The Crystal Structure of $PrH_3(SeO_3)_2(Se_2O_5)$, a Compound with Selenite and Diselenite Groups

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The crystal structure of praseodymium trihydrogen biselenite diselenite, $PrH_3(SeO_3)_2$ (Se_2O_5), has been determined by X-ray methods. The compound crystallizes in the monoclinic space group $P2_1/c$ with $Z=4$. The cell dimensions are $a=12.933(3)$, $b=7.334(2)$, $c=10.811(2)$ Å and $\beta=91.68(1)°$. The structure was solved by direct methods and refined to $R=0.054$.

The compound consists of a two-layered structure parallel to the bc plane in which the diselenite and one of the two non-equivalent selenite groups join the praseodymium atoms into an infinite two-dimensional network. Six diselenite and three selenite O atoms are coordinated to each Pr. Two of the diselenite oxygens around a praseodymium are three-coordinated: one is bonded to one Pr and two Se atoms and the other to one Se and two Pr atoms.

During the crystallization experiments with the isomorphous series $LnH(SeO_3)_2.2\frac{1}{2}H_2O$,[1] tabular crystals containing the lanthanoid and selenium in the molar ratio 1:4 were formed by La and Pr in concentrated solutions of selenous acid. The combination of analytical data leads to two possible formulae for the praseodymium compound, namely $Pr_2(Se_2O_5)_3$.- $2H_2SeO_3.H_2O$ and $PrH_3(SeO_3)_2(Se_2O_5)$. A structure determination was initiated to obtain more information on the structural aspects of the compound not previously reported in the literature.

EXPERIMENTAL

Preparation of the compound. The compound was crystallized from 0.1 g of praseodymium hydrogenselenite, prepared as described in Ref. 1, $0.3-0.4$ g of SeO_2 and $0.5-0.6$ g of H_2O. The mixture was kept in an ampoule at

$120-130$ °C for $2-4$ days, during which time, green, tabular crystals were formed. This method of preparation applied to neodymium did not yield the corresponding compound while lanthanum, under these same conditions, formed isomorphous crystals.

Crystal data. Praseodymium trihydrogen biselenite diselenite, $PrH_3 (SeO_3)_2(Se_2O_5)$, M.W. $=635.73$.

Space group $P2_1/c$ (No. 14)
$a=12.933(3)$ Å $b=7.334(2)$ Å $c=10.811(2)$ Å
$\beta=91.68(1)°$ $V=1025.0$ Å³
$Z=4$ $D_{calc}=4.12$ g/cm³
$\mu(MoK\alpha)=188.6$ cm⁻¹

Structure analysis. The X-ray measurements were carried out with a Syntex P2₁ (Fortran-version) automatic diffractometer using the $\theta/2\theta$ scanning technique and graphite mono-chromatized $MoK\alpha$ radiation. The size of the mounted crystal was $0.3 \times 0.3 \times 0.1$ mm. The scan speed was 1°/min, and the intensity data were collected in the interval $5° < 2\theta < 60°$. The cell dimensions were determined from 14 reflections measured with the diffractometer at 25 °C. The space group was determined to be $P2_1/c$ according to systematic absences in the original intensity data. Reflections for which the net count was greater than four times the respective standard deviation were accepted as observed. With this criterion a total of 1517 independent reflections were obtained.

Absorption correction was made from the ϕ-scan data, after which the Lorentz and polarization corrections were carried out. The positions of the Pr and Se atoms were obtained by direct methods with the computer programs of the X-ray 1976 package;[2] the atomic scattering factors were taken from the International Tables.[3] After four cycles of refinement the value of R was 15.1 %. All the oxygens appeared in the difference Fourier map, and the structure was refined using isotropic temperature factors to an R value of 7.0 %. Final atomic parameters and anisotropic temperature factors were then

Table 1. Atomic coordinates and anisotropic temperature parameters U_{ij} (Å²) in the form exp[$-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})$] with estimated deviations. The values of U_{ij} are multiplied by 10⁴.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pr	0.3374(1)	0.9539(1)	0.4487(1)	90(1)	104(4)	74(5)	−10(4)	15(4)	−2(5)
Se1	0.7413(1)	0.0362(3)	0.2115(2)	91(8)	115(9)	134(9)	−13(7)	−1(8)	13(9)
Se2	0.0501(2)	0.9731(3)	0.3467(2)	119(8)	150(10)	208(11)	−27(8)	44(8)	−6(9)
Se3	0.7090(1)	0.5684(3)	0.3922(2)	108(8)	140(9)	97(9)	−16(8)	16(7)	−5(9)
Se4	0.4882(1)	0.8067(3)	0.1706(2)	91(8)	105(8)	106(9)	−16(7)	41(8)	−19(8)
O1	0.7671(11)	0.0799(26)	0.3593(15)	86(65)	404(105)	256(87)	−12(68)	1(65)	129(84)
O2	0.8550(12)	0.9104(22)	0.1842(18)	182(75)	145(77)	555(120)	16(65)	70(82)	−150(84)
O3	0.2209(12)	0.7229(22)	0.3604(16)	162(70)	192(81)	292(89)	−18(63)	50(68)	−136(76)
O4	0.0366(10)	0.6426(23)	0.1040(16)	52(60)	278(87)	319(95)	−6(61)	20(67)	4(79)
O5	0.1546(10)	0.0737(21)	0.3982(16)	62(58)	163(75)	394(97)	35(57)	−105(66)	40(77)
O6	0.0589(14)	0.0458(26)	0.1879(16)	381(98)	282(92)	253(90)	−56(84)	−1(78)	109(86)
O7	0.3333(14)	0.2340(22)	0.0155(17)	385(100)	112(75)	409(108)	74(73)	210(88)	13(80)
O8	0.6645(10)	0.6247(22)	0.2496(15)	53(58)	233(78)	235(81)	−17(57)	15(61)	33(72)
O9	0.3833(11)	0.8875(20)	0.0667(14)	142(67)	186(75)	155(75)	95(60)	−68(61)	−67(67)
O10	0.4275(11)	0.7609(20)	0.3001(15)	163(70)	131(70)	247(83)	−58(59)	155(67)	24(69)
O11	0.4870(10)	0.6080(18)	0.0980(14)	36(53)	166(59)	282(81)	−17(49)	89(60)	−64(62)

Table 2. Selected bond lengths (Å) and bond angles (°) with standard deviations in parentheses.

Pr−O1	2.523(16)	O1−Se1−O2	96.7(8)
Pr−O3	2.443(16)	O1−Se1−O3	103.8(9)
Pr−O5	2.566(14)	O2−Se1−O3	95.4(8)
Pr−O7	2.401(16)		
Pr−O8	2.482(16)	O4−Se2−O5	96.1(7)
Pr−O9	2.865(15)	O4−Se2−O6	97.9(8)
Pr−O10	2.460(15)	O5−Se2−O6	96.7(8)
Pr−O11	2.599(13)		
Pr−O11	2.524(14)	O7−Se3−O8	105.1(8)
		O7−Se3−O9	98.8(8)
Se1−O1	1.654(16)	O8−Se3−O9	101.0(7)
Se1−O2	1.769(16)	O9−Se4−O10	102.9(7)
Se1−O3	1.656(16)	O9−Se4−O11	89.8(7)
		O10−Se4−O11	102.9(7)
Se2−O4	1.766(16)		
Se2−O5	1.624(14)	Se3−O9−Se4	123.8(8)
Se2−O6	1.805(18)		
Se3−O7	1.673(18)		
Se3−O8	1.681(16)		
Se3−O9	1.847(15)		
Se4−O9	1.835(15)		
Se4−O10	1.659(16)		
Se4−O11	1.655(14)		

obtained after four more cycles of refinement; the final value of R was 5.4 %. The F_o and F_c listing is available from the authors upon request.

DISCUSSION OF THE STRUCTURE

The atomic coordinates and anisotropic temperature parameters are given in Table 1 and selected interatomic distances and bond angles in Table 2.
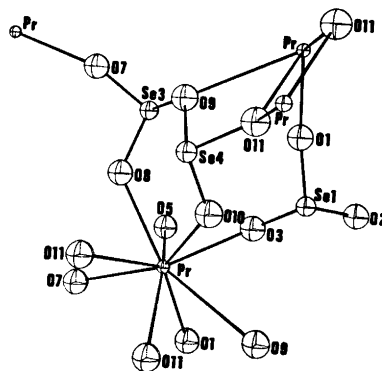

Fig. 1. Bonding scheme of the chain-forming diselenite and selenite groups.

Table 3. A comparison of interatomic distances and bond angles in compounds containing the diselenite ($Se_2O_5{}^{2-}$) ion. O′ denotes the oxygen bridging the two selenium atoms.

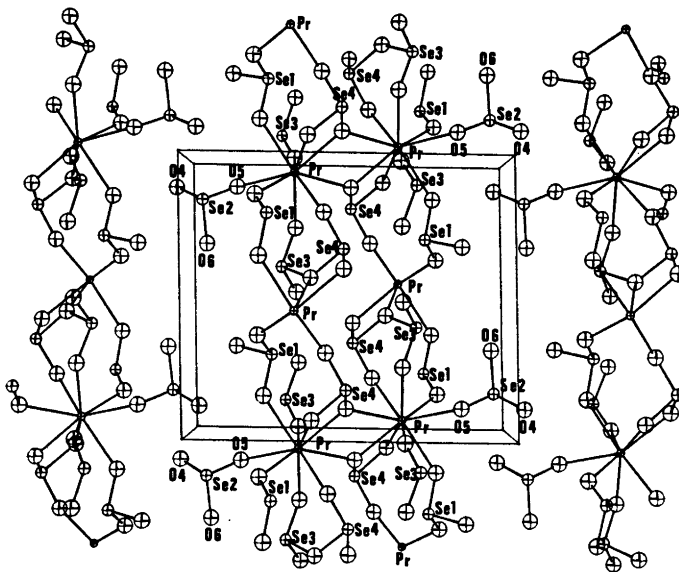| Compound	Range of Se−O distances (Å)	Range of Se−O′ distances (Å)	Range of O−Se−O′ angles (°)	Range of Se−O′−Se′ angles (°)	Ref.
VSe_2O_6	1.657−1.710	1.768−1.822	96.0−103.4	119.6	5
$ZnSe_2O_5$	1.658−1.693	1.827	96.3−102.4	121.6	6
$MnSe_2O_5$	1.644−1.674	1.831	95.9−102.8	121.6	7
$CuSe_2O_5$	1.668−1.670	1.831	101.4−103.1	122.4	8
$PrH_3(SeO_3)_2(Se_2O_5)$	1.655−1.681	1.835−1.847	89.8−102.9	123.8	Present work

Fig. 2. Perspective view of the double-layer structure of $PrH_3(SeO_3)_2(Se_2O_5)$ along the *b*-axis. The unit cell is indicated in the drawing.

There is no water of crystallization in the structure, since all the oxygens belong to either the diselenite or selenite groups. This leads to the formula $PrH_3(SeO_3)_2.(Se_2O_5)$ for the compound. The coordination number of the Pr(III) ion is nine. Six diselenite and three selenite oxygen atoms form a distorted monocapped square antiprism. There are eight oxygens at distances 2.401−2.599 and one, O9, at 2.865 Å. These Pr−O distances are only slightly larger than those in a similar coordination polyhedron within a Pr complex containing both singly and doubly ionized IMDA (IMDA = HN(CH₂COOH)₂); in this compound the corresponding distances are 2.34−2.58 Å and 2.75

Å.[4] The "cap" is formed by the oxygen bonding the two seleniums in the diselenite group; it is thus coordinated to three atoms simultaneously. This situation is unique among the diselenites reported so far.[5-8]

Four praseodymium(III) ions are linked with one diselenite group into a two-dimensional array (see Fig. 1). Two of the five oxygens are coordinated to the same Pr(III) ions, two others to two different Pr(III) ions, and the fifth oxygen is coordinated to two Pr(III) ions simultaneously. Pr(III) ions are situated on two planes parallel to the *bc* plane, and the result is a two-layered structure, which is essentially held together by the three-coordi-

nated oxygens (see Fig. 2). This double-layer can also be viewed as pairs of edge-sharing coordination polyhedra (the vertices of the common edge being the two O11), which are linked by selenium(IV) ions into a layer network. The layer structure is further strengthened by additional chains formed by the bridging one of the two nonequivalent selenite ligands. The other selenite group does not form a chain-structure, but acts as a monodentate ligand to one Pr(III) ion.

Table 3 compares the diselenite bond distances and angles with those given in Refs. 5 − 8. The values are compatible with one exception: in the present work one of the angles (O9 − Se4 − O11) is markedly smaller (89.8°) than the corresponding ones in other compounds. This distortion is probably caused by the unique position held by O11, which is within bonding distance of the selenium in the diselenite group (1.655 Å) as well as of two different Pr(III) ions (2.524 and 2.599 Å).

An interesting phenomenon is observed in the Se − O distances within the selenite groups. If the oxygen is coordinated to Pr(III) ion, the bond length is between 1.624 and 1.656 Å, which is somewhat shorter than usual for selenite ions. In $MnSeO_3.2H_2O$ and $CuSeO_3.2H_2O$, where all the oxygen atoms of the selenite group are coordinated to the metal, the distances are 1.692 − 1.713 Å and 1.72 − 1.78 Å, respectively.[9,10] If the oxygens are not coordinated to praseodymium, the bond lengths are 1.766 − 1.805 (see Table 2). This stretching of the Se − O bond can be attributed to the formation of hydrogen bonds, although the positions of the hydrogens could not be identified from the Fourier maps. A similar feature has been observed in crystalline H_2SeO_3, where the distances were 1.643 and 1.735 − 1.743 Å for Se − O and Se − OH, respectively.[11]

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