INORGANIC COMPOUNDS

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Neodymium Diselenite Selenious Acid Dihydrate: Structure and Conformation of the Se_2O_5 Group

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Abstract

The title compound, $Nd_2(Se_2O_5)_3.H_2SeO_3.2H_2O$, is a new rare earth hydrogen selenite. Its crystal structure is built up of polar layers parallel to the *ab* plane. Each layer is formed by edge-sharing NdO_9 polyhedra and bridging diselenite groups. Selenious acid and water molecules occur on only one side of the layer. The other side contains flanking diselenite groups only. A complex network of hydrogen bonds holds the layers together. The configuration of Se_2O_5 is defined and compared with the diselenite moieties of related compounds.

Comment

In the course of a study of the ternary system Nd_2O_3–Se_2O_3–H_2O at 373 K and different concentrations of selenious acid, we established the existence of three crystalline phases by X-ray diffraction. The phase formed above 80% H_2SeO_3 has lattice parameters (determined on a CAD-4 diffractometer) a = 12.933 (2), b = 7.334 (3), c = 10.811 (1) Å and β = 91.68 (4)°, and is isostructural with the monoclinic compound $PrH_3(SeO_3)_2.(Se_2O_5)$ (Koskenlinna & Valkonen, 1977*a*). A compound isostructural with $SmH(SeO_3)_2.2H_2O$ (Koskenlinna *et al.*, 1994) crystallizes at H_2SeO_3 concentrations below 20%. Its lattice parameters, refined from a powder pattern, are a = 6.718 (1), b = 7.096 (1) and c = 16.460 (2) Å (PDF 46-450; International Centre for Diffraction Data, 1996). In the intermediate concentration area, we established the presence of a previously unknown phase with the chemical composition $Nd_2(Se_2O_5)_3.H_2SeO_3.2H_2O$. The present paper outlines the crystal structure of this interesting new phase and reviews the geometry of the diselenite group in various compounds.

The new rare earth selenite is built up of polar layers parallel to the *ab* plane (Fig. 1). The inner part of the layer consists of edge-sharing pairs of NdO_9 polyhedra, oriented along the *c* axis, and bridging diselenite groups. The layer is 'decorated' by selenious acid and water molecules on one side and flanking diselenite groups on the other side. The layers are held together by an extensive network of hydrogen bonds.

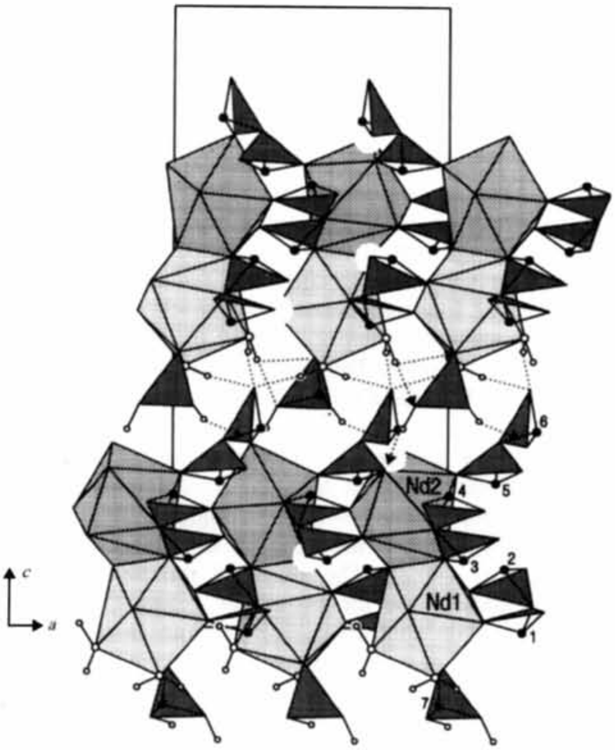

Fig. 1. Projection of the structure down the *b* axis showing the layer organization. Nd1 and Nd2 polyhedra are shaded. The SeO_3 pyramids are symbolized by dark O_3-base triangles and numbered Se apices. Hydrogen bonds are drawn as dotted lines.

Each of the two crystallographically non-equivalent Nd atoms has a tricapped trigonal prismatic environment. The Nd1 polyhedron is formed by six O atoms from diselenite groups, one from selenious acid and two from water molecules, and has almost regular geometry, with Nd—O distances varying between 2.417 (5) and 2.475 (6) Å in the trigonal bases, and between 2.542 (5) and 2.669 (6) Å for the capping atoms. The more distorted Nd2 polyhedron is built up of diselenite O atoms only; the corresponding Nd—O distances vary between 2.395 (5) and 2.523 (5) Å, and 2.537 (5) and 2.914 (6) Å, respectively. The common edge of the two polyhedra is formed by atoms O22 and O32. The Nd1···Nd2 distance in the Nd_2O_{16} bipolyhedron is 4.32 (2) Å and the angles $O22^{ii}$—Nd1—$O32^{iii}$ and $O22^{ii}$—Nd2—$O32^{iii}$ are 62.2 (2) and 61.5 (2)°, respectively (Table 1).

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The pyramidal SeO_3 parts of the diselenite groups have regular geometries, similar to those in YNO_3-$(Se_2O_5).3H_2O$ (Valkonen & Ylinen, 1979), PrH_3-$(SeO_3)_2.Se_2O_5$ (Koskenlinna & Valkonen, 1977*a*), $MnH(SeO_3).Se_2O_5$ (Koskenlinna & Valkonen, 1977*b*) and $CdSe_2O_5$ (Valkonen, 1994). The distances between Se and the central O atom vary between 1.805 (6) and 1.852 (5) Å, and are longer than those between Se and the terminal O atoms [1.635 (6)–1.679 (5) Å]. The Se_2O_5 groups of most of the diselenites investigated previously coordinate without use of their central O atom. There are only two previously known compounds, $PrH_3(SeO_3)_2.Se_2O_5$ and $CuSe_2O_5$ (Meunier *et al.*, 1976), in which the diselenite groups are pentadentate. In the present neodymium diselenite, two of the diselenite groups, *i.e.* O_2Se1–O–$Se2O_2$ and O_2Se3–O–$Se4O_2$, also act as pentadentate ligands; both play a similar structural role. They form six-membered Nd–$(OSe)_2$–O rings typical for inorganic diselenites. Additional coordination of the common O atom leads to the formation of four-membered Nd–$(O)_2$–Se rings. Similar four-membered rings occur only in the structure of $PrH_3(SeO_3)_2(Se_2O_5)$. The third 'decorating' diselenite group, O_2Se5–O–$Se6O_2$, is the first example of a tridentate ligand.

Analysis of the Se_2O_5 moiety in several inorganic diselenites shows that it has two rigid fragments: the SeO_3 pyramid and the Se—O—Se angle, of about 121°. The only exception is the structure of $CdSe_2O_5$, where this angle is 140.3°. The shape of the Se_2O_5 group differs mainly in the torsion angles τ and τ' (defined in Fig. 2). The conformational freedom is illustrated in Table 3 for several compounds. The angles τ and τ' are such that $|\tau| \geq |\tau'|$. The total skewness of the Se_2O_5 group is denoted by $|\tau + \tau'|$. For the first four compounds (Table 3), in which the diselenite groups do not form six-membered rings, the τ sum has values in the range 289.1–340°. For the diselenite groups forming six-membered rings, this value decreases and falls close to zero in $CuSe_2O_5$ (Meunier *et al.*, 1976), where two such rings are formed.

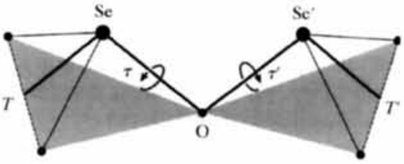

Fig. 2. Definition of the torsion angles describing the conformation of the diselenite group. *T* and *T′* are the midpoints between the terminal O atoms.

Experimental

Light-violet tabular crystals of the title compound were prepared from 2 g of Nd_2O_3 and 50 ml of a 57.5% solution of H_2SeO_3 by tempering in an evacuated glass ampoule at 373 K for a month.

Table 1. *Selected geometric parameters (Å, °)*

Nd1—O11	2.417 (5)	Se1—O13	1.819 (5)
Nd1—O12^{i}	2.436 (6)	Se2—O21	1.661 (6)
Nd1—O21	2.449 (6)	Se2—O22	1.676 (5)
Nd1—O71	2.468 (6)	Se2—O13	1.845 (5)
Nd1—O22^{ii}	2.474 (5)	Se3—O31	1.666 (5)
Nd1—O*W*2	2.475 (6)	Se3—O32	1.679 (5)
Nd1—O32^{iii}	2.542 (5)	Se3—O33	1.852 (5)
Nd1—O*W*1	2.588 (6)	Se4—O42	1.655 (6)
Nd1—O13^{ii}	2.669 (6)	Se4—O41	1.657 (5)
Nd2—O31^{ii}	2.395 (5)	Se4—O33	1.805 (6)
Nd2—O42	2.409 (5)	Se5—O51	1.659 (6)
Nd2—O51	2.440 (6)	Se5—O52	1.675 (5)
Nd2—O41^{ii}	2.452 (5)	Se5—O53	1.824 (6)
Nd2—O52^{i}	2.465 (5)	Se6—O62	1.650 (6)
Nd2—O32^{iii}	2.523 (5)	Se6—O61	1.665 (6)
Nd2—O22^{ii}	2.537 (5)	Se6—O53	1.824 (6)
Nd2—O61^{ii}	2.603 (6)	Se7—O71	1.636 (6)
Nd2—O33^{iii}	2.914 (6)	Se7—O73	1.733 (7)
Se1—O12	1.635 (6)	Se7—O72	1.736 (7)
Se1—O11	1.673 (5)		
O12—Se1—O11	103.5 (3)	O51—Se5—O52	105.1 (3)
O12—Se1—O13	99.7 (3)	O51—Se5—O53	95.4 (3)
O11—Se1—O13	98.7 (3)	O52—Se5—O53	98.5 (3)
O21—Se2—O22	103.1 (3)	O62—Se6—O61	105.5 (3)
O21—Se2—O13	100.9 (3)	O62—Se6—O53	96.7 (3)
O22—Se2—O13	88.2 (2)	O61—Se6—O53	99.4 (3)
O31—Se3—O32	100.2 (3)	O71—Se7—O73	96.5 (3)
O31—Se3—O33	102.0 (3)	O71—Se7—O72	100.7 (3)
O32—Se3—O33	90.7 (3)	O73—Se7—O72	95.0 (4)
O42—Se4—O41	104.5 (3)	Se1—O13—Se2	121.6 (3)
O42—Se4—O33	98.9 (3)	Se4—O33—Se3	122.7 (3)
O41—Se4—O33	101.8 (3)	Se5—O53—Se6	120.1 (3)

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

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O72—H72···O61^{i}	0.87	1.84	2.705 (9)	178.7
O73—H73···O52^{ii}	1.00	1.71	2.703 (8)	177.6
O*W*1—H*W*11···O62^{iii}	0.92	2.04	2.933 (9)	162.3
O*W*1—H*W*12···O62^{iv}	0.98	1.97	2.928 (8)	165.9
O*W*2—H*W*21···O73^{v}	0.95	2.11	3.031 (10)	160.9
O*W*2—H*W*21···O71^{v}	0.95	2.41	2.999 (9)	119.4
O*W*2—H*W*22···O62^{iv}	0.95	1.94	2.770 (9)	145.2

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

Crystal data

$Nd_2(Se_2O_5)_3.H_2SeO_3.2H_2O$
$M_r = 1167.25$
Orthorhombic
$Pna2_1$
$a = 10.665\ (5)$ Å
$b = 7.219\ (2)$ Å
$c = 23.662\ (3)$ Å
$V = 1821.8\ (10)$ Å^3
$Z = 4$
$D_x = 4.256$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 22 reflections
$\theta = 20.49$–$21.65°$
$\mu = 19.722$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.13 × 0.13 × 0.06 mm
Violet

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: Gaussian (*ABSORB*; DeTitta, 1985)
$T_{\min} = 0.075$, $T_{\max} = 0.255$

4057 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.050$
$\theta_{\max} = 27.91°$
$h = 0 \rightarrow 14$
$k = -9 \rightarrow 9$
$l = -31 \rightarrow 31$

Table 3. *Geometric parameters of various diselenite groups (Å, °)*

	Se—O	Se′—O	Se···Se′	Se—O—Se′	τ	τ'	$\lvert\tau+\tau'\rvert$
SeO_2[a]	1.786	1.786	3.154	124.0	170.0	170.0	340.0
$CaSe_2O_5$[b]	1.801	1.857	3.232	124.2	−164.4	−152.8	317.2
$Au(SeO_3)_2.(Se_2O_5)$[c]	1.823	1.823	3.080	115.3	−144.7	−144.7	289.4
$Se(5/6)_2O_5$[d]	1.824 (6)	1.824 (6)	3.160 (1)	120.1 (3)	−151.0 (3)	−112.0 (3)	263.0
$ZnSe_2O_5$[e]	1.827	1.827	3.191	121.6	−83.1	−83.1	166.2
$MnSe_2O_5$[f]	1.830	1.830	3.195	121.6	−83.1	−83.1	166.2
$YNO_3(Se_2O_5).3H_2O$[g]	1.844	1.816	3.240	124.5	88.4	73.9	162.1
$Se(1/2)_2O_5$[c]	1.819 (5)	1.845 (5)	3.199 (1)	121.6 (3)	119.3 (3)	37.1 (4)	156.4
$PrH_3(SeO_3)_2.(Se_2O_5)$[h]	1.848	1.834	3.248	123.8	103.8	55.3	159.1
$CdSe_2O_5$[i]	1.800	1.800	3.387	140.3	74.4	74.4	148.8
$VOSe_2O$[j]	1.768	1.822	3.104	119.6	145.1	−10.1	135.0
$(NH_4)Se_2O_5$[k]	1.814	1.843	3.164	119.7	−136.1	26.8	109.3
$PbSe_2O_5$[l]	1.844	1.828	3.130	117.0	−131.4	42.4	89.0
$MnH(SeO_3).(Se_2O_5)$[m]	1.803	1.782	3.200	126.4	−71.3	1.4	69.9
$Se(3/4)_2O_5$[c]	1.852 (5)	1.805 (6)	3.209 (1)	122.7 (3)	71.3 (4)	−33.0 (3)	38.3
$CuSe_2O_5$[n]	1.830	1.830	3.209	122.4	0.5	0.5	1.0

References: (*a*) Wyckoff (1965); (*b*) Delage *et al.* (1982); (*c*) Jones *et al.* (1981); (*d*) this work; (*e*) Meunier & Bertaud (1974); (*f*) Koskenlinna *et al.* (1976); (*g*) Valkonen & Ylinen (1979); (*h*) Koskenlinna & Valkonen (1977*a*); (*i*) Valkonen (1994); (*j*) Meunier *et al.* (1974); (*k*) Chomnilpan (1980); (*l*) Koskenlinna & Valkonen (1995); (*m*) Koskenlinna & Valkonen (1977*b*); (*n*) Meunier *et al.* (1976).

8562 measured reflections
4380 independent reflections
(includes Friedel pairs)

3 standard reflections
frequency: 120 min
intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.071$
$S = 0.897$
4380 reflections
263 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.05$ e Å^{-3}
$\Delta\rho_{\min} = -1.23$ e Å^{-3}

Extinction correction:
*SHELXL*97 (Sheldrick, 1997)
Extinction coefficient:
0.00373 (13)
Scattering factors from
International Tables for Crystallography (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.022 (14)

The least-squares refinement with anisotropic displacement parameters for the non-H atoms led to $R = 0.035$ and $wR = 0.045$. At this point, the bond-valence sums around the selenite O atoms were calculated using the program *BROWN* (Macíček, 1989; unpublished). The sums of the bond valences around the selenite O72 and O73 atoms were 1.262 and 1.295, respectively, which indicated unambiguously that these atoms were bonded to H atoms. The subsequent difference Fourier calculations supported this finding. Although the water H atoms could not be located, the geometry of the *OW* environment allowed us to predict the positions of the H atoms. All H atoms were further refined as riding atoms with fixed $U_{\rm iso} = 0.0500$ Å^2.

Data collection: *CAD*-4 *Users Manual* (Enraf–Nonius, 1988). Data reduction: *DATARED* (Vassilev, 1997; unpublished). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, 1992; unpublished).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1466). Services for accessing these data are described at the back of the journal.

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