm1$^{\rm iv}$ | 132.9 (7) |
| Se1—O5—Sm1$^{\rm vi}$ | 100.2 (6) | Se1—O6—Sm1 | 129.7 (7) |
| O6—Se1—O1 | 101.7 (7) | O6—Se1—O5 | 102.5 (7) |
| O1—Se1—O5 | 94.9 (6) | O3—Se2—O2 | 102.5 (8) |
| O3—Se2—O4 | 96.2 (7) | O2—Se2—O4 | 99.3 (8) |

Symmetry codes: (i) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $1+x, y, z$; (iii) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iv) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (v) $x-\frac{1}{2}, \frac{1}{2}-y, 2-z$; (vi) $x-1, y, z$; (vii) $2-x, y-\frac{1}{2}, \frac{3}{2}-z$.

Data collection and cell refinement: Rigaku AFC-7 software. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SIR*92 (Burla *et al.*, 1992). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1994). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1078). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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